Thermodynamics
and
Statistical Mechanics

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Chapter 1

Preliminaries

The word “Thermodynamics” is derived from the greek words *therme*, meaning “heat”, and *dynamikos*, meaning force or power. It is the area of physics that deals with the relationship of “heat” to other forms of energy and to mechanical work, and examines how these quantities are related to the measurable properties of a **thermodynamic system**. A thermodynamic system is a macroscopic portion of the universe, by which we mean that it consists of a very large number of more elementary constituents, each of which is able to carry mechanical energy. In contrast, the rest of the universe is called the **environment** and the separation between the “system” and the “environment” is generally assumed to occur via a boundary separating the two. Thermodynamics assumes from the start that the elementary constituents of the system and its environment are so many that fluctuations about their average behavior can be completely ignored.

Every thermodynamic system is able to store energy by virtue of the fact that its elementary constituents possess mechanical energy. A fundamental objective of thermodynamics is to describe the interaction of such a system with the environment or the interaction between different systems among themselves. Such interactions inevitably lead to an exchange of energy between them and there are broadly two ways in which this can occur: (i) either energy enters or leaves the system because an external mechanical constraint is changed (this occurs, for example, when a gas expands or is compressed and its volume changes) or (ii) energy spontaneously moves across the boundary by transfer on the molecular level (for instance, when a hot body is brought in contact with a cold body). We say that the first kind of energy transfer occurs by **useful work**, the second occurs by **Heat**.

The possibility of transforming heat into useful work and vice-versa had been recognized for a very long time, in fact even before the nature of heat as a transfer of energy was understood. Heat was originally supposed to be a kind of fluid, called “caloric”, flowing from one body to another. This understanding was replaced in the mid and late nineteenth century by the more modern mechanical theory of heat, thanks to the work of Mayer, Joule, Maxwell, Boltzmann and others. Since every macroscopic system is made up of elementary constituents, exchanges of energy must eventually be mechanical processes occurring on a microscopic scale. Understood in this way thermodynmics becomes a special branch of mechanics: the mechanics, classical or quantum as the need may be, of very many elementary constituents interacting with each other.

Anyone who has tried to solve the equations of motion for more than two interacting particles knows already that this is an extremely difficult, if not impossible task. The general N body problem contains $6N$ variables. Subtracting the ten first integrals of the motion (one for energy, three for the motion of the center of mass, three for the total momentum, three for the total angular momentum) leaves us with $6N - 10$ variables, subject to the same number of initial conditions, to contend with. If the system has on the order of Avogadro's number (6.023×10^{23}) of elementary constituents then the problem is computationally unfeasable, even assuming that the initial conditions could all be obtained experimentally, which itself is possibly still less feasable a task. Yet, one should be sensitive to the fact that even if such a solution could be obtained, it would give us information that is far in excess of what we can reasonably measure or control. In fact, we are able in practice to impose only very coarse constraints on a macroscopic system and to measure only a very small number of its properties (an example would be the pressure, volume and temperature of a gas) compared to the number of mechanical variables involved in a microscopic treatment. The treatment via mechanics, even if it could be accomplished, would therefore be quite useless from a practical standpoint. A way out, originally proposed by Boltzmann, is to treat the mechanical system statistically *i.e.,* asking not detailed questions concerning the motion of the individual constituents but rather asking questions about the *average* behavior of the system. This microscopic approach, combining mechanics and statistics, leads to "Statistical Mechanics", a part of which we will examine in the latter half of this text.

Because we measure and control a very small number of properties of the system, some of which are related only statistically to its underlying microscopic properties, it is worth asking how far we can go if we simply *ignore* the underlying mechanics. This is the approach of Thermodynamics, which concentrates only on relationships between the measurable properties of the system. Of course it requires us to define clearly the properties (variables) we use in our description of the macroscopic system by describing instruments to precisely measure them. Once this is accomplished, the sole task of thermodynamics is to codify experiment by postulating a set of principles relating these "thermodynamic varables". On the surface at least this sort of description would seem to have little to do with the theory of dynamical systems. It is an interesting fact then that Thermodynamics admits a rather elegant formulation as a dynamical system in its own right. We will show this in a forthcoming chapter.

Both approaches have their advantages and disadvantages. In the microscopic approach (Statistical Mechanics) the system must be modeled mechanically in a fairly detailed fashion and our understanding of it is proportionally more profound, but the mathematical difficulties involved in the actual transition from theoretical model to experimental predictions and vice versa are also greater. In the macroscopic approach (Thermodynamics, as conceived by Mayer, Carnot, Clausius, Kelvin and many others) our understanding of the actual processes between the elementary constituents is sacrificed for mathematical simplicity. It is remarkable indeed that many deep results can yet be obtained *without* any reference whatsoever to the underlying mechanics. This must be understood as evidence of the power of statistical averaging: when very large numbers are involved statistical fluctuations become vanishingly small and Thermodynamics becomes an excellent effective but nevertheless complete and internally consistent theory, within its realm of applicability.

1.1 Equilibrium States and State Variables

A thermodynamic state is the macroscopic condition of a thermodynamic system as described by the values of a small number of variables, such as the temperature, pressure, density, volume, composition and others that will be defined in the following chapters. These are called the **state variables** and together the state variables span the **thermodynamic phase space** of the system. They are always few in number when compared to the number of mechanical variables that would be required, and generally may be strictly defined only when the system is in "equilibrium" (equilibrium refers to a situation in which there is no change of the state variables in time.) They define a space of possible **equilibrium states** of the system. An essential task of thermodynamics is to discover a reasonably "complete" set of state variables for the given system.

Thermodynamic variables are often divided into two categories: the **intensive** variables, which are independent of the system size or the quantity of matter contained in the system and the **extensive** variables whose values, by contrast, do depend on the system size or the amount of matter in the system. For example, temperature is an intensive property of a thermodynamic system. The same applies to the density of a homogeneous system since if the size (volume) of such a system is scaled by some factor, then its mass is scaled by the same factor and therefore the density stays constant. On the other hand, the total energy of a system of weakly interacting particles, or of particles with very short range interactions, is extensive.

Now volume is a geometric quantity for which we have a well developed intuition and the mass density, $\rho(\vec{r})$, defined according to

$$M = \int_V d^3\vec{r}\rho(\vec{r}), \tag{1.1.1}$$

is likewise well understood. Let us precisely define two other basic of state variables, *viz.,* the pressure, and the temperature. Others will be defined as the subject unfolds.

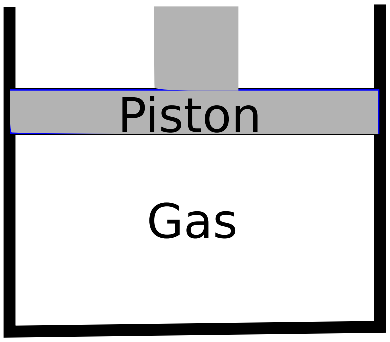

Figure 1.1: A gas is confined in a chamber with a piston at one end

1.1.1 Pressure

Imagine that the gas is confined in a container with a piston at one end. The piston gives us some measure of control over the volume of the gas (see figure 1.1). The gas exerts a force on the piston, which can be measured by placing weights on the piston until the upward force of the gas on the piston balances its weight. In this state of mechanical equilibrium we may crudely define the **pressure** of the gas as the force, F, exerted by it per unit area, A, of the piston

$$p = \frac{F}{A} \tag{1.1.2}$$

but this expression is really only the definition of the *average* pressure. Note that the direction of the force is perpendicular (normal) to the surface bounding the gas, equivalently that of the piston. A more general definition of pressure may be given by expressing the above relationship in terms of infinitesimal quantities. Consider any macroscopic, continuous system and a surface within the system or bounding it. Let $d\vec{S}$ be an infinitesimal, directed element of this surface (the direction is taken to be the outward normal, the word "outward" signifying that it points into the environment). Let the force on this infinitesimal element of surface and normal to it be $d\vec{F}_n$, then define the pressure as the proportionality in the relationship

$$d\vec{F}_n = p d\vec{S} \tag{1.1.3}$$

between $\vec{F}_n$ and $d\vec{S}$. Thus the force on a finite area of *any* surface would be

$$\vec{F}_n = \int_S p d\vec{S} \tag{1.1.4}$$

where the integral is taken over the portion of the surface under consideration. If the pressure is constant we obviously recover the simple definition in (1.1.3). We say that two systems in contact with one another are in **mechanical equilibrium** when their pressures are equal.

1.1.2 The Zeroeth Law and Temperature

Temperature is more subtle. We have an intuitive understanding of temperature in terms of “hot” and “cold” or better still a number we can read on a “thermometer”. For the purposes of physics, however, this is not enough and we must give a precise meaning to temperature. Consider two thermodynamic systems, A and B, one of which is “hotter” than the other. Now bring them into contact with one another, allowing them only to exchange energy through an immovable partition so that no mechanical work is done by one system on the other, then experience tells us that the “hotter” system becomes “colder” and the “colder” system becomes “hotter” until finally, after a very long time (which depends on the composition of the systems), the two bodies are equally “hot”. At this point they have ceased to exchange energy between themselves on the average and we say that they are in **thermal equilibrium**. Thermal equilibrium is an equivalence relation between systems: first we specify that every thermodynamic system must be in thermal equilibrium with itself so that thermal equilibrium is a reflexive relation, then we claim that it is also *right-Euclidean*, and codify this claim in so-called **zeroeth law** of thermodynamics:

Zeroeth Law: If two thermodynamic systems are in thermal equilibrium with a third system then they are in thermal equilibrium with each other.

Any relation that is reflexive and Euclidean is an equivalence relation (the zeroeth law of thermodynamics guarantees that thermal equilibrium is both symmetric and transitive) and every equivalence relation divides a set into disjoint subsets. In this case, the disjoint subsets of the set of all thermodynamic systems would consist of all the systems in thermal equilibrium with one another. These disjoint subsets may be labeled, and “Temperature” is just the variable used in the labeling process. So we may give the following definition:

Temperature is that variable of thermodynamic systems, whose equality ensures that that they are in thermal equilibrium and whose inequality ensures that they are not in thermal equilbrium with each other. Systems that are not in thermal equilibrium with each other will exchange energy between themselves if they are brought in contact with one another, even if no mechanical work is done in the process.

Note that the zeroeth law of thermodynamics does not guarantee order (with respect to “hot” or “cold”) or continuity of the temperature, but these are properties that we will nevertheless associate with this variable. With this operational definition of temperature, we now ask how we should quantify it. There are many properties of matter that depend monotonically on the temperature and that can be measured directly. For example, we know that materials expand and contract when heated and cooled respectively at fixed pressure, so length, area and volume which can be measured geometrically are examples of such properties.[1] Likewise, the pressure of a gas kept at a fixed volume will increase with increasing temperature, so pressure is also such a property. Another example would be the electrical resistance of materials which grows with temperature. Properties of materials that change monotonically with the temperature are called **thermometric** properties.

We can use thermometric properties to build thermometers as follows. Let X be the thermomentric property of some material we wish to turn into a thermometer. We simply *define* the scale of temperature in such a way that the variation of the thermometric property is a linear function of the temperature, then

$$X(T) = X_0 + \alpha^{-1}(T - T_0) \tag{1.1.5}$$

Clearly X_0 represents the value of X at T_0 and α determines the slope of the scale. Inverting we have

$$T(X) = T_0 + \alpha(X - X_0) \tag{1.1.6}$$

The two constants that define this linear scale must be fixed by choosing two phenomena which are known to always occur at the same temperature. It's also best to choose them in such a way that they are very easily reproducible. Since water is ubiquitous on our planet, choose two phenomena connected with water. The candidates could be the boiling of pure water at sea level and the freezing of pure water (more accurately, its tripple point, *i.e.,* when water coexists in equilibrium with water vapor, and ice), again at sea level. Call the temperatures associated with these events T_b and T_f respectively and the values of X associated with these events X_b and X_f. Then, replacing (X_0, T_0) with (X_f, T_f), we have

$$T_b = T_f + \alpha(X_b - X_f) \Rightarrow \alpha = \frac{T_b - T_f}{X_b - X_f} \tag{1.1.7}$$

and so

$$T = T_f + \frac{T_b - T_f}{X_b - X_f}(X - X_f) \tag{1.1.8}$$

The thermometric property, X, is easily measured and so we fix the values of X_f and X_b. Finally complete setting up the temperature scale by choosing convenient values for T_f and T_b. A particularly simple choice would be $T_f = 0$ and $T_b = 100$, then

$$T^{(C)} = \frac{100}{X_b - X_f}(X - X_f) \tag{1.1.9}$$

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[1] A notable exception is water, which contracts as the temperature rises from 0°C to about 4°C and then expands monotonically until it vaporizes at 100°C.

gives the temperature for any value of X once X_f and X_b are determined. This is the Celsius scale (C), named after the astronomer Anders Celsius who developed it in 1742. Alternatively, by choosing $T_f = 32$, $T_b = 212$, we get the Fahrenheit scale (F),

$$T^{(F)} = 32 + \frac{180}{X_b - X_f}(X - X_f), \tag{1.1.10}$$

which is named after Daniel Gabriel Fahrenheit who proposed it in 1724.[2]

Both the Celsius and Fahrenheit scales are *linear* scales and can be directly compared to one another. Using C and F to represent temperatures measured in the Celsius and the Fahrenheit scales respectively (instead of $T^{(C)}$ and $T^{(F)}$) we see that

$$\begin{aligned} C &= \frac{5}{9}(F - 32) \\ F &= 32 + \frac{9}{5}C \end{aligned} \tag{1.1.11}$$

There is nothing special about either of the scales above and nothing special about the choice of fixed points. All that is important is to remember that they are linear scales. In general we could choose $T = T(X, \alpha, \beta)$ to be a more complicated monotonic function with two arbitrary constants that could subsequently be determined as above. This would not lead to any new physics. The linear function is the simplest monotonic function and therefore the best choice.

1.1.3 The Thermodynamic or Absolute Temperature Scale

Because we never prescribed the material or thermometric property that we would use, an implicit assumption that has been made in the above discussion is that the temperature can be defined as a linear function of *all* thermometric properties of *all* materials. Actually this is not the case, for if we were to assume a linear relationship between the temperature and a particular thermometric property of some material and construct a thermometer from it, we should find that another thermometric property of the same material or the same thermometric property of a different material would no longer be a linear function of the temperature as measured by our thermometer. We must therefore choose *one* thermometric property of *one* particular substance which we then take as our standard. The standard material chosen is an **ideal gas** (which will be precisely defined later and which can be approximated in the laboratory to excellent precision by real gases at very

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[2] Fahrenheit actually did not use the two fixed points we mention in this text. Instead he used a certain mixture of ice, water and ammonium chloride, which is known to achieve a fixed temperature regardless of the initial temperatures of its constituents (such mixtures are called *frigorific* mixtures), for the lower fixed point and called it $T_f = 0$. He then used the tripple point of water as the upper fixed point and called it $T_b = 32$.

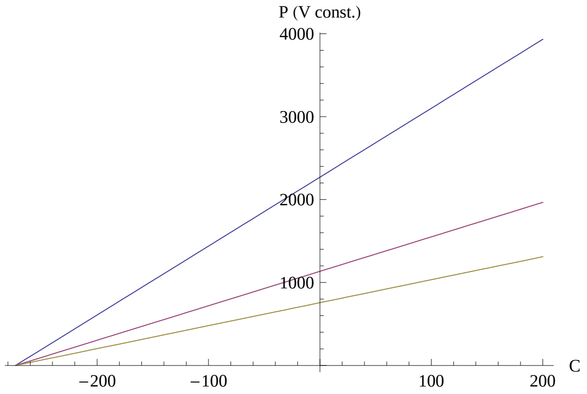

Figure 1.2: Pressure vs Temperature for different gases at constant volume

low densities; experiments show that the behavior of gases at very low densities is nearly independent of the molecular structure of the gas provided that the temperature is above the point at which the gas liquefies). The standard thermometric property chosen is generally the pressure of the gas at constant volume and the thermometer so constructed is called a constant volume gas thermometer.[3]

If we now plot the pressure vs. the temperature as measured by our thermometer for different gases (low densities and fixed but different volumes), we get straight lines similar to those shown in figure 1.2. The different lines refer to the different (constant) volumes of the gases. Notice that in all cases the lines intersect the T axis at a fixed point, *i.e.,* $C = -273.16$ Celsius. At this temperature the pressure would be exactly zero. If we were to attempt to extend the line to the left, the pressure would end up being negative. Since pressure cannot be negative, we must consider the temperature -273.16°C to be the absolute minimum temperature attainable. It is often referred to as absolute zero and serves as a basis for a new scale (the absolute or Kelvin scale, K) in which the size of one degree is taken to be precisely the same as the size of one degree Celsius. Therefore the conversion between these temperatures is

$$K = C + 273.16 \tag{1.1.12}$$

Our definition of temperature via the pressure of a constant volume gas thermometer means that p is proportional to T at constant volume (for an ideal gas).

Again, plots of volume vs. temperature as measured by our thermometer for different gases (low densities and fixed but different pressures), also turn out to be straight lines as shown in figure 1.3 and plots of pressure vs. volume holding the temperature as measured

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[3] See any elementary text for a description of how the constant volume gas thermometer is built.

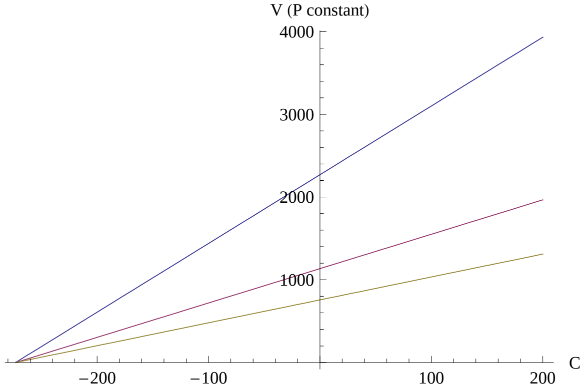

Figure 1.3: Volume vs Temperature for different gases at constant pressure

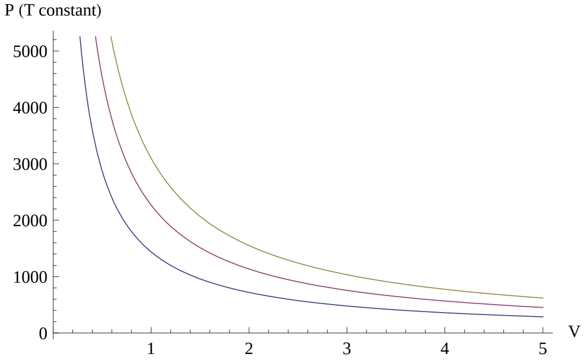

Figure 1.4: Pressure vs Volume for different gases at constant temperature

by our thermometer fixed for different gases (low densities and fixed but different temperatures) gives the set of curves shown in figure 1.4. These plots indicate that we should expect a relationship between the pressure, volume and temperature of ideal gases of the form

$$f(p, V, T) = 0, \tag{1.1.13}$$

where f is some function. Such an equation is a constraint that defines a hypersurface in the space of thermodynamic variables, showing that not all points in this space are acceptable equilibrium states but only those that lie on the constraint surface. A careful examination of the curves in 1.2, 1.3 and 1.4 leads to the famous ideal gas law of Boyle, Charles and Guy-Lussac,

$$pV = \nu RT \tag{1.1.14}$$

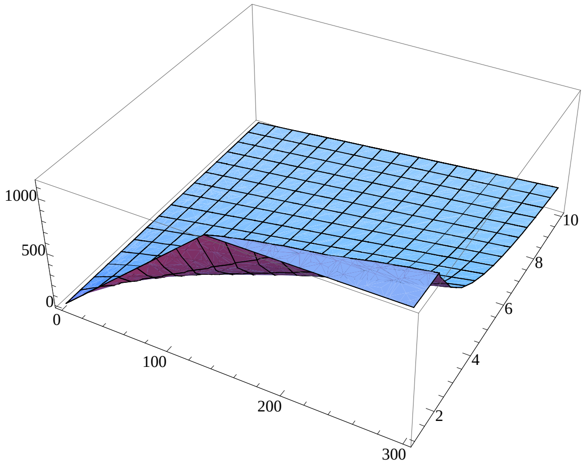

Figure 1.5: Hypersurface of acceptable equilibrium states of an ideal gas

where p is the pressure of the gas, V is its volume, T its *absolute* temperature (measured in Kelvins), ν is the number of moles present and R is the ideal gas constant $R = 8.31$ J/mol·K. The surface on which acceptable equilibrium states of the gas live is shown in figure 1.5

Although we have considered a pure gas, made of a single type of molecule, the calculations above are straightforwardly generalized to a homogeneous mixture of (ideal) gases. Let us define the **partial pressure** of a gas in a mixture of gases as the pressure that the gas would exert if it alone occupied the entire volume occupied by the mixture. Then **Dalton's law** states that the pressure exerted by a mixture of gases is the sum of the partial pressures exerted by the components of the mixture. Thus consider a mixture of N gases, occupying a volume V. If j labels the gases, the partial pressure of each satisfies the relation

$$p_j V = \nu_j RT \tag{1.1.15}$$

where ν_j is the number of moles in of type j in the mixture. By Dalton's law, the pressure exerted by the mixture is

$$p = \sum_{j=1}^{N} p_j = \frac{RT}{V} \sum_{j=1}^{N} \nu_j \tag{1.1.16}$$

and so the equation of state for the mixture is the same as that of the pure gas,

$$pV = \nu RT \tag{1.1.17}$$

with the understanding that $\nu = \sum_j \nu_j$.

1.2 Thermodynamic Processes

A **thermodynamic process** is any process that takes a macroscopic system from one equilibrium state to another. Since every equation of state is a constraint on the state variables, together they define a hypersurface in the thermodynamic phase space, much like the Hamiltonian of a conservative mechanical system defines a hypersurface in the mechanical phase space upon which all the dynamics occurs. Allowed thermodynamic states are represented by points in the hypersurface and thermodynamic processes are trajectories in it. The dimension of the hypersurface is the number of state variables less the number of equations of state.

Broadly, thermodynamic processes may be divided into two classes, which we can motivate by considering the following examples. Consider a gas which is enclosed inside a container of volume V_1. Suppose that the container has a stopcock which is closed but which may be opened at any time and that the container is itself enclosed inside a larger container of volume V_2 which is vacuous. Wait for long enough so that the gas inside V_1 is in equilibrium, then suddenly open the stopcock. The gas will immediately rush out of the opening and fill the entire volume V_2. For a time after the stopcock is opened the gas is not in an equilibrium state, in fact the variables p, V and T, and especially T, cannot be measured because measuring them requires equilibrium. It is said to be in a **dynamical** state. Yet, if we wait long enough the gas will achieve a new equilibrium state with a new pressure, volume and temperature. Therefore, the process of expansion has transformed the gas from one equilibrium state to another equilibrium state, but itself cannot be described by the equilibrium variables. It is one example of a thermodynamic process.

Because the process described above cannot be described by the equilibrium variables, Thermodynamics, which relies on relationships between equilibrium variables, will have little to say about it. However, we can imagine that the gas is made to expand slowly. So slowly, in fact, that it can be treated *as though* it is always in equilibrium. To accomplish this imagine opening the stopcock for a very short interval of time so that only an infinitesimal quantity of gas is released. Then wait for the system to come to equilibrium. Repeat the process a very large number of times, each time releasing only an infinitesimal quantity of gas and then waiting for equilibrium. In this way we will end up with a final equilibrium state that will in general *not* be the same as the state we ended up with in the first process. Nevertheless we still have a thermodynamic process taking the system from an initial equilibrium state to a final equilibrium state, and this process occurs slowly enough that the gas may always be considered to exist in equilibrium. Such a thermodynamic process is called a **quasi-static** process. During a quasi-static process the successive states of the transformation differ infinitesimally from each other and the equilibrium variables can be used to describe the evolution of the system. The first kind of process, during which the change occurs so rapidly that equilibrium is never achieved until the final state is reached making the thermodynamic variables meaningless during the process itself is **non-quasi-static**.

1.2.1 Work

We will be concerned with energy conservation in thermodynamic processes. An essential part of our considerations will involve the work done by a thermodynamic system on the environment or, conversely, the work that the environment does on the system during any process. Let S be the (closed) boundary of our system and let $\vec{F}_n$ be the net force exerted by the system on an infinitesimal area $d\vec{S}$ of the boundary. Suppose that the boundary experiences a deformation, so that the infinitesimal area $d\vec{S}$ is displaced by $d\vec{r}$. The infinitesimal work done by the system on the boundary is then

$$đW = \vec{F}_n \cdot d\vec{r} = p(d\vec{S} \cdot d\vec{r}), \tag{1.2.1}$$

using our definition of pressure. Now the quantity $d\vec{S} \cdot d\vec{r}$ may be interpreted as the infinitesimal contribution to the change in the volume of the closed surface S by the displacement of $d\vec{S}$ along $d\vec{r}$. Thus

$$đW = pdV \tag{1.2.2}$$

is the work done by the system on the environment in changing its volume by dV. $đW$ is not an exact differential because its integral depends on the "path" that is taken in the phase space of the system as it goes from its initial state to its final state. In other words, the integral of $đW$ depends on the process.

As a simple example, consider a quasi-static process in which the volume of an ideal gas inside a container changes. Suppose that the initial state is given by the pair (p_i, V_i) and the final state by the pair (p_f, V_f), then the work done *by the system on the environment* is just

$$đW = pdV, \quad W_{if} = \int_i^f pdV \tag{1.2.3}$$

We are able to evaluate the integral only once the process of going from i to f is known.

Obviously no work is done during a constant volume or **isovolumetric** process for then $dV = 0$. If the process occurs at a constant temperature, *i.e.,* it is **isothermal**, then because $p = \nu RT/V$ we find

$$W_i f = \nu RT \int_i^f \frac{dV}{V} = \nu RT \ln\left(\frac{V_f}{V_i}\right) \tag{1.2.4}$$

Naturally, we could express this result in terms of the initial and final pressures as well by using the equation of state,

$$W_{if} = \nu RT \ln\left(\frac{p_f}{p_i}\right), \tag{1.2.5}$$

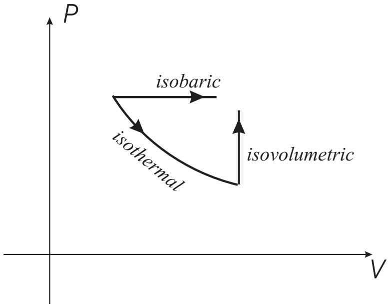

Figure 1.6: Constant T, p and V processes in a $p-V$ diagram.

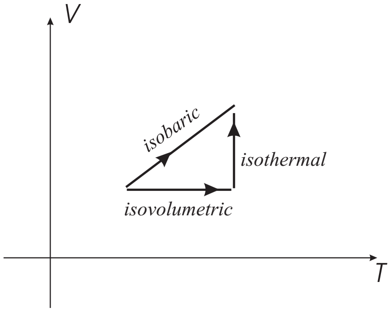

Figure 1.7: Constant T, p and V processes in a $V-T$ diagram.

since the temperature is constant throughout. On the other hand, if the process is **isobaric** *i.e.,* occurs at constant pressure, then

$$W_{if} = p\int_i^f dV = p(V_f - V_i) \tag{1.2.6}$$

This could be expressed in terms of the change in temperature as well by using the equation of state,

$$W_{if} = \nu R(T_f - T_i) \tag{1.2.7}$$

since the pressure is held fixed. In both processes treated, if $V_f < V_i$ then the work done is negative. Negative work done *by* the gas on the environment is the same as positive work done by the environment *on* the gas.

The processes considered above are special types of trajectories in the three dimensional thermodynamic phase space of the ideal gas. Because there is one equation of state, all processes will occur in a two dimensional hypersurface, which we might take to be spanned by any of the three possible pairs: (p, V), (p, T) or (V, T). The three trajectories considered in the example, *viz.,* isobaric, isothermal and isovolumetric, are drawn first in the (p, V) plane in figure 1.6 and next in the (V, T) plane in figure 1.7. A more general thermodynamic process will be a more complex curve connecting the initial and final states of the system, but the work done will always simply be the area under the curve in the $p-V$ plane.

In general, the infinitesimal work done by a thermodynamic system will have the form

$$đW = \sum_i p_{X_i} dX_i \tag{1.2.8}$$

where X_i are some extensive variables (different from the energy) governing the system and p_{X_i} are the "**generalized forces**" associated with their deformation. For example, one can show that the work done by the surface tension, σ, during an interfacial expansion, is

$$đW = \sigma dA. \tag{1.2.9}$$

In some cases this may actually be the major contribution to the work done, more important than the pdV term.[4] Other examples of mechanical work are the work done by friction, $\vec{f}$,

$$đW = f ds, \tag{1.2.10}$$

where ds is an infinitesimal displacement tangent to the path of the body and the work done by the tension, τ, in a wire of length L in elongating it by dL is

$$đW = \tau dL. \tag{1.2.11}$$

Likewise, the work done by an external applied electric field in polarizing a dielectric is

$$đW = \vec{E} \cdot d\vec{P}, \tag{1.2.12}$$

where $\vec{P}$ is the electric polarization vector of the dielectric and $\vec{E}$ is the applied external electric field and the work done by the electric field of a charge distribution during the addition of a charge dq to it is

$$đW = \Phi dq \tag{1.2.13}$$

where Φ is the electric potential of the distribution.[5] "Generalized forces" are intensive variables.

1.2.2 Heat

As mentioned in the introduction, **Heat** is energy transferred into or removed from a macroscopic system on the molecular level, as opposed to the direct application of mechanical work on the system by deformations of its macroscopic parameters. While the transfer of energy may occur because of an existing difference in temperatures between two macroscopic systems, this is not the only way in which the transfer may occur. For example, friction transfers energy from a mechanical system into its environment: a block sliding along the rough surface of a table transfers mechanical energy to the table although no work is done on the table. Stirring liquid in a cup or shaking it in a flask transfers mechanical energy from the stirring or shaking device to the liquid, as evidenced by the

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[4] Problem: Consider a bubble of water vapor expanding in water at 300 K from 1μm to 1.1μm. The vapor pressure of water at 300 K is approximately 0.0234 atm and $\sigma = 0.0724$ N/m. Determine the work done by the volume expansion and by the surface expansion. Which is larger?

[5] Problem: Convince yourself that all these are correct by performing a similar analysis as given here for $đW = pdV$.

rise it temperature of the liquid. Again, no work is done on the liquid since its volume remains unchanged. In both cases, the energy is transferred by heat.

This understanding of the relationship between "heat" and energy is relatively modern. It was Sir Benjamin Thomson (Count Rumford) who, while supervising the manufacture of canons for the government of Bavaria, noticed that the more the canons were bored the more the water that was required to cool them. Noticing that the supply of "heat" from boring a canon was inexhaustible and that no chemical change had actually occurred in the material of the bored canon, he associated heat with the mechanical energy that went into the boring process because, he argued, it was impossible to generate an indefinite amount of caloric by the boring process. Nearly fifty years later Helmholtz declared that heat is a "form of energy" and that all forms of energy are equivalent and interchangeable. However, while one form of energy can be exhanged for another or transferred from one subset of the universe to another, energy itself cannot be created nor destroyed and the total amount of energy present within the universe is constant.

Back when heat was considered a fluid (caloric) a unit of heat was defined as the amount of caloric required to raise the temperature of one gram of pure water at standard pressure from 14.5°C to 15.5°C. This unit was called the **calorie**. Today, we simply say that a calorie is the amount of energy that must be transferred to pure water by heat at standard pressure to raise its temperature from 14.5°C to 15.5°C.

Notice that it is necessary to specify the material, its mass, the temperature range (including the starting temperature) and the pressure in order to have a precise definition of the calorie. This is because of the well-known experimental fact that the amount of heat required to raise the temperature of a substance by one degree Kelvin (or Celsius) depends on all of these factors. We define the **heat capacity** of a thermodynamic system as the amount of energy required to be transferred by heat to raise the temperature of the system by one degree Kelvin (the letter Q is generally used to represent "heat")

$$C = \frac{\Delta Q}{\Delta T} \to \frac{đQ}{dT} \tag{1.2.14}$$

where ΔQ (or $đQ$) is the energy transferred by heat and ΔT (or dT) is the change in temperature, and is measured in cal/°C. We have used $đQ$ instead of dQ because ΔQ depends on the process by which energy is transferred. It follows that, even apart from the composition of the system, the temperature range over which the energy is transferred and other external factors, such as the pressure, etc., C will also depend on the process by which the energy is transferred.

If the system is homogeneous, its heat capacity will depend linearly on its mass, m. We can eliminate this dependence on the mass of the system by defining the **specific heat** as the heat capacity of a unit mass,[6],[7]

$$c = \frac{1}{m}\frac{đQ}{dT} \tag{1.2.15}$$

Naturally, the specific heat will depend on all the other factors upon which C depends. Alternatively, we can define the **molar heat capacity** as the heat capacity of one mole of the substance,

$$\mathcal{C} = \frac{1}{\nu}\frac{đQ}{dT}. \tag{1.2.16}$$

The molar heat capacity is measured in cal/mol·°C. For example, the molar heat capacity of pure water at STP is $\mathcal{C}_w = 18$ cal/mol·°C. Again, the molar heat capacity will depend on the substance, the process by which the substance is heated, the temperature range over which the heating occurs and other external parameters.

In terms of the specific heat,

$$c(T) = \frac{1}{m}\frac{đQ}{dT} \Rightarrow Q_{if} = m\int_i^f c(T)dT \tag{1.2.17}$$

If it is known that $c(T)$ is approximately constant during the process of heating, then

$$Q_{if} = mc(T_f - T_i) \tag{1.2.18}$$

but if, for example, it is determined that $c(T) = a + bT^2$ for a particular system undergoing a particular process then the average specific heat of the system in the range $[T_i, T_f]$ is

$$c_{\text{av}} = \frac{1}{T_f - T_i}\int_i^f (a + bT^2)dT = a + \frac{b}{3}(T_f - T_i)^2 \tag{1.2.19}$$

which differs considerably from its value at T_i or at T_f unless $b \ll a/(T_f - T_i)^2$. The heat absorbed by the system (of mass, say, m) is

$$Q_{if} = m\int_i^f c(T)dT = mc_{\text{av}}(T_f - T_i) = m(T_f - T_i)\left[a + \frac{b}{3}(T_f - T_i)^2\right]. \tag{1.2.20}$$

For many substances and processes of interest $c(T)$ is a slowly varying function of the temperature and as long as temperature does not change too much it is a good approximation to replace $c(T)$ by c_{av}.

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[6] More precisely, if the material is inhomogeneous, one can define the specific heat via the equation

$$C = \int_{\text{system}} dm(\vec{r})c(\vec{r}) = \int_V d^3\vec{r}\rho(\vec{r})c(\vec{r})$$

[7] By definition, one calorie of energy was required to be transferred by heat to pure water at standard pressure to raise its temperature by 1°C, so the specific heat of pure water is 1 cal/g·°C.

The heat capacity of a system is a useful concept so long as the process involves a temperature change. Yet, energy may be absorbed or released from a system during isothermal processes as well. In a class of such processes a substance changes phase, say from solid to liquid and vice-versa or liquid to gas and vice-versa or from solid to gas ("sublimation") and vice-versa. Such processes are reffered to as **phase transitions**. During phase transition, the temperature of the substance remains constant but energy must continue to be transferred either into or out of the system for the process to continue. For example, if the source of energy (the stove) is turned off during the boiling of water the process ceases. This shows that heat is required to be absorbed by the water in order to maintain the boiling, yet the temperature of the water itself remains constant throughout. The energy that is being absorbed by the water is required to convert the liquid into vapor

We define the **latent heat** as the heat required to change the phase of one gram of a substance,

$$L = \frac{\Delta Q}{m} \tag{1.2.21}$$

and is measured in cal/g. The latent heat is associated with a particular kind of phase transition and a particular substance. For example, the latent heat of the vaporization of water is $L_v = 540$ cal/g, *i.e.,* it takes 540 calories of heat to vaporize one g of water. When the vapor condenses, every gram will then release 540 calories. Similarly, the heat released from water when one gram freezes to form one gram of ice at standard pressure is 80 calories, *i.e.,* the latent heat of fusion of water is $L_f = 80$ cal/g. When ice melts at standard pressure it absorbs 80 cal/g.

1.3 Calorimetry

Heat capacities, specific heats and latent heats of substances are measured using **Calorimetry**. Generally speaking a calorimetric experiment involves the transfer of energy between two or more thermodynamic systems while the combination of the systems is kept isolated from the rest of the universe. Devices in which the exchange of energy occurs are called **calorimeters**, their main function being to isolate whatever is placed inside. Since the combination of thermodynamic systems is kept isolated, the calorimetric process satisfies

$$\Delta Q \equiv 0 \tag{1.3.1}$$

where ΔQ represents the energy exchanged by the combination with the rest of the universe. Denoting the systems by the subscript "j", this means that

$$\Delta Q = \sum_j \Delta Q_j \equiv 0 \tag{1.3.2}$$

where ΔQ_j is the energy absorbed (positive) or liberated (negative) by system j. Consider the following two examples.

Example 1. A copper block of mass 75 g is taken from an oven and placed in a glass of mass 300 g which contains 200 g of water. The initial temperature of the glass and water is 12°C and the temperature rises to 27°C. Determine the temperature of the oven.

The process does not involve changes of state. Assuming that no energy is lost to the environment (a somewhat strong assumption) and that there is no vaporization of the water during the process, energy is only exchanged between the copper block, the glass and the water. We have

$$\begin{aligned}&\Delta Q = \Delta Q_{\text{copper}} + \Delta Q_{\text{glass}} + \Delta Q_{water} \equiv 0 \Rightarrow\\&m_{\text{Cu}}c_{\text{Cu}}(T^{\text{fin}} - T^{\text{in}}_{\text{Cu}}) + m_{\text{gl}}c_{\text{gl}}(T^{\text{fin}} - T^{\text{in}}_{\text{gl}}) + m_{\text{w}}c_{\text{w}}(T^{\text{fin}} - T^{\text{in}}_{\text{w}})\end{aligned} \tag{1.3.3}$$

We need $T^{\text{in}}_{\text{Cu}}$. Solving,

$$T^{\text{in}}_{\text{Cu}} = \frac{(m_{\text{Cu}}c_{\text{Cu}} + m_{\text{gl}}c_{\text{gl}} + m_{\text{w}}c_{\text{w}})T - (m_{\text{gl}}c_{\text{gl}} + m_{\text{w}}c_{\text{w}})T^{\text{in}}_{\text{w}}}{m_{\text{Cu}}c_{\text{Cu}}} \approx 540.04^\circ\text{C} \tag{1.3.4}$$

where we used the fact that $T^{\text{in}}_{\text{gl}} = T^{\text{in}}_{\text{w}}$.

Example 2. Two 50 g icecubes are dropped into 200 g of water in a calorimeter. If the temperature of the water was initially 25°C and the temperature of the ice was initially −15°C. Determine the specific heat of ice (at constant pressure) assuming that it is constant over the interval $[-15, 0]^\circ$C if the final temperature of the mixture is 12.5°C

Since all the energy transfer occurs exclusively between the water and the ice (assuming an ideal calorimeter), we have

$$\begin{aligned}&\Delta Q = \Delta Q_{\text{ice}} + \Delta Q_{\text{water}} = 0 \Rightarrow\\&m_{\text{i}}c_{\text{i}}(0 - T^{\text{in}}_{\text{i}}) + m_{\text{i}}L_f + m_{\text{i}}c_{\text{w}}(T^{\text{fin}} - 0) + m_{\text{w}}c_{\text{w}}(T^{\text{fin}} - T^{\text{in}}_{\text{w}}) = 0\end{aligned} \tag{1.3.5}$$

(since, in the final equilibrium state, the temperatures of the water and ice coincide, T^{fin} carries no subscript). Solving for c_{i} we find

$$c_{\text{i}} = \frac{m_{\text{i}}L_f + m_{\text{i}}c_{\text{w}}(T^{\text{fin}} - 0) + m_{\text{w}}c_{\text{w}}(T^{\text{fin}} - T^{\text{in}}_{\text{w}})}{m_{\text{i}}T^{\text{in}}_{\text{i}}} \approx 0.5 \text{ cal/gm} \cdot^\circ \text{C} \tag{1.3.6}$$

In this example the ice melts and the ensuing water warms to the final temperature, so we had to take into account the latent heat of fusion of water. We have ignored the heat released by the calorimeter itself.

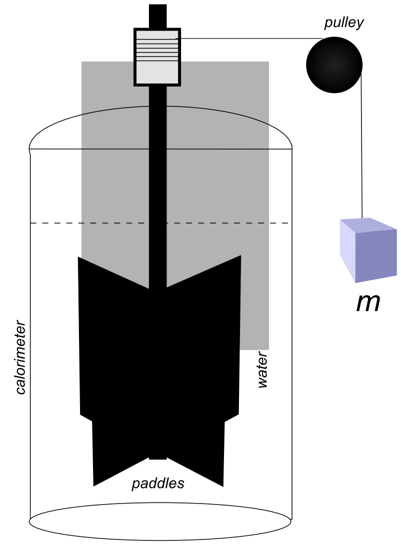

Figure 1.8: The Joule experiment

1.4 Mechanical Equivalent of Heat

We have seen that it is possible, by friction, to transfer energy from a mechanical system to a macroscopic system causing the latter's temperature to rise. It should therefore be possible to define a unit of heat in terms of the mechanical unit of energy, the Joule. Recall that the calorie was defined as the amount of heat necessary to raise the temperature of one gram of pure water from 14.5°C to 15.5°C at standard pressure. Suppose we consider the aparatus of figure 1.8 in which a falling weight is made to turn a paddle which stirs a liquid placed in a calorimeter. Stirring the liquid transfers the initial potential energy of the falling weight to the liquid in the calorimeter by friction. By measuring the mass of the falling weight and the height through which it should fall in order to raise the temperature of 1 gram of water from 14.5°C to 15.5°C at standard pressure we can determine the relationship between the calorie and the Joule. One finds that 1.0 calorie = 4.184 Joules.

1.5 Energy Transfer as Heat

Energy transfer between macroscopic systems broadly occurs in three ways as Heat.

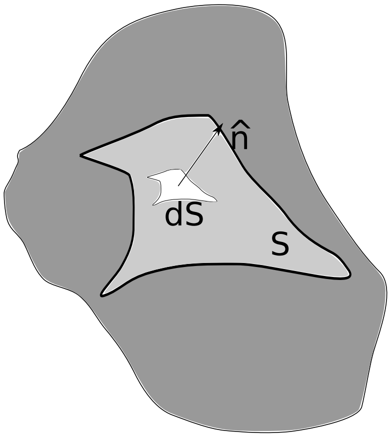

Figure 1.9: Heat conduction across any cross section of a solid

1.5.1 Conduction: Newton's Law

Energy transfer between two macrscopic systems due to a difference in temperature between them and which does *not* involve the gross movement of matter is called **conduction**. This process bears primary responsibility for energy transfer in solids. Conduction can be understood on the microscopic scale as the direct exchange of mechanical energy from a region of higher temperature to a region of lower temperature by molecular collisions at the boundary, *without* recourse to the bulk motion of the substance. It is most effective in solids and can occur in liquids but not it gases because of their low molecular density, which implies that molecular collisions simply do not occur frequently enough.

Take a piece of some solid material and consider a cross sectional area S as shown in figure 1.9. Let $d\vec{S}$ represent an infinitesimal, directed element of S, then **Newton's Law** of heat conduction says that, assuming there is a temperature gradient across S, the rate at which energy is transferred across S is given by

$$H = \frac{\partial Q}{\partial t} = -k \int_S d\vec{S} \cdot \vec{\nabla} T \tag{1.5.1}$$

where H, measured in Watts, is the rate of energy flow across the surface and k is a constant characterizing the material of which the solid is made. k is called the coefficient of heat conduction ($[k] = \mathrm{W/m{\cdot}^\circ C}$) or conductivity. The direction of the area element $d\vec{S}$ is chosen to be the direction of the energy flow if $H > 0$ and opposite the energy flow if $H < 0$.

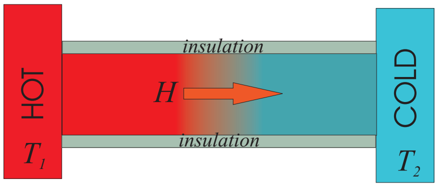

Figure 1.10: Heat conduction across a solid of uniform cross sectional area.

Examples

In the **steady state** the temperature does not depend on time. This is possible only if the quantity of energy flowing into any region is precisely equal to the energy flowing out of that region. Suppose we are able, by symmetry, to find surfaces $\xi(\vec{r}) =$ const. of normal $\hat{n}$ which are such that $\hat{n} \cdot \nabla T$ is constant along the hypersurface. If the area of the hypersurfaces is denoted by $A(\xi)$, Newton's law will read

$$H = \frac{\partial Q}{\partial t} = -kA(\xi)\frac{dT}{d\xi} \tag{1.5.2}$$

A simple example of its application occurs in a solid rod of uniform cross-sectional area as shown in 1.10, one end of which (the left) is maintained at a high temperature (source) and the other end (right) at a lower temperature (sink). Energy will flow uniformly across planes from left to right, *i.e.,* from source to sink, and the symmetry indicates that the surfaces satisfying the condition above are described by $x =$ const. We have

$$H = \frac{\partial Q}{\partial t} = -kA\frac{dT}{dx} \tag{1.5.3}$$

with constant H. Since the cross sectional area is uniform throughout the rod, it follows that dT/dx must also be constant. Then we could replace

$$\frac{dT}{dx} = \frac{T_2 - T_1}{L} \tag{1.5.4}$$

where $T_{1,2}$ are the temperatures of the extremities as shown. Notice that dT/dx is negative if energy is flowing to the right. This justifies the negative sign: its presence indicates that energy flows in the direction of decreasing temperature. Thus,

$$H = -\sigma(T_2 - T_1) \tag{1.5.5}$$

where $\sigma = kA/L$ is called the **thermal conductance** of the material ($[\sigma]=$ W/°C). Its reciprocal is called the **thermal resistance** (or R value), R, of the material ($[R] =$°C/W).

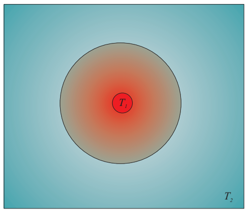

Figure 1.11: A homogeneous spherical conductor.

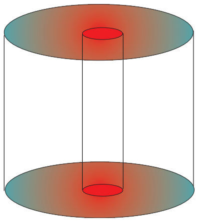

Figure 1.12: A homogeneous cylindrical conductor.

For another example, consider a homogeneous, spherical conductor of radius r_2 with a heat source at a constant temperature, T_1, of radius $r_1 < r_2$ located at its core and a sink surrounding the sphere at temperature T_2 (figure 1.11). Heat flows radially outwards, from the core to the surface and spherical symmetry suggests that the surfaces of interest are given by $r =$ const. Therefore

$$H = \frac{\partial Q}{\partial t} = -4\pi k r^2 \frac{dT}{dr} \tag{1.5.6}$$

with constant H. In the steady state, integrating from r_1 to r_2

$$\int_{r_1}^{r_2} \frac{dr}{r^2} = -\frac{4\pi k}{H}(T_2 - T_1) \;\Rightarrow\; H = -\frac{4\pi k r_1 r_2}{r_2 - r_1}(T_2 - T_1) = -\sigma(T_2 - T_1) \tag{1.5.7}$$

where the thermal conductance is now given by $\sigma = 4\pi k r_1 r_2/(r_2 - r_1)$. A similar argument for cylinders of length L (figure 1.12) will yield

$$H = -\sigma(T_2 - T_1), \quad \sigma = \frac{2\pi k L}{\ln(r_2/r_1)}. \tag{1.5.8}$$

The thermal conductance depends not only on the material but also sensitively on the geometry.

We might also imagine two rods of conductances σ_1 and σ_2 respectively, connected in series as shown in figure 1.13, so that the left surface is kept at temperature T_1 and the right surface at T_2 (one could equally well consider concentric spheres or coaxial cylinders). Then if T_x is the temperature at the boundary between the rods

$$H_1 = -\sigma_1(T_x - T_1), \quad H_2 = -\sigma_2(T_2 - T_x) \tag{1.5.9}$$

represent the energy flux by conduction across the two rods. In the steady state $H_1 = H_2 = H$, so we can eliminate T_x,

$$T_x = \frac{\sigma_1 T_1 + \sigma_2 T_2}{\sigma_1 + \sigma_2} \tag{1.5.10}$$

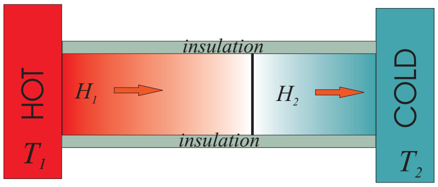

Figure 1.13: Heat conductors in series.

and substitute back into either expression for H to find

$$H = -\sigma_{\text{eff}}(T_2 - T_1) \tag{1.5.11}$$

where

$$\frac{1}{\sigma_{\text{eff}}} = \frac{1}{\sigma_1} + \frac{1}{\sigma_2} \tag{1.5.12}$$

and therefore $R_{\text{eff}} = R_1 + R_2$. The argument may be made for an arbitrary number of conductors in series,[8] so we have

$$\frac{1}{\sigma_{\text{eff}}} = \sum_{j=1}^{N} \frac{1}{\sigma_j}, \quad R_{\text{eff}} = \sum_{j=1}^{N} R_j \tag{1.5.13}$$

for N conductors in series (in the steady state).

On the other hand, imagine that the rods are arranged in parallel as shown in figure 1.14. The net energy transferred is the sum of

$$H_1 = -\sigma_1(T_2 - T_1), \quad H_2 = -\sigma_2(T_2 - T_1) \tag{1.5.14}$$

or

$$\begin{aligned} & H = H_1 + H_2 = -\sigma_{\text{eff}}(T_2 - T_1) \Rightarrow \\ & \sigma_{\text{eff}} = \sigma_1 + \sigma_2, \\ & \frac{1}{R_{\text{eff}}} = \frac{1}{R_1} + \frac{1}{R_2} \end{aligned} \tag{1.5.15}$$

These expressions may likewise be generalized to describe N conductors in parallel by the method of induction,

$$\sigma_{\text{eff}} = \sum_{j=1}^{N} \sigma_j$$

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[8] Use induction to prove this.

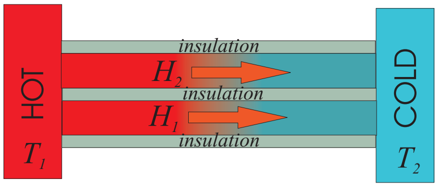

Figure 1.14: Heat conductors in parallel.

$$\frac{1}{R_{\text{eff}}} = \sum_{j=1}^{N} \frac{1}{R_j} \tag{1.5.16}$$

Similarities between these expressions for the effective resistances and the corresponding expressions in resistive electric networks (Ohm's Law) should be obvious.

1.5.2 Conduction: The Heat Equation

Let S be a closed surface within the material, bounding a volume V, and let $d\vec{S}$ be an *inward* directed surface element on S. According to Newton's law, the rate at which energy flows *into* the volume, V, will be

$$\frac{\partial Q}{\partial t} = -k \oint_S d\vec{S} \cdot \nabla T. \tag{1.5.17}$$

If there are no other means of energy transfer into the volume then conservation of energy says that the left hand side must be the rate at which the energy content of the material in this volume is changing. Therefore, if c_p is the specific heat of the material (under constant pressure, for example) and ρ is its mass density then

$$\frac{\partial Q}{\partial t} = \int_V c_p \frac{\partial T}{\partial t} \rho dV. \tag{1.5.18}$$

which means that

$$\int_V \rho c_p \frac{\partial T}{\partial t} dV = -k \oint_S d\vec{S} \cdot \nabla T = k \int_V \nabla^2 T dV, \tag{1.5.19}$$

where we used Gauss' law in the last step. The change of sign occurs because $d\vec{S}$ was chosen to be inward directed. As our volume is arbitrary, we obtain

$$\frac{\partial T}{\partial t} = \frac{k}{\rho c_p} \nabla^2 T, \tag{1.5.20}$$

which will be recognized as the diffusion equation. If we take c_p and ρ to be approximately constant then $\alpha = k/\rho c_p$ is called the coefficient of thermal diffusivity.

Examples

The boundary value problem for $T(t,\vec{r})$ seeks a solution inside some region, R, bounded by a set of surfaces that we will collectively denote by ∂R. The equation is linear, therefore, by the principle of superposition, any linear combination of solutions is also a solution. Furthermore, a unique solution can be obtained only if the initial temperature distribution, $T(0,\vec{r})$, is specified along with Dirichlet or Neumann boundary conditions on ∂R. Dirichlet boundary conditions require specifying the temperature on the bounding surfaces, whereas Neumann boundary conditions require specifying the normal derivative of the temperature on ∂R and apply principally to an insulated boundary.

Returning to the steady state examples of the previous section, we use the heat equation to determine T as a function of the distance from the source. In the steady state, we solve Laplace's equation subject to appropriate boundary conditions. Therefore, in the case of the rod, exploiting the rectangular symmetry and setting $T = T(x)$, we have

$$\frac{d^2T}{dx^2} = 0 \;\Rightarrow\; T = ax + b \tag{1.5.21}$$

where a and b are constants, which must be fixed by the Dirichlet conditions $T(0) = T_1$ and $T(L) = T_2$. This gives

$$T(x) = (T_2 - T_1)\frac{x}{L} + T_1 \tag{1.5.22}$$

which agrees with (1.5.4). For the spherical conductor in the steady state we have $T = T(r)$ and express the Laplacian in spherical coordinates. This gives

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dT}{dr}\right) = 0 \;\Rightarrow\; \frac{dT}{dr} = \frac{a}{r^2} \;\Rightarrow\; T(r) = -\frac{a}{r} + b. \tag{1.5.23}$$

Applying the Dirichlet boundary conditions $T(r_{1,2}) = T_{1,2}$ gives

$$T(r) = \frac{r_1 r_2}{r_2 - r_1}\left(\frac{1}{r} - \frac{1}{r_1}\right)(T_1 - T_2) + T_1 \tag{1.5.24}$$

and it is easy to recover (1.5.7).[9]

Except in the steady state, the temperature will depend on time, $T = T(t,\vec{r})$. One useful method to solve the heat equation is to look for "separable" solutions, $T(t,\vec{r}) = A(t)\Phi(\vec{r})$, which is inserted as an ansatz into the heat equation. We arrive at

$$\frac{\dot{A}}{A} = \frac{\alpha}{\Phi}\nabla^2\Phi \tag{1.5.25}$$

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[9] Problem: Repeat the exercise for the cylindrical conductor: find the temperature as a function of the cylinder radius, then recover its conductance.

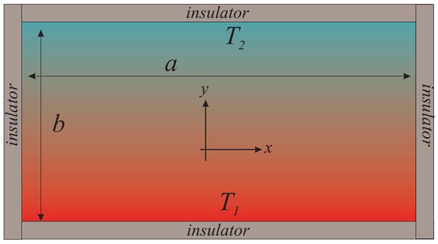

Figure 1.15: A rectangular lamina.

Because the left hand side depends only on t and the right hand side only on $\vec{r}$, they must each equal the same constant,

$$\frac{\dot{A}}{A} = \frac{\alpha}{\Phi}\nabla^2\Phi = -\lambda \tag{1.5.26}$$

so that a general (separable) solution would have the form

$$T(t, \vec{r}) = e^{-\lambda t}\Phi(\vec{r}) \tag{1.5.27}$$

where $\Phi(\vec{r})$ satisfies

$$\nabla^2\Phi(\vec{r}) + k\Phi(\vec{r}) = 0, \quad k = \frac{\lambda}{\alpha}, \tag{1.5.28}$$

which must be solved subject to appropriate boundary conditions.

As an example of the application of this method, consider the rectangular lamina shown in figure 1.15. The plate is heated so that at the initial time, $t = 0$, the temperature on the lamina satisfies

$$T(0, x, y) = T_1 + (T_2 - T_1)\frac{y}{b} \tag{1.5.29}$$

then the sides are kept insulated. We wish to find the way in which the temperature gets redistributed on the lamina. Because the sides are insulated, we will apply Neumann conditions on the edges. In rectangular coordinates, the Helmholtz equation reads

$$\Phi_{xx}(x, y) + \Phi_{yy}(x, y) + \kappa\Phi(x, y) = 0 \tag{1.5.30}$$

so let us seek a separable solution of this equation as well. Let $\Phi(x, y) = A(x)B(y)$, then

$$\frac{A_{xx}}{A} = -\frac{B_{yy}}{B} - \kappa \tag{1.5.31}$$

Again we have a situation in which the left hand side may depend only on x and the right hand side only on y, so they must both be equal to the same constant we call μ. Then

$$A_{xx} - \mu A = 0 \;\Rightarrow\; A(x) = Ce^{\sqrt{\mu}\,x} + De^{-\sqrt{\mu}\,x}, \quad A_x(0) = 0 = A_x(a) \tag{1.5.32}$$

where C and D are complex constants to be determined. Likewise

$$B_{yy} + (\kappa+\mu)B = 0 \;\Rightarrow\; B(y) = Ee^{i\sqrt{\kappa+\mu}\;y} + Fe^{-i\sqrt{\kappa+\mu}\;y}, \quad B_y(0) = 0 = B_y(b) \tag{1.5.33}$$

where E and F are also complex constants to be determined.

Applying the boundary conditions on $A(x)$ we find that $A_x(0) = 0 \;\Rightarrow\; C = D$ and $A_x(a) = 0 \;\Rightarrow\; \sqrt{\mu}a = in\pi$, for integer n, which gives

$$A_n(x) = 2C_n \cos\left(\frac{n\pi x}{a}\right) \tag{1.5.34}$$

in terms of a real constant C_n. In the same way, $B_y(0) = 0 \;\Rightarrow\; F = E$ and $B_y(b) = 0 \;\Rightarrow\; \kappa + \mu = m^2\pi^2/b^2$ for integer m and

$$B_m(y) = 2E_m \cos\left(\frac{m\pi y}{b}\right).$$

for some real E_m. Solutions for $T(t, x, y)$ satisfying the insulated boundary conditions depend on two integers, (m, n), and may be written as

$$\Phi_{mn}(t, x, y) = A_{mn}e^{-\lambda_{mn}t} \cos\left(\frac{n\pi x}{a}\right) \cos\left(\frac{m\pi y}{b}\right) \tag{1.5.35}$$

where

$$\lambda_{mn} = \alpha\kappa_{mn} = \alpha\left(\frac{n^2}{a^2} + \frac{m^2}{b^2}\right). \tag{1.5.36}$$

We now use the fact that the heat equation is linear and the solutions are superposable to write the most general separable solution satisfying the given boundary conditions in terms of a double Fourier series,

$$\Phi(t, x, y) = \sum_{m,n=-\infty}^{\infty} \left[A_{mn}e^{-\lambda_{mn}t} \cos\left(\frac{n\pi x}{a}\right) \cos\left(\frac{m\pi y}{b}\right)\right] \tag{1.5.37}$$

and must now ensure that it also satisfies the initial condition of (1.5.29), *i.e.,*

$$T_1 + (T_2 - T_1)\frac{y}{b} = \sum_{m,n=-\infty}^{\infty} \left[A_{mn} \cos\left(\frac{n\pi x}{a}\right) \cos\left(\frac{m\pi y}{b}\right)\right] \tag{1.5.38}$$

Since the left hand side does not depend on x, we may safely set $A_{mn} = 0$ when $n \neq 0$. We are left with the Fourier series

$$T_1 + (T_2 - T_1)\frac{y}{b} = \frac{1}{2}B_0 + \sum_{m=1}^{\infty} B_m \cos\left(\frac{m\pi y}{b}\right) \tag{1.5.39}$$

The coefficients can then be evaluated in terms of the integrals

$$\begin{aligned} B_0 &= \frac{2}{b}\int_0^b \left(T_1 + (T_2 - T_1)\frac{y}{b}\right) dy = (T_1 + T_2) \\ B_m &= \frac{2}{b}\int_0^b \left(T_1 + (T_2 - T_1)\frac{y}{b}\right) \cos\left(\frac{m\pi y}{b}\right) dy = \frac{2[1-(-)^m]}{m^2\pi^2}(T_1 - T_2) \end{aligned} \tag{1.5.40}$$

so we finally get the (unique!) solution

$$T(t,y) = T_{\text{av}} + 2(T_1 - T_2)\sum_{m=1}^{\infty} \frac{[1-(-)^m]}{m^2\pi^2} e^{-\alpha m^2 t/b^2} \cos\left(\frac{m\pi y}{b}\right). \tag{1.5.41}$$

where T_{av} is the average of the boundary temperatures, $T_{\text{av}} = (T_1 + T_2)/2$. After a time $t \gg b^2/\alpha$, the temperature of the lamina approaches a constant value equal to T_{av}.[10],[11]

1.5.3 Convection

Energy transfer between two or more macroscopic systems, or within a single macroscopic system that is not in equilibrium, by the gross movement of the substance(s) composing the system(s), is called **convection**. A typical example of convection occurs when boiling water in a vessel from below. Energy is transferred to the lowest layer of the water in the vessel by conduction. As the layer warms up it expands and its density decreases causing it to rise by Archimedes' principle. Cooler layers above it descend to take its place and get warmed by contact with the base of the the vessel. In this way there is a gross movement of the water which eventually transfers the energy being supplied through the base to the entire volume of water in the vessel. Convection is employed by radiators, which warm a room by warming the air in contact with them. The hot air then rises allowing colder air to take its place close to the radiator, thus setting up a circulation. Wind currents, ocean currents etc., are all examples of convection. Convection is responsible for energy transfer in the sun and in any main sequence star,[12] occurring in a spherical shell, whose thickness

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[10] Problem: Solve the steady state heat equation for the lamina given the following Dirichlet conditions: $T(0,y) = 0,\ T(a,y) = 0,\ T(x,0) = 0,\ T(x,b) = f(x)$, where $f(x) = Ax(a-x)$.

[11] Problem: Many solutions, but not all, can be obtained using the technique of separation of variables. Show that

$$T(t,x) = \frac{1}{\sqrt{\kappa t}} e^{-x^2/(4\kappa t)}$$

solves the one dimensional heat equation. Determine the initial ($t \to 0$) temperature distribution. What happens to the distribution as $t \to \infty$?

[12] A main sequence star is one that exists in hydrostatic equilibrium, *i.e.,* one in which the tendency of matter to collapse gravitationally is balanced by the outward pressure that results from the fusion (of Hydrogen) occurring in its core.

is about 200,000 km, that lies between a region dominated by radiation and adjacent to the fusing core, called the radiation zone, and the photosphere, which is, roughly speaking, the thin, visible layer (about 100 km) of gas on the surface of the sun from which photons are able to escape freely. The range of radii in which the energy is transferred primarily by convection is called the "convection zone". In this region, mass movement of the plasma within the star forms a circular current in which the heated plasma at the bottom rises and cooler plasma that has passed its energy into the photosphere descends. Convective heat transfer occurs whenever there is the possibility of a flow and when the temperature gradient is high enough. Unfortunately, however, a quantitative discussion of convection involves the theory of fluid dynamics and lies beyond the scope of these notes. Details may be found in the notes on Classical Dynamics in this same series.

1.5.4 Radiation

A third means of energy transfer is by **thermal radiation**. In a hot body, energy is distributed randomly between its constituent atoms and molecules. This energy causes the charges within the body to oscillate and the oscillating charges then emit electromagnetic waves. When the ensuing radiation is in thermal equilibrium with its source, it is said to be "thermal".

Every radiating body can be characterized by its **absorptivity** and its **emissivity**. The absorptivity, a, of a body is the fraction of incident radiant energy that it is able to absorb. An ideal **black body** is defined to be a perfect absorber, *i.e.,* one that absorbs *all* of the incident radiant energy, so for such a body $a = 1$. We will use the subscript "B" to denote the black body. Real objects have some reflectivity and are not perfect black bodies. The closest approximation to a perfect black body would be a "cavity", *i.e.,* a small hole leading to the inside of a hollow object that is coated with some amorphous black material, such as soot. Radiation incident on the hole from the outside is reflected a large number of times on the interior walls as shown in figure (1.16); during each collision the walls will absorb some of the incident radiation and hence the cavity acts as a near-perfect absorber. If the temperature of the cavity is above that of its environment, radiation may leave the cavity only after multiple reflections with the walls during which it achieves thermal equilibrium with them. It is therefore characterized exclusively by the temperature of the cavity walls and does not depend on the material of which they are made. The spaces within the pores of hot charcoal behave like small cavities, absorbing incident radiation and emitting radiation that is characterized only by the temperature of the coal.

The emissivity of a body is defined as the ratio of the energy radiated by the body to the energy radiated by a perfectly black body at the same temperature. No body is as efficient an emitter as a black body. This can be proved quite easily if we consider two bodies, A and B, one of which (say B) is a black body, which are able to exchange energy with each other by radiation only and exist in thermal equilibrium at temperature

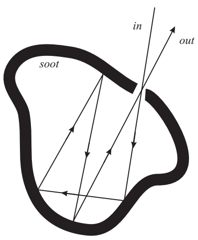

Figure 1.16: A "cavity"

T. Let P_B be the energy radiated by the black body per second and assume that *all* of it is incident on body A. If a is the absorptivity of A then the energy absorbed by A will be $P_{\rm abs} = aP_B$. But, since A and B are in thermal equilibrium at a fixed temperature, A must be radiating back the same amount of energy, otherwise it would be a net absorber or emitter of energy and either warm up or cool down, which is not allowed because A and B are in thermal equilibrium by assumption. Thus $P_{\rm rad} = P_{\rm abs} = aP_B$. By definition then

$$e = \frac{P_{\rm rad}}{P_B} = a \tag{1.5.42}$$

The statement that the emissivity of a body in thermal equilibrium is equal to its absorptivity is known as **Kirchoff's law** of thermal radiation. It follows that the emissivity can only take values between zero and unity and if the emissivity of a body is unity then it is a black body. In general, the absorptivity and emissivity will depend on the temperature, the wavelength of the radiation and the angle of incidence or emission. However, to a very good approximation they change only slowly with these variables and can often be taken to be constant.

Now it has been known, since the late nineteenth century, that the total power radiated by a black body depends only on the temperature of the source according to

$$P = \sigma A T^4, \tag{1.5.43}$$

where A is the surface area of the source and T is its absolute temperature. This is the **Stefan-Boltzmann** law of thermal radiation and the constant σ is called the **Stefan-Boltzmann constant**. It has the value $\sigma = 5.67\times10^{-8}$ W·m^{-2}·K^{-4}. Its origin is quantum mechanical and it can be determined directly in terms of the fundamental constants $\hbar$, (Planck's constant), the speed of light, c, and Boltzmann's constant, k_B. It follows that the total power radiated by *any* body in thermal equilibrium at the same temperature will be

$$P = \sigma e A T^4, \tag{1.5.44}$$

where e is its emissivity. The total radiated power does not give us any of the details of the

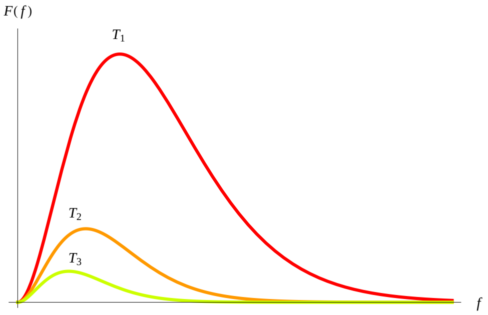

Figure 1.17: The spectral radiancy of a black body for temperatures $T_1 > T_2 > T_3$.

radiation itself. For instance, it says nothing about the amount of radiation emitted by a black body within different frequency ranges. For this purpose one defines the **spectral radiancy**, $\mathcal{F}(f,T)$, so that $\mathcal{F}(f,T)df$ represents the energy radiated per unit time per unit area of the radiating surface (the **flux**) in the frequency range between f and $f+df$. By definition, it should satisfy the condition

$$\mathcal{F}(T) = \int_0^\infty \mathcal{F}(f,T)df = \sigma T^4, \quad P = A\mathcal{F}(T) \tag{1.5.45}$$

for a black body. Experimentally, $\mathcal{F}(f,T)$ can be easily determined by passing the radiation emitted from the source through filters of known frequency bandwidth before measuring the flux and is given by the curves in figure (1.17). These curves have the interesting feature that each depends *exclusively* on the temperature of the black body, *i.e.,* it is sufficient to know just two points on any curve to determine the curve entirely. Furthermore, the radiancy at every temperature rapidly approaches zero both at the low and at the high frequency ends of the spectrum (which is essential for the area under the curves to remain finite) and each curve peaks at a frequency that depends, once again, only on the temperature of the source. **Wien's displacement law** says that this frequency, at which the radiated flux is maximum, is directly proportional to the temperature,

$$f_{\max} = \delta_W T \tag{1.5.46}$$

where δ_W is Wien's constant, with value $\delta_W = 5.88 \times 10^{10}$ Hz/K. It may also be stated in terms of the wavelength at which the radiated flux peaks; one finds

$$\lambda_{\max} = \frac{b_W}{T} \tag{1.5.47}$$

where $b_W = 2.898 \times 10^{-3}$ m·K.

For example, it is known that the radiation intensity from our sun peaks at around $\lambda_{\text{max}} = 500$ nm. According to Wien's displacement law, assuming that the sun behaves roughly like a black body[13] and that the radiation we receive arrives from the photosphere, this would mean the the photosphere's temperature is on the average about 5796 K. Actually the temperature of the photosphere varies from above 6000 K near the convection zone down to around 4500 in its outermost layers, with an average temperature of about 5800 K. Knowing the temperature of the photosphere, we can estimate the radiation flux from the surface as $\mathcal{F} = \sigma T^4 \approx 64 \times 10^6$ W/m^2, and therefore its total power output or **Luminosity** as

$$L = 4\pi R_s^2 \mathcal{F} \approx 3.9 \times 10^{26} \text{ W},$$

given that its mean radius is $R_s \approx 6.96 \times 10^8$ m.[14]

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[13] Actually the sun is not a perfect black body, having an emissivity of about 0.95.

[14] Problem: Considering that the energy emitted by the sun is predominantly obtained by repeatedly converting four Hydrogen nuclei (protons) into one Helium nucleus whose mass is $3.97m_p$, determine the number of reactions that must be carried out in the core per second to sustain the sun's luminosity. Determine the Hydrogen consumption per second and, assuming that roughly 10% of the sun's mass will be used during the main sequence, determine for how long the sun can be expected to remain stable.

Chapter 2

The First Law

2.1 The Internal Energy

The first law of thermodynamics is essentially a law of conservation of energy for macroscopic systems. "Conservation" can be imposed by requiring that the variation of the total energy of the system and its environment is identically zero. However, in order to make this line of thinking precise one should be able to say what exactly the energy of a macroscopic system is in the first place. Now every macroscopic system is eventually a mechanical system, albeit composed of a very large number of constituents, and it is reasonable to say that its energy is just the average total mechanical energy, *i.e.,* the sum of the kinetic and potential energies of its constituents. Call this energy the **internal energy**, U, of the system and assume that it is a function of the state of the system, *i.e.,* $U = U(\vec{Z})$, where $\vec{Z}$ is used to denote all the state variables, intensive and extensive. If the system is isolated both thermally and mechanically so that it exchanges no energy with the environment and then transforms from some initial state, i, to some final state, f, then one may further assume that $U(\vec{Z}_i) = U(\vec{Z}_f)$. If some external forces are acting upon the system by virtue of its interaction with the environment then there is no reason to assume that the internal energy would stay constant because then our system may do work upon the environment or have work done upon it by the environment via the external forces, in which case one may argue that the change in internal energy should be equal to the work done,

$$\Delta U = U(\vec{Z}_f) - U(\vec{Z}_i) = -W_{if}, \tag{2.1.1}$$

or, in infinitesimals,

$$dU(\vec{Z}) = -đW = -\sum_i p_{X_i} dX_i \tag{2.1.2}$$

where p_{X_i} is the "pressure" associated with the deformation of the extensive variables X_i of the system (eg., if X_i is the volume, p_{X_i} is the usual pressure). We have chosen our sign conventions in such a way that W_{if} would be positive when the system does work and negative when work is done upon it.

Equation (2.1.1) would hold true only if the work done were independent of the actual transformation process in going from the initial state, i, to the final state, f, because we have assumed that the internal energy is a function of the state variables (a function of state) and so the left hand side of (2.1.1), dU, is an exact differential. But we have already noted that the right hand side, $đW$, is not an exact differential, so we can expect that the change in internal energy will *not* always be the work done by the system. For example, when an ideal gas is compressed isothermally work is done on the gas but its internal energy remains unchanged – as we will see shortly. Situations like this would mean one of two things: either energy is not conserved or the system is able to exchange energy with its environment in a form that is different from mechanical work. If we assume that energy is conserved[1] and take into account energy transfer on the molecular level, then we write

$$dU = -đW + đQ. \tag{2.1.3}$$

where $đQ$ is the "heat". It cannot be an exact differential because $đW$ is not an exact differential, but the sum of $đQ$ and $đW$ must be an exact differential. We have thus arrived at the **first law** of Thermodynamics, which states simply that there is a function of state, called the internal energy (our function $U(\vec{Z})$), which satisfies

$$dU = đQ - đW, \quad \text{or} \quad đQ = dU + đW \tag{2.1.4}$$

Let's pause to reiterate the sign conventions being used here:

- $đQ$ is positive when energy is transferred into the system, negative when energy is released by the system into the environment.
- $đW$ is positive when work is done by the system, negative when work is done on the system by the environment
- dU is positive when the internal energy increases and negative when the internal energy decreases.

For the example of the ideal gas undergoing isothermal compression: since we know that $dU = 0$ and $đW < 0$ it follows that $đQ < 0$ and hence energy is being released from the gas into a "heat reservoir" (environment), which is being used to keep it at a fixed temperature.

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[1] The **law of conservation of energy**, which says that energy can neither be created nor destroyed, is an empirical law of physics having a long and sometimes confused history. Today, by "energy" we mean all forms of it, including matter energy, according to Einstein's famous relation $E = mc^2$, which comes into play when processes such as fusion, in which mass is converted into radiation, are involved.

A deeper, more microscopic way to see how the first law arises is to realize that because the variables determining the thermodynamic states are small in number compared to the number of microscopic, mechanical variables required for a complete mechanical description of it, there will in general exist a very large number of "microstates" (states defined by the allowed values of the $6N - 10$ variables) that are all consistent with any given thermodynamic state. Let us label these microscopic states by α, then we associate the internal energy with the average value of the mechanical energy E_α associated with the microstates. Thus

$$U = \sum_\alpha P_\alpha E_\alpha \tag{2.1.5}$$

where P_α represents the probability that the system is in the microstate α. Any change in U arises for one or both of two reasons: either the distribution of probabilities changes or the energies associated with the microstates changes. In other words,

$$dU = \sum_\alpha (dP_\alpha) E_\alpha + \sum_\alpha P_\alpha (dE_\alpha) \tag{2.1.6}$$

The right hand side consists of two inexact differentials. The first term is associated with changes in the occupation probability distribution *i.e.,* the probabilities with which the different microstates are occupied, while the energies of the states themselves remain unchanged. The second term is associated with changes in the energies of the microstates, holding the occupation probability distribution fixed. The second sum is associated with the mechanical work that is done on the system,

$$đW = -\sum_\alpha P_\alpha (dE_\alpha), \tag{2.1.7}$$

where the negative sign accounts for the fact that if the energies associated with the states decrease then the system does work on the environment and vice versa. The first term is associated with the "heat", *i.e.,*

$$đQ = \sum_\alpha (dP_\alpha) E_\alpha \tag{2.1.8}$$

Note that the sum of probabilities is constrained to be unity because the system must occupy one of its microstates at any time, therefore $\sum_\alpha dP_\alpha = 0$. Thus $đQ > 0$ only if the probability to occupy higher energy states increases causing the probability of occupying lower energy states to correspondingly decrease. Conversely, $đQ < 0$ if the reverse occurs. With these definitions, (2.1.6) is precisely (2.1.4) and, in this way of looking at it, heat is associated with the redistribution of the probabilities with which the system occupies its various microstates, holding the energy of the microstates fixed.

2.2 Simple Applications to Gases

Consider a gas, not necessarily ideal, whose macrostates are labeled by the set (p, V, T) and governed by some equation of state $f(p, V, T) = 0$. Evidently we can use the equation of state to eliminate one of the three variables and express the internal energy in terms of the other two. This can be done in three ways; if we eliminate p then the internal energy gets expressed as $U(V, T)$

$$đQ = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V} + p\right)_T dV \tag{2.2.1}$$

where the suffices tell which variable is held fixed during the differentiation. Likewise, if we chose to elliminate V, we would get

$$đQ = \left(\frac{\partial U}{\partial T} + p\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial U}{\partial p} + p\frac{\partial V}{\partial p}\right)_T dp \tag{2.2.2}$$

and finally, ellimating T,

$$đQ = \left(\frac{\partial U}{\partial p}\right)_V dp + \left(\frac{\partial U}{\partial V} + p\right)_p dV \tag{2.2.3}$$

These three relations have some interesting physical applications as we now see.

2.2.1 Heat Capacities of Gases

By definition, the heat capacity of the gas is $đQ/dT$ but, because $đQ$ is inexact, the heat capacity will be process dependent. Two heat capacities are of interest, *viz.,* (i) the heat capacity at constant volume, C_V and (ii) the heat capacity at constant pressure, C_p. (i) is defined as the heat capacity during an isovolumetric process and (ii) as the heat capacity during an isobaric process. It is easy to see then that

$$C_V = \left(\frac{đQ}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \tag{2.2.4}$$

by (2.2.1), where we have set $dV = 0$, since the process is isovolumetric. To find C_p we can use the second equation with the same reasoning to get

$$C_p = \left(\frac{đQ}{dT}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p \tag{2.2.5}$$

If we restrict attention to ideal gases we can use the equation of state,

$$pV = NkT.$$

Later, we will argue that the equation of state implies that the internal energy can be a function only of the absolute temperature. This was known early on an experimental basis following Joule: two isolated chambers A and B are joined by a tube with a stop-cock seperating them. Chamber B is very much larger than champer A. Chamber A is filled with an ideal gas up to a certain pressure whereas chamber B is a vacuum. The stop-cock is suddenly opened so that the gas flows freely from A to B. In doing so the gas does no work, so by the first law of thermodynamics

$$đQ = 0 = dU + đW \Rightarrow dU = 0 \tag{2.2.6}$$

Now the final temperature, volume and pressure of the gas are measured and it is found that $dT = 0$, *i.e.,* the process occurs isothermally. Neither dp nor dV are vanishing, so we conclude that $U = U(T)$, for an ideal gas. Thus we can write

$$C_V = \frac{dU}{dT} \Rightarrow \Delta U = U_f - U_i = \int_i^f C_V(T)dT \tag{2.2.7}$$

For a more general equation of state, C_V could depend on both T and V so we should have

$$U(T,V) = \int_{V,i}^f C_V(T,V)dT + \mathcal{U}(V) \tag{2.2.8}$$

where the subscript "V" on the integral means that we integrate with respect to T keeping V fixed, and where $\mathcal{U}$ is a function only of V. Returning to the ideal gas, the first law takes the form

$$đQ = C_V dT + pdV \tag{2.2.9}$$

for *all* processes. Now if the process is isobaric then either from the first law above or according to (2.2.5) (applying the equation of state) we should have

$$C_p = C_V + Nk \tag{2.2.10}$$

2.2.2 Adiabatic Equation of State

A process in which no energy is transferred to a system except by work is said to be **adiabatic** and the system is then said to be *thermally isolated.* During an adiabatic process, $đQ = 0$, and for an ideal gas

$$\begin{aligned} \left(\frac{\partial T}{\partial p}\right)_V &= \frac{V}{Nk} \\ \left(\frac{\partial T}{\partial V}\right)_p &= \frac{p}{Nk} \end{aligned} \tag{2.2.11}$$

so by (2.2.3), using $U = U(T)$,

$$\frac{C_V}{Nk} V dp + \left(\frac{C_V}{Nk} + 1\right) pdV = \frac{C_V}{Nk} V dp + \frac{C_p}{Nk} pdV = 0 \tag{2.2.12}$$

and therefore

$$\frac{dp}{p} = -\frac{C_p}{C_V}\frac{dV}{V} \tag{2.2.13}$$

The quantity $\gamma = C_p/C_V$ is of some interest in thermodynamics, and is related to the number of **degrees of freedom** of the elementary constituents as we shall soon see. (The number of degrees of freedom of a molecule is the number of ways in which it can store energy.) Integrating the above we find

$$pV^\gamma = \text{const.} \tag{2.2.14}$$

This is an alternative equation of state, applicable only to ideal gases undergoing adiabatic processes. Knowing the process is equivalent to having an additional constraint on the system, which can be used to eliminate yet another variable of state. Thus, in the case of the ideal gas, only one of the three thermodynamic variables remains independent during any given process (this is why the process is a path in the p-V plane). The resulting equation of state will, of course, be applicable only to the given process. Other examples are the isovolumetric process in which the equation of state takes the form $p/T = $ const. (law of Charles), the isobaric process during which $V/T = $ const. (law of Gay-Lusac), and the isothermal process during which $pV = $ const. (law of Boyle).

2.3 Elementary Kinetic Theory of Gases

We will now embark on a simplistic treatment of ideal gases which, nevertheless, gives a remarkably accurate picture of their behavior. This is a digression into elementary Kinetic theory, a topic we shall return to in some detail in a forthcoming chapter.

2.3.1 Basic Postulates and Results

We take the microscopic point of view, making the following assumptions about what an ideal gas really is.

- An ideal gas is made up of molecules, all of which are identical.
- The molecules obey Newton's laws.
- The number of molecules is large, so that the laws of statistics apply

- Although the number of molecules is large, the volume they occupy is vanishingly small compared to the total volume of the gas.
- There are no interactions between the molecules except by hard-body collisions.
- The time during which the molecular collisions occur (the collision time) is negligibly small compared with the the time spent by the molecules as free particles (free time).

First consider a one-dimensional gas in a one-dimensional box, of length L. Let the length of the box lie along the $x-$axis and consider a single molecule travelling along this axis, for convenience from left to right. Upon colliding with the wall on the right, the molecule will change direction, moving to the left. If the box is rigid, much heavier than the moelcule and if the collision is elastic, the molecule's recoil speed will be the same as its original speed. It's direction is reversed, however, so if v_x is its speed prior to collision,

$$\Delta p = p_f - p_i = -2mv_x \tag{2.3.1}$$

The molecule must travel a distance $2L$ before returning to the same wall for another collision with it, so it returns after a time $\Delta t = 2L/v$. Thus, we can estimate the rate at which the wall imparts momentum to the molecule as

$$F_{\text{wall}} = \frac{\Delta p}{\Delta t} = -\frac{mv_x^2}{L} \tag{2.3.2}$$

By Newton's second law, this must be the force exerted by the wall on the molecule and by Newton's third law it is the force that the molecule exerts upon the wall (in the opposite direction), *i.e.*,

$$F_{\text{mol}} = +\frac{mv_x^2}{L} \tag{2.3.3}$$

If there are N molecules in the box, the rate at which momentum is imparted to the wall, or the force on the wall, is

$$\langle F \rangle = \frac{Nm\langle v_x^2 \rangle}{L}, \tag{2.3.4}$$

where the angular brackets denote that we are speaking about the average behavior. The pressure on the wall is then just the force divided by the cross-sectional area of the wall,

$$p = \frac{Nm\langle v_x^2 \rangle}{LA} = \frac{Nm\langle v_x^2 \rangle}{V} \Rightarrow pV = Nm\langle v_x^2 \rangle \tag{2.3.5}$$

In general, molecules do not travel exclusively in one direction. We expect motion in all directions, randomly distributed between the three linearly independent directions of space. In other words,

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle \tag{2.3.6}$$

(where we have used mean square components because the *average* of each component can be expected to vanish, $\langle v_x\rangle = \langle v_y\rangle = \langle v_z\rangle = 0$, it being equally probable for a molecule to be traveling to the left as to the right otherwise one direction in the gas would be preferred over another). Because

$$\langle v^2\rangle = \langle v_x^2\rangle + \langle v_y^2\rangle + \langle v_z^2\rangle \tag{2.3.7}$$

it then follows that

$$\langle v_x^2\rangle = \langle v_y^2\rangle = \langle v_z^2\rangle = \frac{1}{3}\langle v^2\rangle \tag{2.3.8}$$

and we could write (2.3.5) as

$$pV = \frac{1}{3}Nm\langle v^2\rangle. \tag{2.3.9}$$

which looks strikingly similar to the equation of state of the ideal gas, if suitable identifications are made.[2]

2.3.2 Internal Energy and Heat Capacities

Indeed, comparing we find that the temperature is to be associated with the mean kinetic energy, $\langle K_{\text{mol}}\rangle$

$$kT = \frac{1}{3}m\langle v^2\rangle = \frac{2}{3}\langle K_{\text{mol}}\rangle \tag{2.3.10}$$

In the first place, we obtain an interesting relationship between the root mean square velocity, v_{rms} and the absolute temperature of the gas,

$$v_{\text{rms}} \overset{\text{def}}{=} \sqrt{\langle v^2\rangle} = \sqrt{\frac{3kT}{m}} \tag{2.3.11}$$

In the second place, since we assumed that there were no interactions between the molecules, the only contribution to the molecular energy comes from the kinetic energy and we have

$$\langle E_{\text{mol}}\rangle = \langle K_{\text{mol}}\rangle = \frac{3}{2}kT \tag{2.3.12}$$

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[2] We have used the non-relativistic approximation in this derivation. If the molecules of the gas are relatvistic (as might occur under extreme conditions as, for example, for the electron gas in a white dwarf) then (2.3.9) gets modified according to

$$pV = \frac{1}{3}Nv_{\text{rms}}p_{\text{rms}},$$

where v_{rms} and p_{rms} are respectively the root-mean-square values of the three velocity and relativistic momentum. Show this, using the relativistic equations of motion, assuming that the box is stationary in the frame of the observer.

Since each (point-like) molecule has but three degrees of freedom, we can say that it has $kT/2$ units of energy per degree of freedom. Finally, dividing (2.3.9) by V and calling n the number density of molecules

$$p = \frac{1}{3}nmv_{\rm rms}^2 = \frac{1}{3}\rho v_{\rm rms}^2 \tag{2.3.13}$$

(2.3.9) gives us a relationship between the pressure of a gas, its density, ρ, and the mean molecular speed.

The internal energy of the gas is just the sum of the individual molecular kinetic energies

$$U = N\langle E_{\rm mol}\rangle = \frac{3}{2}NkT \tag{2.3.14}$$

which, as mentioned earlier, depends only on the temperature. It also immediately follows that the heat capacity of the gas at constant volume is,

$$C_V = \frac{dU}{dT} = \frac{3}{2}Nk \tag{2.3.15}$$

and therefore the heat capacity at constant pressure must be

$$C_p = C_V + Nk = \frac{5}{2}Nk \tag{2.3.16}$$

Thus the ratio of heat capacities has the value

$$\gamma = \frac{C_p}{C_V} = \frac{5}{3} \tag{2.3.17}$$

for an ideal gas of point-like molecules. Point-like molecules are idealizations, of course. If the molecules have additional structure, we must learn to take it into account. For instance, point-like molecules carry energy only by virtue of their translational motions. With additional structure a molecule may carry energy in internal vibrations as well as in rotational motion about its center of mass.

2.3.3 Law of Equipartition of Energy

We have seen that the average energy of each molecule in a gas is $3kT/2$, and that the factor of "3" can be attributed to the three translational degrees of freedom of a point like molecule, so that each degree of freedom carries an average of $kT/2$ units of energy. The law of **equipartition** of energy declares that the same holds true for vibrational and rotational degrees of freedom as well.

As examples, consider a diatomic molecule and assume that the bond between its constituent atoms is effectively rigid. The molecule has three translational degrees of freedom (center of mass motion). In addition it has two rotational degrees of freedom corresponding to rotations about the two axes orthogonal to the axis of symmetry of the molecule (the line joining its atoms). Of course, we exclude rotations about the axis of symmetry itself, since such rotations carry no energy on account of the fact that the moment of inertia about this axis vanishes. The internal energy of the gas of diatomic molecules is the

$$U = \frac{5}{2}NkT \tag{2.3.18}$$

gving $C_V = 5Nk/2$, $C_p = 7Nk/2$ and $\gamma = 7/5$. For polyatomic molecules, all three rotational degrees of freedom are to be counted and we find $U = 3NkT$, $C_V = 3Nk$, $C_p = 4Nk$ and $\gamma = 4/3$. The counting of vibrational degrees of freedom must take into account the fact that energy is stored both in the kinetic and potential energy of the oscillator, so there are generally two vibrational degrees of freedom per space dimension or six for a general polyatomic molecule. In general, let g be the number of degrees of freedom per molecule, then

$$E = \frac{g}{2}NkT \Rightarrow C_V = \frac{g}{2}Nk, \quad C_p = \frac{g+2}{2}Nk, \quad \gamma = \frac{g+2}{g} \tag{2.3.19}$$

so γ is related to the number of degrees of freedom per molecule, as promised earlier.

In practice, one has to take into account the quantum theory which requires that the energy of motion with closed or periodic phase space orbits is quantized. What this means is that although a molecule may possess rotational and vibrational degrees of freedom, it can be excited to higher rotational and vibrational energy levels only by the absorption of discrete packets of energy. If the minimum energy required for a jump between energy levels is not available to the molecule, the rotational and vibrational energy levels cannot be excited. Therefore, at low temperatures the energy a molecule may gain by collisions with other molecules is generally not large enough to raise it to the first excited state of either rotation or vibration. As a consequence, at low temperatures, a molecule will have only three effective (translational) degrees of freedom. As the temperature is raised, a fraction of the molecules may be able to acquire enough energy through collisions to excite them to the first rotational state. The fraction of excited molecules will rise with the temperature and the specific heat will also begin to rise. This continues until the temperature is high enough that *all* the molecules are able to obtain energy enough to rotate. At this point the number of effective degrees of freedom per molecule is five or six depending of whether the molecule is diatomic or polyatomic. Rotational degrees of freedom contribute in most gases at around room temperature. However, the temperature must be raised significantly (to about 10^3 K) to begin to excite vibrational energies, which begin to contribute fully to the specific heat of the gas only at above 10^4 K.

2.3.4 The Mean Free Path

In our simple model above, we assumed that the molecule travels freely from one end of the box to another. In fact this cannot be the case if the molecule has a non-vanishing collision cross-section, *i.e.,* a finite size. One can guess how far a molecule would travel collision-free, if it had an effective diameter d as follows. The estimate is easily made on more or less dimensional grounds, for in travelling a distance D a spherical molecule sweeps out a cylinder of radius $d/2$ and length D. Another molecule would collide with it if the centers of the two molecules were to come within a distance d from one another. This means that the number of collisions that a particular molecule experiences in traveling a distance D would be approximately the number of molecules that lie within a cylinder of radius d and length D. Let n be the number density of molecules in the gas and N_D the number of collisions in a distance D

$$N_D = nV_D = n\pi d^2 D \Rightarrow D = \frac{N_D}{n\pi d^2} \tag{2.3.20}$$

The distance over which one collision may be expected (called the **mean free path**, $\langle l\rangle$) is then

$$\langle l\rangle = \frac{1}{n\pi d^2} \tag{2.3.21}$$

This rather ad-hoc calculation is in the spirit of the "derivation" of the internal energy in the previous section. However, the result is not so far from that obtained from a more robust calculation we shall do later in this text. If one takes into account the motion of all the molecules (we have essentially assumed that only one – "our" – molecule is in motion relative to the gas as a whole and that all the other molecules in the gas are at rest relative to it!) one finds the Clausius formula

$$\langle l\rangle = \frac{1}{\sqrt{2}n\pi d^2} \tag{2.3.22}$$

To get an idea of the magnitude of the mean free path, let us compute it for an average molecule of air at 20°C and 1 atm pressure. The average molecule of air has mass (20% Oxygen and 80% Nitrogen)

$$\langle m\rangle = [0.2m_O + 0.8m_N]m_p = [(0.2)(32) + (0.8)(28)] \times 1.67 \times 10^{-27} = 4.81 \times 10^{-26} \text{ kg} \tag{2.3.23}$$

The density of dry air at STP[3] is $\rho \approx 1.29$ kg/m^3, therefore the number density of molecules is

$$n = \frac{\rho}{\langle m\rangle} = \frac{1.29}{4.81 \times 10^{-26}} = 2.68 \times 10^{25} \text{ /m}^3 \tag{2.3.24}$$

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[3] We ae using NIST's definition of STP here.

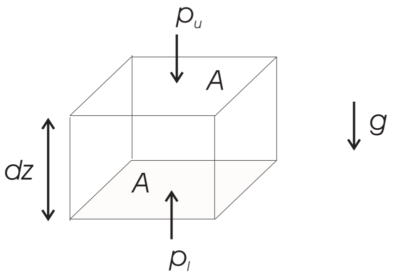

Figure 2.1: A rectangular piped of surface area A and height dz in a gravitational field

Take the diameter of the average molecule to be $d \approx 3.5 \times 10^{-10}$ m. Plugging all this information into the expression for $\langle l \rangle$ gives $\langle l \rangle = 6.9 \times 10^{-6}$ cm.[4]

Now if we know the mean free path, we can compute the **mean free time** τ, which is the time between collisions, as the name suggests,

$$\tau = \frac{\langle l \rangle}{v_{\text{rms}}} \tag{2.3.25}$$

and the **collision frequency**, defined as the reciprocal of the mean free time, becomes $f = 1/\tau = v_{\text{rms}}/\langle l \rangle$. For the example of air at STP we find that $v_{\text{rms}} \approx 508.167$ m/s and so $f \approx 7.4 \times 10^9$ s^{-1}. A molecule of air is collision free for less than a nanosecond!

2.3.5 Maxwell-Boltzmann distribution of Molecular Velocities

We mentioned taking averages in the previous section, but with no word about the distribution of probabilities over which the averages were taken. Yet, we must assume that there is a certain probability distribution over the velocities of molecules at any given temperature. In this section we consider what that distribution might look like.

This so-called molecular velocity distribution was first discussed by J.C. Maxwell in 1859, however we shall follow L. Boltzmann's derivation. Consider a volume of some ideal gas in the shape of a rectangular parallelpiped and situated in an external gravitational field which we assume for convenience to be constant and directed "downward", as shown in figure 2.1. From elementary hydrostatics, we know that the pressure of the gas at the lower surface of the cube will not be the same as the pressure at the upper surface. Let $n = n(z)$ represent the number density of molecules, p_u and p_l the pressures on the upper and lower surfaces, each of which has area A, and let dz be the height of the rectangular

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[4] Problem: This answers a question we may have had about the applicability of classical mechanics. Quantum effects become important when the wave functions of molecules overlap leading to interference. Argue (i) that a typical molecule of air at STP is non-relativistic and (ii) that its de Broglie wavelength is many orders of magnitude smaller than its mean free path.

parallelpiped. Evidently, in equilibrium we must have

$$(-p_u + p_l)A = nmgAdz, \tag{2.3.26}$$

where m is the molecular mass of the molecules. Then if we let $p_u - p_l = dp$,

$$\frac{dp}{dz} = -nmg \tag{2.3.27}$$

and from the equation of state, $p = nkT$, assuming that T does not change with height,

$$\frac{dn}{dz} = -\frac{nmg}{kT} \tag{2.3.28}$$

gives the number density of molecules at any height z in terms of the number density n_0 at $z = 0$. As the temperature is assumed uniform throughout our gas, integration yields

$$n = n_0 e^{-\frac{mgz}{kT}} \tag{2.3.29}$$

and applying the equation of state,

$$p = p_0 e^{-\frac{mgz}{kT}}. \tag{2.3.30}$$

We see that the isothermal gas does not have a well defined boundary, but it becomes more diffuse with increasing height.

What if the gas is isolated instead of isothermal? Returning to (2.3.27), replace n by p/kT to get

$$\frac{dp}{dz} = -\frac{p}{kT}mg \tag{2.3.31}$$

The equation of state for adiabatic processes, in the form $p^{1-\gamma}T^{\gamma} = \text{const.}$, can be rewritten in the form

$$\frac{dp}{p} = \frac{\gamma}{\gamma - 1}\frac{dT}{T} \tag{2.3.32}$$

so (2.3.31) becomes

$$\frac{dT}{dz} = -\frac{\gamma - 1}{\gamma}\frac{mg}{k}, \tag{2.3.33}$$

which is trivially integrated from the surface to z, with solution

$$T = T_0\left[1 - \frac{\gamma - 1}{\gamma}\frac{z}{z_0}\right], \tag{2.3.34}$$

where T_0 is the surface level temperature and $z_0 = kT_0/mg$. The solution is valid so long as $z \leq \gamma z_0/(\gamma - 1)$. The pressure can now be given as

$$p = p_0\left[1 - \frac{\gamma - 1}{\gamma}\frac{z}{z_0}\right]^{\frac{\gamma}{\gamma-1}} \tag{2.3.35}$$

so we see that the adiabatic gas possesses a sharp boundary, in contrast with the isothermal gas.

For the atmosphere, $z_0 \approx 29.4$ km. Earth's atmosphere behaves more or less adiabatically up to about 20 km, at which point we enter the stratosphere. Above 20 km, *i.e.,* in the stratosphere, it behaves isothermally, and the pressure falls off exponentially with increasing height.

Now the change in n with height has a simple meaning: not every molecule of the gas is able to rise to any given altitude. Consider a single molecule which starts off from some (arbitrary) height z' with speed v'. Simply from the point of view of its total mechanical energy, it would reach a height $z > z'$ only if $v'^2 \geq 2g(z-z')$. If its speed is large enough it could even cross z, but if its speed is not large enough it will not get to z. Put in another way, the number of molecules at z, will be a function of the mean molecular speed at z'. So we expect that the number density obtained above as a function of z is really telling us about the velocity distribution of the molecules in the gas.

The molecules that arrive at z are the molecules that interest us. Conserving energy,

$$\frac{1}{2}m\vec{v}^2 + mgz = \frac{1}{2}m\vec{v}'^2 + mgz' \tag{2.3.36}$$

We can take $z' = 0$ and, since we're interested in the molecules that *just* make it to z, take $\vec{v} = 0$ as well. Thus, to get to z a molecule must have kinetic energy larger than mgz at $z' = 0$. In differential form

$$\vec{v}' \cdot d\vec{v}' = gdz \Rightarrow \frac{1}{2}d\vec{v}'^2 = gdz, \tag{2.3.37}$$

which says that a change in the height z, would necessitate a corresponding change in the speed that a molecule would have to have had at $z' = 0$ in order to arrive at z. We can now write a velocity distribution as follows. If $n(\vec{v}')$ is the number density of molecules with velocities between $\vec{v}'$ and $\vec{v}' + d\vec{v}'$, then the number of molecules with velocities in this interval would be $n(\vec{v}')d^3\vec{v}'$. But, inserting (2.3.37) into (2.3.28) we get

$$2\frac{dn}{d\vec{v}'^2} = -\frac{nm}{kT}, \tag{2.3.38}$$

which is integrated holding the temperature fixed to give

$$n(\vec{v}') = n_0 e^{-\frac{m\vec{v}'^2}{2kT}}, \tag{2.3.39}$$

where n_0 represents the number of molecules with zero speed. The number of molecules having velocities between $\vec{v}'$ and $\vec{v}' + d\vec{v}'$ should be

$$n(\vec{v}')d^3\vec{v}' = n_0 e^{-\frac{mv'^2}{2kT}} d^3\vec{v}'. \tag{2.3.40}$$

Henceforth drop the primes, remembering that the distribution is valid at $z' = 0$ where the gravitational potential energy is zero. Assuming local rotational symmetry in velocity space, which is certainly reasonable in equilibrium as no particular direction is preferred over another, we can replace $d^3\vec{v}$ by $4\pi v^2 dv$,

$$n(\vec{v})d^3\vec{v} = 4\pi n_0 e^{-\frac{mv^2}{2kT}} v^2 dv \overset{\text{def}}{=} n(v)dv \tag{2.3.41}$$

where $n(v)dv$ can be thought of as the distribution in *speeds*. Recall that here n_0 represents the number of molecules having zero velocity. To estimate its value note that the integral of $n(\vec{v})d^3\vec{v}$ over *all possible* velocities should yield the total number of molecules. Thus

$$N = 4\pi n_0 \int_0^\infty e^{-\frac{mv^2}{2kT}} v^2 dv = n_0 \left(\frac{2\pi kT}{m}\right)^{3/2} \tag{2.3.42}$$

and so

$$n(\vec{v})d^3v = 4\pi N \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mv^2}{2kT}} v^2 dv \tag{2.3.43}$$

is the desired distribution of molecular velocities. It allows us to compute the expectation (average) values used in the previous sections. In fact, any function $f(\vec{v})$ would have an expectation value given by

$$\langle f(\vec{v})\rangle = \frac{1}{N}\int f(\vec{v})n(\vec{v})d^3\vec{v} \tag{2.3.44}$$

For example, the average velocity of any molecule is obviously identically zero because the integral defining it,

$$\langle \vec{v}\rangle = \frac{1}{N}\int \vec{v}n(\vec{v})d^3\vec{v} \tag{2.3.45}$$

is odd for every component. On the other hand,

$$\langle v^2\rangle = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty e^{-\frac{mv^2}{2kT}} v^4 dv = \frac{3kT}{m} \tag{2.3.46}$$

so

$$v_{\text{rms}} = \sqrt{\frac{3kT}{m}} \tag{2.3.47}$$

which is just (2.3.11). We should note that the rms speed of the molecules is different from their mean speed, since

$$\langle v\rangle = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty e^{-\frac{mv^2}{2kT}} v^3 dv = \sqrt{\frac{8kT}{\pi m}}, \tag{2.3.48}$$

and that both of these are different from their *most probable* speed, which is defined as the speed that maximizes the distribution in speeds,

$$\left.\frac{dn(v)}{dv}\right|_{\widetilde{v}} = 0 \Rightarrow \widetilde{v} = \sqrt{\frac{2kT}{m}} \tag{2.3.49}$$

Thus we have three different quantities, all of which characterize the mean speed of the molecules. Which of these is meaningful depends always on the particular problem that is being addressed.

2.4 Thermodynamic Cycles: Engines and Refrigerators

A **Thermodynamic Cycle** is a process in which the thermodynamic system (we will sometimes refer to the thermodynamic system as the **working substance**) periodically returns to its original macrostate. As we will shortly show, any system undergoing a cyclic process will either do work on the environment or have work done upon it by the environment. By the first law of thermodynamics, if work is done by the cycle then the energy for the work done must be extracted from some external source. To simplify matters we will work with **heat reservoirs**: a "heat reservoir" is a thermodynamic system with a very large heat capacity compared with the working substance, so that any exchange of heat between the substance and the reservoir will result in no significant change in the reservoir's temperature. Thus heat reservoirs maintain their temperature no matter how much energy is extracted or deposited into them. We define a **Heat Engine** as any thermodynamic cycle which extracts energy from a reservoir in the form of heat and performs mechanical work. On the other hand, a **Refrigerator** will be any cyclic thermodynamic process which transfers energy in the form of heat from a reservoir at a lower temperature to a reservoir at a higher temperature. We will soon see that any thermodynamic cycle that operates as a heat engine will operate as a refrigerator if the cycle is reversed.

We had begun our study of Thermodynamics by saying that one of its principle objectives is to better understand processes that transform heat into useful work and vice-versa. Let us therefore get a better look at these processes. A cyclic process would be represented by a closed curve in the thermodynamic phase space. This follows from the requirement that the thermodynamic system should periodically return to its initial state. Upon completion of a cycle, the state properties do not change and the engine is able to repeat the cycle. However, path dependent quantities, such as Heat and Work do change during each cycle, and so may change indefinitely as the cycle repeats itself. The closed curve representing a cycle separates the $p-V$ plane into two regions, an "interior" and an "exterior". The work done,

$$W = \oint_C p dV, \tag{2.4.1}$$

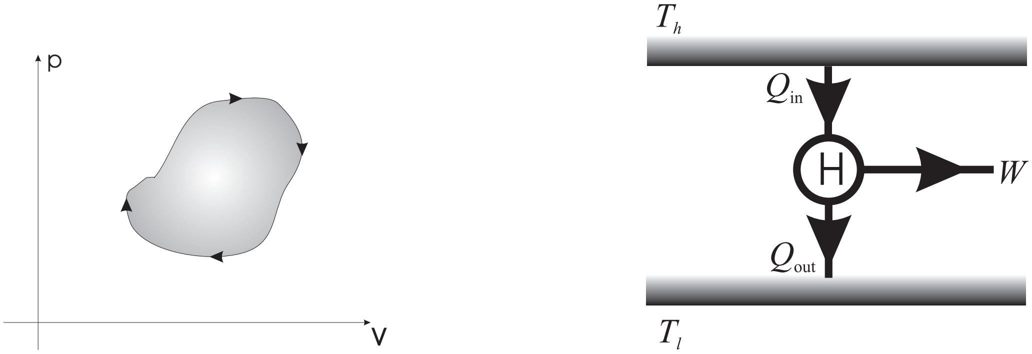

Figure 2.2: A cycle and schematic representing a heat engine: $T_h > T_l$

where C represents the closed curve in the $p - V$ plane will always be the area of the interior region. This assumes that the only way a system may do external work is via changes in the volume. In general there may be several external parameters, X_i, whose change requires the system to do work on the environment. In that case,

$$đW = \sum_i p_{X_i} dX_i \Rightarrow W = \oint_C \sum_i p_{X_i} dX_i \tag{2.4.2}$$

should replace (2.4.1), where p_{X_i} represents the "generalized force" corresponding to changes in X_i. The generalized force p_{X_i} is said to be **conjugate** to the external parameter X_i. Pressure in a fluid is just one example of a "generalized force" in thermodynamics, being the generalized force conjugate to the volume. In what follows, the expression pdV will be understood to represent $\sum_i p_{X_i} dX_i$ whenever we work with systems in which the volume is not the only external variable whose change involves external work.

If the cycle operates in a clockwise direction then the work done is positive. In this case the cycle is a heat engine (see figure 2.2). On the contrary, if it operates in a counterclockwise direction the work done is negative and the cycle will be a refrigerator. Since the internal energy is a function only of the state variables, the energy added by heat to the cycle must be given by

$$Q = W \tag{2.4.3}$$

at the completion of each cycle, according to the first law of Thermodynamics. Now in general the energy transferred by heat can be divided into two parts: the energy transferred by heat *to* the cycle from some reservoir, which we call Q_{in}, and the energy transferred by heat *out* of the cycle and into some other reservoir. We call this energy Q_{out}, then

$$Q = Q_{\text{in}} + Q_{\text{out}}. \tag{2.4.4}$$

is the energy added by heat to the cycle.

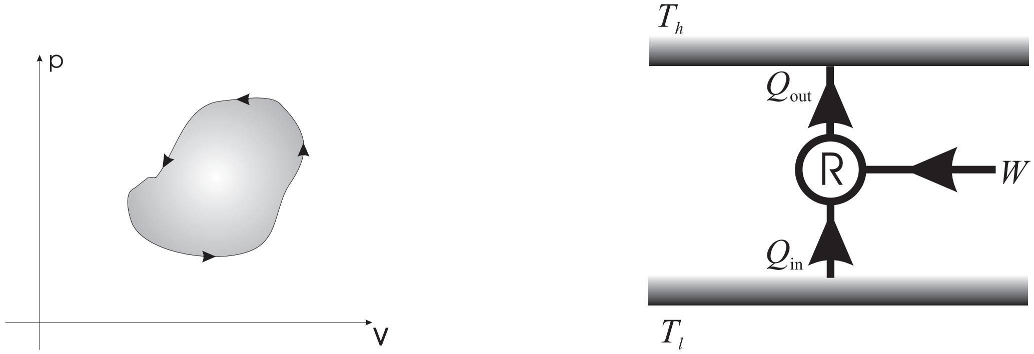

Figure 2.3: A cycle and schematic representing a refrigerator: $T_h > T_l$

The **efficiency** of the cycle is defined differently depending on whether the cycle is operating as a heat engine (clockwise) or as a refrigerator (counterclockwise). The efficiency is supposed to provide some measure of how well the cycle accomplishes its purpose, so it is quite generally defined by the ratio

$$e = \frac{\text{design output}}{\text{design input}} \tag{2.4.5}$$

The purpose of the heat engine is to do useful work. To do so we must supply the engine with energy in some form, which costs money and is thus not desirable. Thus the efficiency of the engine would be

$$e_h = \frac{W}{Q_{\text{in}}} = \frac{Q_{\text{in}} + Q_{\text{out}}}{Q_{\text{in}}} = 1 + \frac{Q_{\text{out}}}{Q_{\text{in}}} \tag{2.4.6}$$

which is always between zero and one, since $Q_{\text{out}} \leq 0$ and $0 \leq |Q_{\text{out}}| \leq Q_{\text{in}}$ as long as work is done ($W \geq 0$). An efficiency of unity would represent an ideal heat engine that is able to convert *all* of the supplied energy into useful work. An efficiency of zero is the other limit in which no work is done for the energy supplied. The purpose of a refrigerator, on the other hand, is to remove energy in the form of heat from some reservoir at a lower temperature and deposit it into a reservoir at a higher temperature. The design output would therefore be the energy *removed* (from the colder reservoir). Doing mechanical work on the cycle to accomplish this would be the input of the process, so the efficiency of the cycle should be defined as

$$e_r = \frac{Q_{\text{in}}}{|W|} = -\frac{Q_{\text{in}}}{Q_{\text{in}} + Q_{\text{out}}} = -\frac{1}{1 + \frac{Q_{\text{out}}}{Q_{\text{in}}}} = \frac{1}{\frac{|Q_{\text{out}}|}{Q_{\text{in}}} - 1}. \tag{2.4.7}$$

Because $W \leq 0$ for the refrigerator we must have $|Q_{\text{out}}| \geq Q_{\text{in}}$ and it follows that the efficiency of a refrigerator can be any non-negative real number. A perfect refrigerator would require no work to be done and so have an infinite efficiency. An efficiency of zero would represent the opposite limit in which an infinite amount of work must be done on the refrigerator to accomplish the transfer of any energy. Let's now consider some concrete examples of heat engines and refrigerators.

2.5 Sample Cycles

Our examples will be idealized because we will neglect some details of processes involved as well as energy losses due to friction and other causes and concentrate only on the essential characteristics of each cycle. This has the advantage of making the calculation of the efficiency in each case tractable while retaining the underlying physics of what is going on. We begin with the standard engine, the Carnot cycle, whose great advantage as we will see later is that it operates between just two heat reservoirs and so two temperatures.

2.5.1 The Carnot Engine

Take an ideal gas for the working substance and imagine that it is enclosed in a container of the following description: it has insulating and rigid walls so that no energy may enter or leave the interior either by mechanical means or by heat through the walls. It also has a conducting base so that energy transfer in the form of heat can occur only through the base. The top of the cylinder is closed by an insulating piston (effectively a movable wall) so that while no energy may be exchanged with the system by heat through the piston, energy exchange via mechanical work may occur.

Let there be two heat reservoirs and let the two reservoirs be at temperatures T_h and T_l such that $T_h \geq T_l$. We will refer to the reservoirs either directly by their temperatures or as the "high temperature" and "low temperature" reservoirs respectively. We now take the working substance through the following four steps, all of which are shown in the $p-V$ diagram of figure 2.4.

1. Place the gas, initially in equilibrium at temperature T_h, on the high temperature reservoir and allow it to expand quasi-statically from state "1" to state "2" by slowly decreasing the weight on the piston. The expansion is isothermal because the gas is continuously in thermal equilibrium with the reservoir. Again, this means that its internal energy is also constant and it absorbs a quantity of energy, Q_{in}, through the base from the reservoir, converting *all* of it into useful work,

$$Q_{\text{in}} = W_{12} = NkT_h \int_1^2 \frac{dV}{V} = NkT_h \ln\left(\frac{V_2}{V_1}\right), \quad U_1 = U_2 \tag{2.5.1}$$

2. Now place the gas on an isulating stand, allowing the gas to continue to expand from "2" to "3" by slowly decreasing the weight on the piston. Because no energy enters

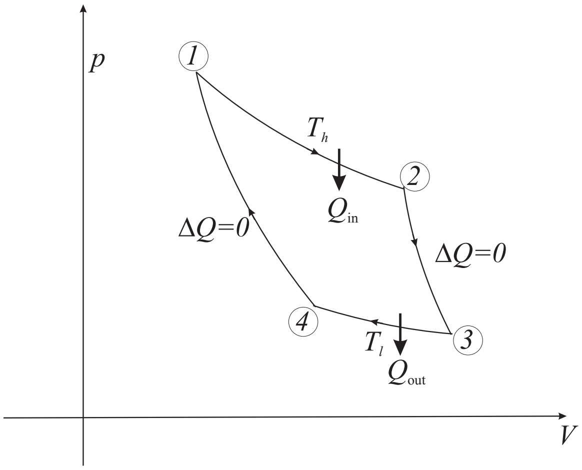

Figure 2.4: A $p - V$ diagram for the Carnot cycle.

or leaves the system by heat, the work done by the gas is at the cost of its internal energy causing its temperature to decrease. Continue the process of expansion until the temperature reaches T_l. Then

$$U_3 - U_2 = -W_{23} = -\int_2^3 pdV = -\alpha \int_2^3 V^{-\gamma} dV = -\frac{\alpha}{(1-\gamma)}(V_3^{1-\gamma} - V_2^{1-\gamma}) \quad (2.5.2)$$

where α is the constant on the right hand side of the adiabatic equation of state (2.2.14). Dividing the ideal gas equation of state $pV = NkT$ by $pV^\gamma = \alpha$, we find

$$\alpha V^{1-\gamma} = NkT \Rightarrow U_3 - U_2 = -W_{23} = -\frac{Nk}{\gamma - 1}(T_h - T_l), \quad \Delta Q = 0 \quad (2.5.3)$$

for this process.

3. Remove the gas from the insulating stand and place it on the low temperature reservoir, slowly compressing the gas by increasing the weight on the piston until it reaches some volume $V_1 < V_4 < V_3$, which we determine by requiring the state "3" and the state "1" to lie on the same adiabatic line. This is always possible. In this step, work is done on the gas at constant temperature. Because the internal energy is held constant energy in the form of heat, Q_{out} is expelled from the gas. By the first law,

$$Q_{\text{out}} = W_{34} = -NkT_l \ln\left(\frac{V_3}{V_4}\right), \quad U_3 = U_4 \quad (2.5.4)$$

4. Finally place the gas once again on the insulating stand and continue to increase the weight on the piston so that the gas continues to be compressed until it achieves the volume V_1. Again, no energy is allowed to enter or leave the gas by heat, so the work done on the gas increases its internal energy and therefore its temperature. In fact,
$$U_1 - U_4 = -W_{34} = \frac{Nk}{\gamma - 1}(T_h - T_l) \tag{2.5.5}$$

To calculate the efficiency of the Carnot engine, we need to compare the total work done by the cycle to the energy absorbed at the hight temperature reservoir. Thus using (2.4.6)

$$e_h = 1 + \frac{Q_{\text{out}}}{Q_{\text{in}}} = 1 - \frac{T_l}{T_h}\frac{\ln(V_3/V_4)}{\ln(V_2/V_1)} \tag{2.5.6}$$

To simplify the expression, relate each of the states by the equations of state appropriate to the process connecting them

$$\begin{aligned} p_1V_1 &= p_2V_2 \\ p_2V_2^\gamma &= p_3V_3^\gamma \\ p_3V_3 &= p_4V_4 \\ p_4V_4^\gamma &= p_1V_1^\gamma \end{aligned} \tag{2.5.7}$$

Multiplying these equations,we find

$$V_1V_2^\gamma V_3V_4^\gamma = V_2V_3^\gamma V_4V_1^\gamma \Rightarrow \left(\frac{V_3}{V_4}\right)^{1-\gamma} = \left(\frac{V_2}{V_1}\right)^{1-\gamma} \tag{2.5.8}$$

so that
$$e_h = 1 - \frac{T_l}{T_h} \tag{2.5.9}$$

and, because $T_l \leq T_h$, $e_h \leq 1$. If it were possible to have a reservoir at $T_l = 0$ temperature, we could create an ideal engine whose efficiency would be precisely one. In the other limit, if $T_l = T_h$ the efficiency is precisely zero.

The Carnot cycle, operating in a clockwise direction had the net effect of removing energy from the high temperature reservoir and converting a portion of it into mechanical work. Now we can think of operating the cycle in reverse [see figure 2.5]. It would then take energy in the form of heat from the low temperature reservoir and pass it on to the high temperature reservoir. The cycle now operates as a refrigerator and work must be done to operate this cycle. The efficiency of the refrigerator can be easily calculated from our earlier results and using the definition in (2.4.7)

$$e_r = \frac{1}{\frac{T_h}{T_l}\frac{\ln(V_2/V_1)}{\ln(V_3/V_4)} - 1} = \frac{1}{\frac{T_h}{T_l} - 1} \tag{2.5.10}$$

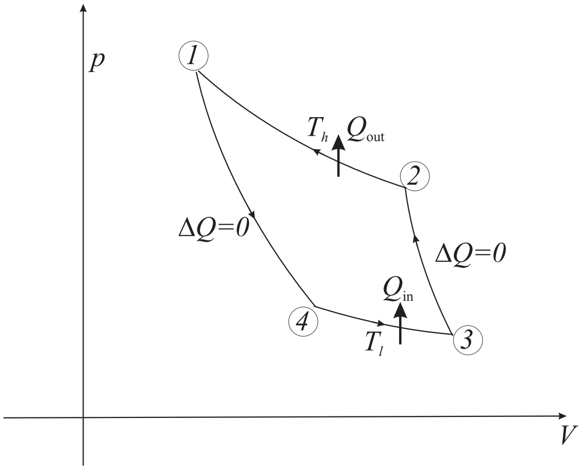

Figure 2.5: A $p-V$ diagram for the Carnot cycle in reverse.

We see that because $T_h/T_l \geq 1$ the efficiency of the refrigerator becomes arbitrarily large as $T_h \to T_l$ but it quickly becomes less than one when $T_h > 2T_l$.[5]

2.5.2 The Otto Cycle (Gasoline Engine)

We consider the four stroke version of the Otto cycle as shown in figure 2.9. The working substance is an mixture of air and fuel. The mixture is forced into a cylinder through one of two valves, which are built into the the cylinder head (at the top of the cyclinder). The other valve is used to release waste gases from the cylinder at the appropriate point in the cycle. Also attached to the cylinder head is a spark plug, whose purpose it is to generate an electric spark when required. The base of the cylinder consists of a piston that is free to move up and down. The piston turns a crankshaft and a flywheel, which stores the mechanical energy that is transferred to it.

The cycle begins at "top dead center", *i.e.,* when the piston is at the top of its motion. Both valves are closed and inside the cyclinder is a mixture of air and fuel that is exploded by generating an electric spark. The explosion causes the pressure to rise very rapidly. We may model this by an isovolumetric process ("1" to "2") because the piston does not have time to move downward during the initial phase of the explosion. Eventually, however,

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[5] It is important to bear in mind what this result says: the work done to accomplish the transfer of energy from the low temperature reservoir to the high temperature one will be less than the quantity of energy transferred in the form of heat provided that the temperature of the high temperature reservoir is less than twice the temperature of the low temperature reservoir.

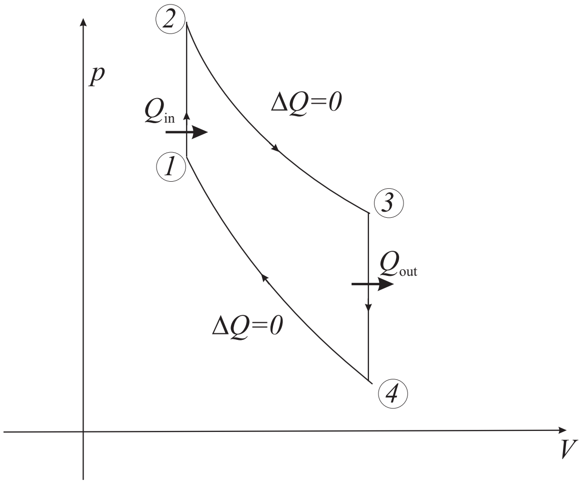

Figure 2.6: A $p-V$ diagram for the Otto Cycle.

the hot gaseous products of the explosion expand, pushing the piston down in a more or less adiabatic process (from "2" to "3"), the so-called "power stroke", and the mechanical energy is trasferred to the flywheel which stores it. When the piston reaches its lowest level, the exhaust valve opens and the (cooler) products of the combustion are released into the atmosphere as the piston continues moving upward in the so-called "exhaust stroke". When it has reached top dead center again, the exhaust valve is closed and the intake valve is opened to let in a fresh batch of the air-fuel mixture as the piston makes its way down again. Both these steps can be represented by the isovolumetric process from "3" to "4". The intake valve is closed when the piston reaches the bottom and, with both valves now closed, the air fuel mixture is compressed (almost) adiabatically until the piston returns to top dead center ("4" to "1"), when the cycle is complete and ready to be repeated.

In our idealized version of events, energy in the form of heat is absorbed by the engine during the first stage, and rejected by the engine during the third stage. Both these process are isovolumetric, the first being at the smallest possible volume, V_i, in the cylinder and the last being at the largest possible volume, V_f. The ratio $b = V_f/V_i$ is generally called the compression ratio and expresses the degree to which the air-fuel mixture is compressed before ignition. The work done by the cycle is

$$W = \alpha_{23} \int_{V_i}^{V_f} V^{-\gamma} dV + \alpha_{41} \int_{V_f}^{V_i} V^{-\gamma} dV \tag{2.5.11}$$

where we use the adiabatic equation of state for the two processes that do work: $pV^\gamma = \alpha$

and the subscript on α refers to the path. Thus[6]

$$W = \frac{Nk}{\gamma - 1}\left[T_2 - T_3 + T_4 - T_1\right] \tag{2.5.12}$$

On the other hand, heat is absorbed during an isovolumetric process and therefore

$$Q_{\text{in}} = U_2 - U_1 = C_V(T_2 - T_1) \tag{2.5.13}$$

so the efficiency of the engine is

$$e_h = \frac{Nk}{C_V(\gamma - 1)}\left[1 - \frac{T_3 - T_4}{T_2 - T_1}\right] \tag{2.5.14}$$

The ratio of the temperatures in the square brackets, can be given in terms of the compression ratio if we recognize that steps “2” to “3” and “4” to “1” are adiabatic, so

$$T_2 V_i^{\gamma-1} = T_3 V_f^{\gamma-1} \;\text{ and }\; T_4 V_f^{\gamma-1} = T_1 V_i^{\gamma-1} \tag{2.5.15}$$

implying that

$$\frac{T_3 - T_4}{T_2 - T_1} = \left(\frac{V_i}{V_f}\right)^{\gamma-1} \tag{2.5.16}$$

and therefore, in terms of the **compression ratio** $b = V_f/V_i$,

$$e_h = 1 - b^{1-\gamma} \tag{2.5.17}$$

where we also used the fact that $\gamma - 1 = (C_p - C_V)/C_V = Nk/C_V$. Clearly $0 < e_h < 1$, because $\gamma > 1$ as we have seen. Observe that the efficiency of the idealized cycle depends only on the compression ratio; the larger the compression ratio the greater the efficiency. Unfortunately, in practice it is not possible to increase the compression ratio indefinitely because one is limited by the volatility of the air-fuel mixture. Excessive compression ratios can cause the mixture to burn prematurely, *i.e.,* before the spark ignites it at top dead center. This will cause the engine to lose power and efficiency.

2.5.3 The Diesel Cycle

The difference between the Otto cycle and the diesel cycle is that the fuel mixture is not ignited suddenly by a spark, but is ignited by the higher compression and is then allowed to burn “slowly”. The resulting idealization of the cycle is shown in figure 2.7 In the figure, “1” represents the point at which the burning begins. The gas then expands pushing the piston down in the power stroke which occurs through two stages, first in

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[6] Again use $\alpha V^{1-\gamma} = NkT$

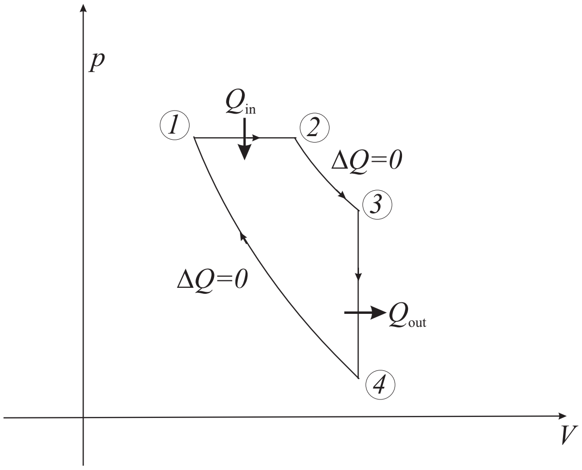

Figure 2.7: A $p-V$ diagram for the Diesel Cycle.

an isobaric process ("1" to "2") as the fuel continues to burn and then in an adiabatic process ("2" to "3") when the fuel is spent and the hot gases continue to expand. The isovolumetric process "3" to "4" occurs when the exhaust valve is opened and the waste gases are eliminated. A fresh batch of the air-fuel mixture is let into the combustion chamber and compressed in last last stage ("4" to "1"), bringing the cycle to completion.

The efficiency is slightly more difficult to calculate than for the Otto cycle, because work is now done in three of the four stages and energy in the form of heat is absorbed during an isobaric process. Thus we have

$$Q_{\text{in}} = C_p(T_2 - T_1) \tag{2.5.18}$$

and

$$Q_{\text{out}} = C_V(T_4 - T_3) \tag{2.5.19}$$

so the efficiency of the cycle is

$$e_h = 1 + \frac{1}{\gamma}\frac{T_4 - T_3}{T_2 - T_1} \tag{2.5.20}$$

Now three volumes are involved in this cycle, *viz.,* V_1, V_2 and $V_3 = V_4$, so let us try to express the ratio of temperatures in terms of them. To do so, we again use the adiabatic lines "2" to "3" and "4" to "1" to get

$$T_2V_2^{\gamma-1} = T_3V_3^{\gamma-1} \quad T_4V_3^{\gamma-1} = T_1V_1^{\gamma-1} \tag{2.5.21}$$

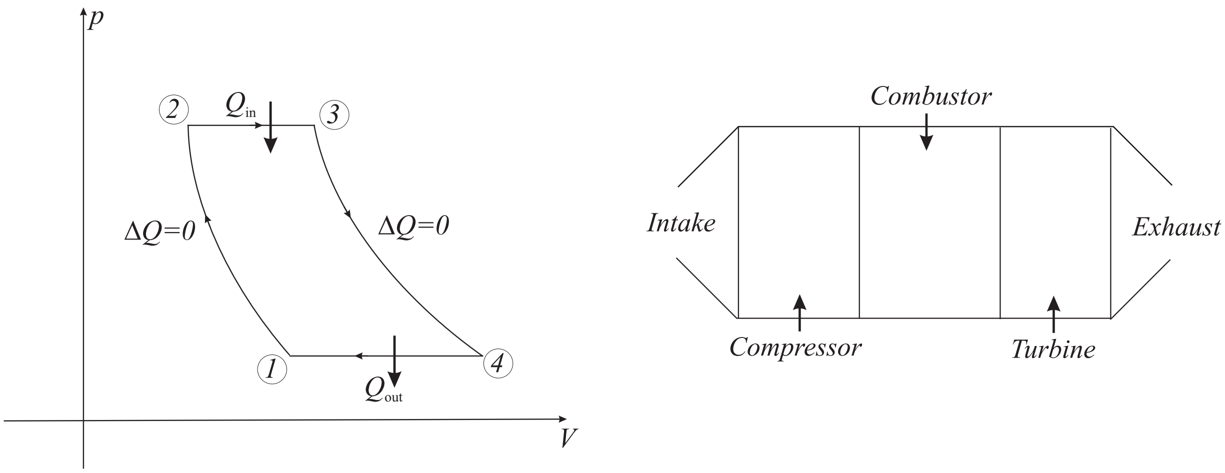

Figure 2.8: A $p-V$ diagram for the ideal Brayton Cycle.

so

$$(T_4 - T_3)V_3^{\gamma-1} = T_1V_1^{\gamma-1} - T_2V_2^{\gamma-1} \tag{2.5.22}$$

or

$$(T_4 - T_3)\left(\frac{V_3}{V_1}\right)^{\gamma-1} = T_1 - T_2\left(\frac{V_2}{V_1}\right)^{\gamma-1} \tag{2.5.23}$$

The ratio $c = V_2/V_1$ is called the “cut-off” ratio. Let $b = V_3/V_1$ and use the effective equation of state during the process “1” to “2”, *i.e.,* $T_1/V_1 = T_2/V_2 \Rightarrow T_2 = cT_1$, to rewrite the above equation in terms of b, c and T_1

$$(T_4 - T_3)b^{\gamma-1} = T_1(1 - c^\gamma) \Rightarrow \frac{(T_4 - T_3)}{T_2 - T_1} = -\frac{b^{1-\gamma}(c^\gamma - 1)}{c - 1} \tag{2.5.24}$$

and so

$$e_h = 1 - \frac{b^{1-\gamma}(c^\gamma - 1)}{\gamma(c - 1)} \tag{2.5.25}$$

Because there is no spark and the fuel burning is slow, the diesel cycle is less stressful on the engine than its sister the Otto cycle. For this reason diesel engines tend to last longer and cost less to maintain than gasoline engines.

2.5.4 The Brayton Cycle

The Brayton (or Joule) cycle represents the operation of a turbine (or jet engine). The idealized cycle consists of the four processes shown in the diagram of figure 2.8. In the first step ("1" to "2") air is taken into the engine and compressed adiabatically in the compressor before passing into the combustor, where fuel is burned at constant pressure ("2" to "3"), adding energy to the gases, which are then allowed to expand adiabatically through a turbine ("3" to "4"). Some of the work done is then used to drive the compressor and the rest is used either for jet propulsion or to turn a generator for electrical power generation. In the last step the gas is released into the reservoir from which the air was extracted, where it cools and contracts at constant pressure, returning to its initial condition.

Energy is absorbed as heat during the combustion ("2" to "3") and released during the isobaric cooling ("3" to "4"). We have

$$Q_{\text{in}} = C_p(T_3 - T_2), \quad Q_{\text{out}} = C_p(T_1 - T_4) \tag{2.5.26}$$

so the efficiency of the engine is

$$e_h = 1 - \frac{T_4 - T_1}{T_3 - T_2} \tag{2.5.27}$$

We would like to express this result in terms of the two pressures that characterize the engine, *viz.,* the atmospheric pressure at "1" and the pressure inside the combustion chamber at "2". This is easily done if we write the equation of state for the adiabatic processes "1" to "2" and "3" to "4", respectively (noting that $p_3 = p_2$ and $p_4 = p_1$)

$$\begin{aligned} p_1^{\frac{1-\gamma}{\gamma}} T_1 &= p_2^{\frac{1-\gamma}{\gamma}} T_2 \\ p_2^{\frac{1-\gamma}{\gamma}} T_3 &= p_1^{\frac{1-\gamma}{\gamma}} T_4 \end{aligned} \tag{2.5.28}$$

so

$$e_h = 1 - \left(\frac{p_2}{p_1}\right)^{\frac{1-\gamma}{\gamma}} \tag{2.5.29}$$

or, using the first of (2.5.28),

$$e_h = 1 - \frac{T_1}{T_2} \tag{2.5.30}$$

Note that T_1 is the atmospheric temperature and T_2 represents the temperature at the compressor exit.

2.5.5 The Stirling Cycle

In the Stirling engine, a working substance, which here will be assumed to be an ideal gas possessing g degrees of freedom per molecule, at initial volume V_1 and temperature T_l takes in energy in the form of heat at constant volume until its temperature reaches

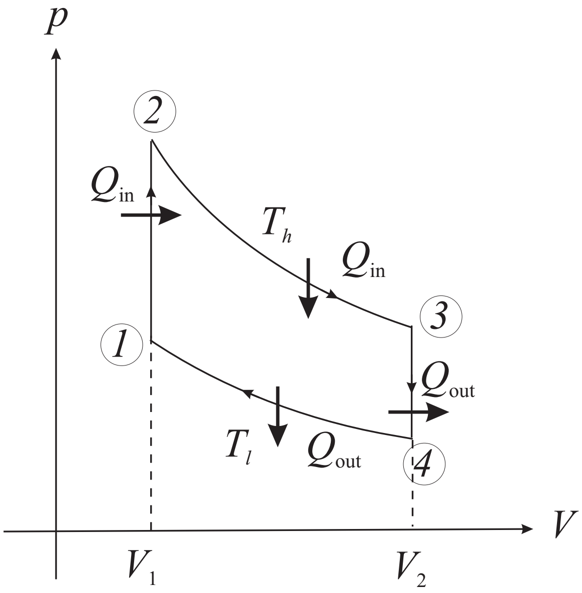

Figure 2.9: A $p-V$ diagram for the Stirling Cycle.

T_h and then expands isothermally to a volume V_2. At this point it gives up some of the energy it absorbed earlier in an isovolumetric process until its temperature drops back to T_l. Finally, it returns to its original state by isothermal compression. We want to compute the efficiency of this cycle.

Energy in the form of heat is supplied during the first two steps (from "1" to "2" and from "2" to "3") so we have

$$Q_{\text{in}} = \frac{g}{2} Nk(T_h - T_l) + NkT_h \ln\left(\frac{V_2}{V_1}\right) \tag{2.5.31}$$

Work is done by the cycle during the two isothermal processes, so

$$W = Nk(T_h - T_l) \ln\left(\frac{V_2}{V_1}\right) \tag{2.5.32}$$

and the efficiency can be directly computed as

$$\frac{1}{e} = \frac{Q_{\text{in}}}{W} = \frac{T_h}{(T_h - T_l)} + \frac{g/2}{\ln(V_2/V_1)} \tag{2.5.33}$$

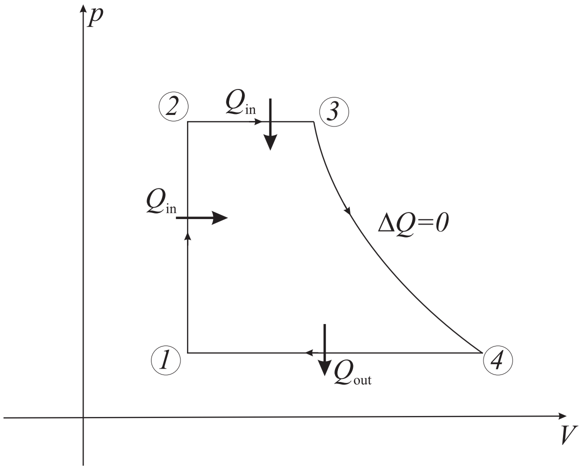

Figure 2.10: A $p-V$ diagram for the ideal Rankine Cycle.

2.5.6 The Rankine Cycle

The Rankine Cycle is an idealized cycle describing the steam engine (see figure 2.10). The steps involved are the following. From “1” to “2” the water (or fluid) is compressed isovolumetrically to the pressure of the boiler, from “2” to “3” the water is injected into boiler where it is heated to boiling point, vaporizes into saturated steam and is superheated to the final temperature (T_3) in an isobaric process. It is then let into the piston chamber where it expands adiabatically pushing the piston and doing work from “3” to “4”. (Alternatively, in modern steam turbines, it is allowed to expand through a turbine, doing work by turning it.) It is then released from the piston chamber into a condenser, where it condenses at constant pressure and is returned to the compressor where it renews the cycle. Energy is absorbed in the form of Heat during stages “1 ” to “2” and “2” to “3”, and it is rejected during the final stage, from “4” to “1”. Calculating the efficiency of the Rankine cycle involves accounting for changes of phase from liquid to gas and vice-versa. This also means that the efficiency is more sensitive to the nature of the working substance. [7]

There are many cycles that we have not explored, but with the few examples that we

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[7] Problem: Imagine an ideal gas undergoing a Rankine cycle. As was the case for the Diesel cycle, its efficiency may be stated exclusively in terms of the ratios $V_3/V_1 = c$ (the “cut-off” ratio) and $V_4/V_1 = b$. Show that

$$e_h = 1 - \frac{\gamma(b-1)}{\left(\frac{b}{c}\right)^{\gamma}[1+\gamma(c-1)]-1}.$$

have looked at it should be clear that no cycle is capable of converting the energy absorbed in the form of heat into useful work *without some other effect.* This “other effect” takes the form of a rejection of some part of the energy absorbed. Neither was it possible to simply transfer energy from a “colder” reservoir to a “hotter” reservoir without some other effect. This other effect takes the form of work that must be done to accomplish the transfer of energy. These simple observations are essentially the two (equivalent) early statements of the second law of thermodynamics which we will examine in the next chapter.

Chapter 3

The Second Law and Entropy

The only restriction that the first law of thermodynamics places on a process is that energy should be conserved. One consequence, for example, is that it prohibits any cyclic process from performing mechanical work without extracting energy (eg. in the form of heat) from some source. A cycle that is capable of performing mechanical work *without* extracting energy from any source, were it possible, would be called a "perpetual motion machine" ("perpetuum mobile") of the first kind. The first law assures us that such a cycle does not exist. However, we could imagine the exciting possibility of a machine that extracts energy from a reservoir of some sort and transforms *all* of the extracted energy into useful mechanical work with no other effect. If this were in fact possible we could build machines that for all practical purposes would have no environmental footprint. We could also (for all practical purposes endlessly) extract energy from some reservoir of energy, convert all the extracted energy into useful work and then transfer that energy back into the reservoir from which we extracted it in the first place. This kind of a cycle is called a "perpetual motion machine" of the second kind. Experience teaches us that a perpetual motion machine of the second kind also does not exist: every heat engine we have built involves a transfer of energy from some "hotter" reservoir of energy (eg. gasoline in an automobile) to a "colder" one (the atmosphere, for most engines). A perpetual motion machine of the second kind would need just one reservoir of energy.

Perpetual motion machines are not the only processes that never seem to occur in nature. A little thought will show that in fact there are many processes that do not occur spontaneously in nature even though the first law would allow them. For example, a lake on a warm summer's day does not simply give up its energy to the atmosphere and freeze, although energy would be conserved in the process.[1] An egg that has been dropped and splattered on the floor does not spontaneously put itself together again even though such

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[1] More generally, if two bodies, A and B, at temperatures T_A and T_B with $T_A \geq T_B$ are placed in thermal contact, it never happens that A spontaneously keeps getting hotter and B colder.

a process may not in fact violate energy conservation. What this is saying is that the first law is only a necessary condition for the occurrence of a thermodynamic process, not a sufficient one. The impossibility of the processes described in the examples above is captured by the second law of thermodynamics.

3.1 The Kelvin and Clausius statements

There are two original statements of the **Second Law** of Thermodynamics. The first is due to the British physicist and engineer William Thomson (Lord Kelvin) and concerns heat engines:

- **Kelvin Statement:** A thermodynamic cycle whose *only* effect is to transform energy extracted from a body in the form of heat into useful work is impossible.

The second is due to the German physicist Rudolf Clausius and concerns refrigerators.

- **Clausius Statement:** A thermodynamic cycle whose *only* effect is to transfer energy in the form of heat from a body at a given temperature to a body at a higher temperature is impossible.

Although these two statements appear different, they are indeed quite rigorously equivalent to each other. Let's prove this in two parts: first we'll show that if Kelvin's statement is *not* true then Clausius' statement cannot be true. Then we'll do the same with Clausius' statement, *i.e.,* we'll show that if it is *not* true then Kelvin's statement cannot be true either.

Let's assume that Kelvin's statement of the second law is *not* true. This means that it is possible in principle to transform energy absorbed as heat from a reservoir at some temperature (say, T_1) into useful work with *no other effect.* Of course, the mechanical work produced can now be transferred to a body at another temperature (say, T_2) by friction (as in the Joule experiment). This transfer of energy takes place *no matter what the temperature,* T_2. In particular T_2 could be greater than T_1 and we would have succeeded in transferring energy in the form of heat from a body at a lower temperature to one at a higher temperature with no other effect. This contradicts the Clausius statement.

Next assume that Clausius' statement of the second law is *not* true. This means that it is possible to transfer heat from a body at a lower temperature, T_l, to a body at a higher temperature, T_h, *with no other effect.* With the help of a Carnot engine operating between T_h and T_l we could then extract the same amount of heat from the body at T_h and convert at least a part of it into useful work. Since the body at T_h absorbs a certain quantity of energy and then releases the same quantity of energy, no change has occurred in its state. The result is that we have a process whose net effect is to transform heat absorbed from the body at T_l into useful work. This contradicts Kelvin's statement, and completes our proof.

Before proceeding to develop this law let us prove that of all engines operating between two temperatures, the Carnot engine is the most efficient. More formally, let C be a Carnot engine operating between the temperatures T_h and T_l ($T_h > T_l$) and let M represent any other heat engine operating between the same two temperatures, then it is always true that

$$\left|\frac{Q_1}{Q_2}\right| \geq \left|\frac{Q_1'}{Q_2'}\right| \tag{3.1.1}$$

where the unprimed quantities refer to C and primed quantities to M, and where Q_1 (Q_1') refers to the energy exchanged as heat with the reservoir at T_h (since energy is absorbed at T_h, $Q_1, Q_1' > 0$) and Q_2 (Q_2') to the energy exchanged as heat with the reservoir at T_l (since energy is discharged at T_l, $Q_2, Q_2' < 0$). Let W (W') be the work done by the two machines in one cycle. By the first law of thermodynamics (we now use absolute values, to avoid confusion with the signs)

$$\begin{aligned} W &= |Q_1| - |Q_2| \\ W' &= |Q_1'| - |Q_2'|. \end{aligned} \tag{3.1.2}$$

Consider the ratio $|Q_1/Q_1'|$. To as good an approximation as we desire this ratio can be approximated by a rational number, *i.e.,*

$$\left|\frac{Q_1}{Q_1'}\right| = \frac{n'}{n} \tag{3.1.3}$$

where n and n' are positive integers. Now consider a process consisting of n' cycles of M and n cycles of C *in reverse* (see figure 3.1). While operating in reverse, C absorbs an amount of energy Q_2 in the form of heat from T_l and an amount of work W, depositing Q_1 into the reservoir at T_h, while M absorbs Q_1' from the reservoir at T_h, does work W' and rejects Q_2' into the reservoir at T_l. The net external work done by our system is then

$$W_{\text{tot}} = n'W' + nW = n'|W'| - n|W| \tag{3.1.4}$$

(recall that W is negative in our convention), the net heat *removed from* T_h is

$$Q_h = n'Q_1' + nQ_1 = n'|Q_1'| - n|Q_1| \tag{3.1.5}$$

(Q_1 is negative because it is *leaving* C, which is operating in reverse) and the net heat *added to* T_l is

$$Q_l = -n'Q_2' - nQ_2 = n'|Q_2'| - n|Q_2| \tag{3.1.6}$$

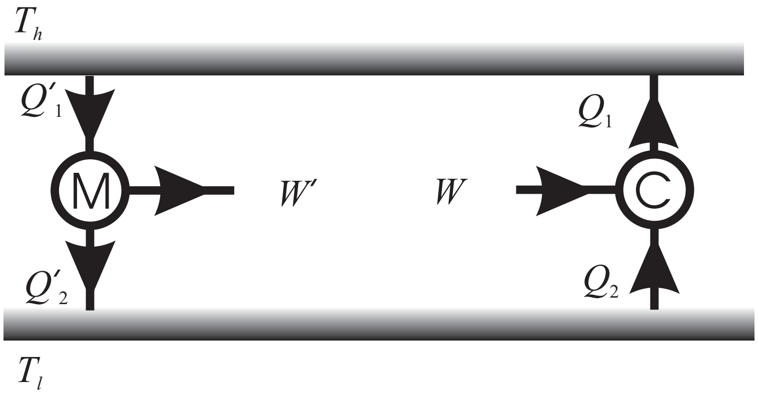

Figure 3.1: Schematic representing M operating as a heat engine and C as a refrigerator.

(Q'_2 is negative because it is *leaving* M). By energy conservation (the first law)

$$W_{\text{tot}} = n'|W'| - n|W| = Q_h - Q_l \tag{3.1.7}$$

but, because we have adjusted

$$|Q_1| = \frac{n'}{n}|Q'_1|, \tag{3.1.8}$$

it follows that $Q_h = 0$ and so

$$W_{\text{tot}} = -Q_l = -n'|Q'_2| + n|Q_2| \tag{3.1.9}$$

Now Kelvin's statement of the second law ensures that $W_{\text{tot}} \leq 0$, for if $W_{\text{tot}} > 0$ we would have a process which extracts a certain amout of heat from the reservoir at T_l and performs useful work, with no other effect. After all, no net heat was added to the high temperature reservoir. But

$$W_{\text{tot}} \leq 0 \Rightarrow Q_l \geq 0 \Rightarrow n'|Q'_2| \geq n|Q_2| \tag{3.1.10}$$

Replacing

$$n' = n\left|\frac{Q_1}{Q'_1}\right| \tag{3.1.11}$$

in the last inequality, we then have the desired result,

$$\left|\frac{Q_1}{Q_2}\right| \geq \left|\frac{Q'_1}{Q'_2}\right|. \tag{3.1.12}$$

Of course, this means that the Carnot engine has the best efficiency of all engines operating between two temperatures.

3.2 Thermodynamic definition of Temperature

We could have made the argument in the opposite way, using M as a refrigerator (*i.e.,* running in reverse) and C as a heat engine. Provided that M, operating as a refrigerator, (i) absorbs the same amount of energy in the form of heat from the colder reservoir as it would reject into the colder reservoir as a heat engine, (ii) absorbs the same amount of energy in the form of useful work as it would perform as a heat engine and (iii) rejects the same amount of energy into the hotter reservoir as it would absorb as a heat engine we could prove that

$$\left|\frac{Q_1'}{Q_2'}\right| \geq \left|\frac{Q_1}{Q_2}\right|. \tag{3.2.1}$$

Of course, (3.1.12) is compatible with (3.2.1) if and only if

$$\left|\frac{Q_1}{Q_2}\right| = \left|\frac{Q_1'}{Q_2'}\right|, \tag{3.2.2}$$

i.e., the efficiencies of the two engines are identical. If conditions (i), (ii) and (iii) are met then the cycle M is called a **reversible** cycle. A reversible process or a reversible cycle will be a process (or cycle) in which both the system and the rest of the universe – its environment – can be returned to the original state (the process can be reversed) by means of quasi-static processes. It is easy to see that the Carnot engine is reversible. Firstly, it is itself made of quasi-static processes. Secondly, per cycle, let the Carnot engine remove $-\delta Q_h$ from the high temperature reservoir and deposit δQ_l to the low temperature reservoir. Run the engine as a refrigerator, then the cycle removes exactly $-\delta Q_l$ from the low temperature rerervoir and deposits $+\delta Q_h$ into the high temperature reservoir per cycle. Since the engine, by definition, returns to its original state and, by running in reverse, is capable of returning the reservoirs to their original states, it must be reversible. We conclude that the efficiencies of reversible cycles operating between two temperatures are identical and equal to the Carnot efficiency. The efficiency of a cycle that is not reversible is always *less than* the efficiency of the Carnot engine.

Because

$$\left|\frac{Q_1}{Q_2}\right| \tag{3.2.3}$$

is the same for all reversible cycles operating between two temperatures (now call them T_1 and T_2, where $T_1 > T_2$), the ratio cannot depend on the cycle but only on the temperatures, *i.e.,*

$$\left|\frac{Q_1}{Q_2}\right| = f(T_1, T_2) \tag{3.2.4}$$

We want to prove that the function $f(T_1, T_2)$ as defined above is multiplicatively separable

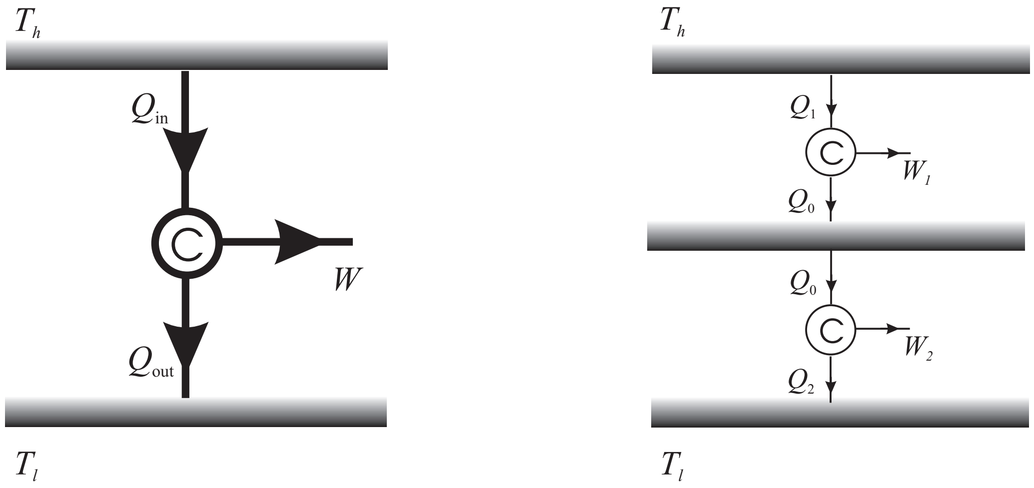

Figure 3.2: A Carnot engine (left) replaced by two Carnot engines (right): $T_1 > T_0 > T_2$

and, moreover, can be written in the form

$$f(T_1, T_2) = \frac{\Theta(T_1)}{\Theta(T_2)} \tag{3.2.5}$$

To prove this, imagine a Carnot engine operating between temperatures T_1 and T_2 ($T_1 > T_2$) that absorbs Q_1 from the hotter reservoir and rejects Q_2 into the colder reservoir. Then replace it by two Carnot cycles, C_1 and C_2, the first one operating between T_1 and T_0 ($T_1 > T_0$) and the other between T_0 and T_2 ($T_0 > T_2$) as shown in figure 3.2. Let C_1 absorb Q_1 from the reservoir at temperature T_1 and reject Q_0 into the reservoir at T_0. It must be true that

$$\left|\frac{Q_1}{Q_0}\right| = f(T_1, T_0). \tag{3.2.6}$$

Likewise, let C_2 absorb Q_0 from the reservoir at temperature T_0 and reject Q_2 into the reservoir at T_2. It will then also be true that

$$\left|\frac{Q_0}{Q_2}\right| = f(T_0, T_2) = \frac{1}{f(T_2, T_0)}. \tag{3.2.7}$$

Multiplying (3.2.6) and (3.2.7) gives

$$\left|\frac{Q_1}{Q_2}\right| = f(T_1, T_2) = \frac{f(T_1, T_0)}{f(T_2, T_0)} \tag{3.2.8}$$

Now T_0 was completely arbitrary and can be viewed as some constant. Letting $\Theta(T_i) = f(T_i, T_0)$, we find

$$\left|\frac{Q_1}{Q_2}\right| = f(T_1, T_2) = \frac{\Theta(T_1)}{\Theta(T_2)} \tag{3.2.9}$$

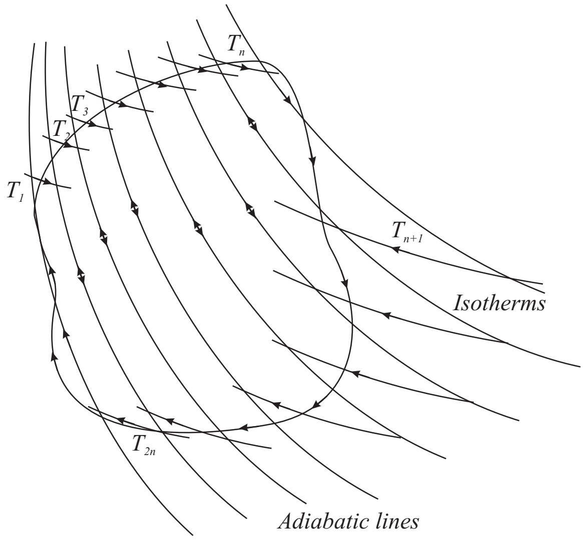

Figure 3.3: An arbitrary *reversible* heat engine broken up into a very large number of Carnot cycles

Our beginning definition of temperature was empirical, based on the an extrapolation to the "ideal" gas. Now we can make it more precise, using $\Theta(T)$ as a new definition of temperature. However, we notice that Θ is defined only upto a constant multiplicative factor. This factor corresponds to the "scale", *i.e.,* what we decide to call "one degree". Θ is called the absolute thermodynamic scale and is independent of the thermodynamic properties of any single thermodynamic substance used in the Carnot cycle. Moreover we have already seen that, for the ideal gas as a working substance,

$$\left|\frac{Q_1}{Q_2}\right| = \frac{T_1}{T_2}, \tag{3.2.10}$$

so if we choose our scale properly we can adjust things so that $\Theta = T$, thus taking the ideal gas temperature to be precisely the thermodynamic scale.

3.3 The Entropy

The next step in our development of the second law will be the concept of entropy in thermodynamics. This is the precursor of the definition of "information", proposed by Shannon.[2] Information is carried, stored and processed by all macroscopic physical sys-

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[2] Shannon, C.E., "A Mathematical Theory of Communication", Bell System Technical Journal, 27, (1948) 379 — 423 & 623 -– 656.

tems and is ultimately governed by the laws of physics, so it is not surprising that physics and information should be closely related to one another. The usefulness of the concept of entropy can hardly be overstated and it is probably fair to say that the connection between physics and information is still not fully exploited. We will look at the microscopic origins of the entropy later in this course; for now we introduce it as a thermodynamic state variable.

Let us consider an arbitrary reversible heat engine, S, and divide the cycle into a very large number of Carnot engines as shown in figure 3.3.[3] An important property of each of the Carnot cycles is that heat is absorbed and rejected by the cycle during isothermal processes and

$$\frac{|Q_{\text{in}}|}{T_{\text{in}}} = \frac{|Q_{\text{out}}|}{T_{\text{out}}} \tag{3.3.1}$$

Taking into account the appropriate signs (Q_{in} is positive, Q_{out} is negative) we can write this as

$$\frac{Q_{\text{in}}}{T_{\text{in}}} + \frac{Q_{\text{out}}}{T_{\text{out}}} \equiv 0 \tag{3.3.2}$$

Each of the Carnot cycles in the figure absorbs and rejects an infinitesimal quantity of energy as heat, δQ_i, at each reservoir. Moreover, the reservoirs come in pairs, so label them from 1 to $2n$ in such a way that the Carnot cycle j operates between temperatures T_j (high) and T_{n+j} (low), where n represents the number of cycles. For the set of cycles shown in figure 3.3 we can say that

$$\sum_{i=1}^{2n} \frac{\delta Q_i}{T_i} = 0, \tag{3.3.3}$$

Of course we are taking the limit as the number of cycles approaches infinity, at which point the series of Carnot engines exactly reproduces the original cycle. This means that the adiabatic lines become infinitesimally close to each other and δQ_i approaches zero at each reservoir, so we have

$$\lim_{n\to\infty} \sum_{i=1}^{2n} \frac{\delta Q_i}{T_i} = \oint_S \frac{đQ}{T} \equiv 0 \tag{3.3.4}$$

Now consider a cycle that is not reversible. This implies that there are one or more portions of the engine that cannot be accurately described by Carnot cycles as depicted in figure 3.3. Consider one such portion, say k. Call the actual energy absorbed as heat at the high temperature reservoir involved in covering this portion $\delta Q'_k$ and the actual

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[3] An analogous division of the region under a curve into rectangles is used in elementary calculus to define the definite integral as the limit of a sum.

energy rejected as heat at the low temperature reservoir $\delta Q'_{k+n}$. We know that

$$\left|\frac{\delta Q'_k}{\delta Q'_{k+n}}\right| \leq \left|\frac{\delta Q_k}{\delta Q_{k+n}}\right| = \frac{T_k}{T_{k+n}} \tag{3.3.5}$$

which means that

$$\frac{\delta Q'_k}{T_k} + \frac{\delta Q'_{k+n}}{T_{k+n}} \leq 0 \tag{3.3.6}$$

To reproduce the cycle, the left hand side of (3.3.3) should be replaced by

$${\sum}'^{2n}_{i=1} \frac{\delta Q_i}{T_i} + \sum_k \left(\frac{\delta Q'_k}{T_k} + \frac{\delta Q'_{k+n}}{T_{k+n}}\right) \tag{3.3.7}$$

where the prime on the first sum indicates that those Carnot cycles overlapping portions of the cycle that are not reversible should be omitted and replaced by the second sum. But, since the first sum is identically zero and the second sum is less than or equal to zero we have

$$\sum_{i=1}^{2n} \frac{\delta Q_i}{T_i} \leq 0 \tag{3.3.8}$$

and in the limit as the number of adiabatic lines approaches infinity,

$$\oint_S \frac{đQ}{T} \leq 0 \tag{3.3.9}$$

The equality holds only when S is reversible. This is **Clausius'** theorem.

We might give an alternative proof of Clausius' theorem as follows. The engine S can be thought of as exchanging energy in the form of heat with a large number, N, of reservoirs at various temperatures which may be labeled as $T_1, \ldots T_i \ldots T_N$. Let Q_i be the energy exchanged with reservoir T_i. Clearly Q_i is larger than zero if energy is absorbed from T_i in the form of heat and is less than zero if energy is rejected in the form of heat into T_i. Connect all the reservoirs to a single reservoir at temperature T_0 by Carnot engines operating either as heat engines or refrigerators, in such a way that the Carnot engine linking the i^{th} reservoir to T_0 supplies to that reservoir (or removes from it) precisely that amount of energy in the form of heat that is removed from (or supplied to) it by S. Thus, if S *absorbs* Q_i from T_i then C_i *gives* Q_i to T_i and vice-versa.

According to our definition of temperature, for each C_i

$$\left|\frac{Q_i}{Q_{i,0}}\right| = \frac{T_i}{T_0} \tag{3.3.10}$$

where $Q_{i,0}$ is the amount of energy given or taken from T_0 by C_i. Then

$$Q_{i,0} = T_0 \frac{Q_i}{T_i} \tag{3.3.11}$$

Notice that the signs take care of themselves: if S absorbs a certain amount of energy from T_i then the Carnot cycle connected to T_i should replace that energy and it can only do so by absorbing $Q_{i,0}$ from T_0. Thus, if $Q_i > 0$ so is $Q_{i,0}$ and vice versa. Now the net exchange of energy at each of the reservoirs T_i by heat is precisely zero in our construction. The net effect of the process is then to take $\sum_i Q_{i,0}$ from T_0 and transform it into useful work. By Kelvin's statement of the second law this would imply that $W = \sum_i Q_{i,0} \leq 0$, or

$$\sum_{i=1}^{N} \frac{Q_i}{T_i} \leq 0 \tag{3.3.12}$$

If S were reversible, then reversing S and all the connected Carnot cycles, we would find that

$$\sum_{i=1}^{N} \left(-\frac{Q_i}{T_i}\right) \leq 0 \tag{3.3.13}$$

which would only be possible if

$$\sum_{i=1}^{N} \frac{Q_i}{T_i} \equiv 0 \tag{3.3.14}$$

Once again, considering infinitesimal exchanges of energy by heat we find that

$$\oint_S \frac{đQ}{T} \leq 0 \tag{3.3.15}$$

for any cycle, where the equality holds for reversible cycles.

Let's consider the implications of this statement. In the first place because

$$\oint_S \frac{đQ}{T} \equiv 0 \tag{3.3.16}$$

for a reversible cycle it follows that the differential $đQ/T$ must be exact (*i.e.,* its integral must be indepdendant of the path). To see this, choose two states i and f on the reversible cycle as in figure 3.4. Then we could write 3.3.15 as

$$\oint_S \frac{đQ}{T} = 0 \Rightarrow \int_{I,i}^{f} \frac{đQ}{T} + \int_{II,f}^{i} \frac{đQ}{T} = 0 \tag{3.3.17}$$

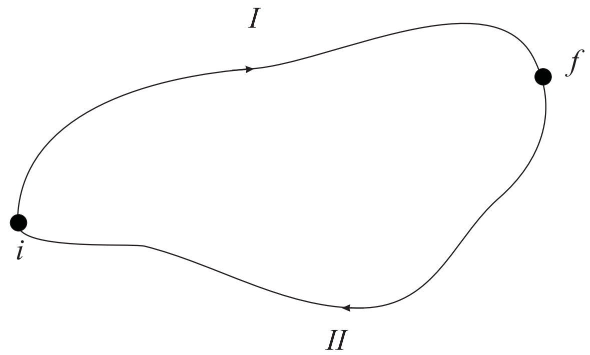

Figure 3.4: A cycle can be thought of as two processes I from i to f and II from f to i

and so, changing direction on path II,

$$\int_{I,i}^{f} \frac{đQ}{T} = \int_{II,i}^{f} \frac{đQ}{T} \tag{3.3.18}$$

i.e., the value of the integral depends only on the end points, i and f and not on the path (process) linking them. This in turn implies that *during a reversible process*

$$đQ = TdS \tag{3.3.19}$$

where S is some function of state,

$$S_f - S_i = \int_{i,(\text{q.s.})}^{f} \frac{đQ}{T} \tag{3.3.20}$$

where we have introduced the suffix "q.s." to emphasize the fact that the integral is to be evaluated along some reversible, quasi-static path from i to f. Note that no further specification of the path is required since, so long as the path is quasi-static the change $S_f - S_i$ will be the same. The function S is called the **entropy** of the system. Equation 3.3.20 tells us how to compute changes in the entropy of a system that has been transformed from a state "i" to a state "f", but tells us nothing of the actual value of the entropy at i or f or anywhere else. However, imagine that we choose a standard state, call it $*$, at which we arbitrarily set the entropy to be numerically equal to zero (like energy in classical mechanics, only changes in entropy are so far relevant), then

$$S(k) = \int_{*}^{k} \frac{đQ}{T} \tag{3.3.21}$$

gives the entropy of any other state, k. A change in our standard from $*$ to $*'$ would introduce a constant, which would be precisely the change in entropy from $*$ to $*'$, because

$$S'(k) = \int_{*'}^{k} \frac{đQ}{T} = \int_{*'}^{*} \frac{đQ}{T} + \int_{*}^{k} \frac{đQ}{T} = S_* + S(k) \tag{3.3.22}$$

Thus we write the entropy of any state k as the indefinite integral

$$S(k) = \int^k \frac{đQ}{T} + S_* \tag{3.3.23}$$

with an arbitrary constant, S_*.

If the cycle S were irreversible then instead of the equality in (3.3.17) we would have an inequality as in (3.3.15). Choose two points on the cycle so that path I from i to f is not quasi-static and path II from f to i is quasi-static. Then

$$\oint_S \frac{đQ}{T} \leq 0 \Rightarrow \int_{I,i}^f \frac{đQ}{T} \leq \int_{II,i}^f \frac{đQ}{T} \tag{3.3.24}$$

Now, by definition, because path II is quasi-static

$$\Delta S_{if} = S_f - S_i = \int_{II,i}^f \frac{đQ}{T} \tag{3.3.25}$$

so we have

$$\Delta S_{if} \geq \int_{I,i}^f \frac{đQ}{T} \tag{3.3.26}$$

In particular, since path I is not restricted to be quasi-static we could take it to be adiabatic (but not quasi-static!). Then $đQ = 0$ and we find that

$$\Delta S_{if} \geq 0 \tag{3.3.27}$$

for isolated systems. We have just proved the third and most modern statement of the second law of thermodynamics

- The entropy of a thermally isolated system undergoing a thermodynamic process *may never decrease.*

It follows that thermally isolated systems achieve equilibrium at the maximum of the entropy, but it is essential to keep in mind that this holds only for thermally isolated systems. In a system consisting of many interacting parts the entropy of an individual part may decrease, although the entropy of the whole, so long as it is isolated, must either increase or stay the same. As a simple example, consider the earth-sun system as reasonably isolated, and only that part of the energy from the sun that is incident upon the earth, ignoring the rest. To a very good approximation both the sun and the earth can be approximated by reservoirs at temperatures T_s and T_e. The net change in entropy of the system when δQ of energy from the sun is absorbed by the earth as heat is

$$\delta S = -\frac{|\delta Q|}{T_s} + \frac{|\delta Q|}{T_e} > 0 \tag{3.3.28}$$

because $T_e \ll T_s$.

Another point worth remembering is that the entropy may increase even during adiabatic processes, if they are not quasi-static. Consider, for example, the free expansion of an ideal gas, *i.e.,* imagine that a gas at high pressure, p_i, inside a chamber of volume V_i is allowed to expand in a vacuum by suddenly opening a stopper. Imagine that this vacuum exists in another, much larger and isolated chamber of volume V_f enclosing the first, so that the expansion is adiabatic but not quasi-static and the gas achieves a final equilibrium state with volume V_f. Since the gas expands freely, no work is done in the process. Moreover, because the process is also adiabatic, the first law guarantees that the internal energy of the gas does not change, therefore the final temperature of the gas will be equal to its initial temperature. To compute the entropy change we need to invent a quasi-static process connecting the initial and final states; we are guaranteed that an isothermal process will do the job because the internal energy stays constant during the expansion. The entropy change is therefore

$$\Delta S = \int_{i,\text{isotherm}}^{f} \frac{đQ}{T} = \int_{i,\text{isotherm}}^{f} \frac{p}{T} dV = Nk \ln \frac{V_f}{V_i} > 0 \tag{3.3.29}$$

where we used the equation of state. The entropy change during a quasi-static and adiabatic process is, of course, identically zero.

Equation (3.3.26) gives us the generalization of (3.3.19) that also applies to irreversible processes,

$$đQ \leq TdS \tag{3.3.30}$$

so, in terms of the entropy, the first law reads

$$TdS \geq dU + pdV. \tag{3.3.31}$$

or more generally,

$$TdS \geq dU + \sum_i p_{X_i} dX_i. \tag{3.3.32}$$

This statement and the statement that $\Delta S \geq 0$ for an isolated system, together summarize the content of the first two laws of thermodynamics. If attention is confined exclusively to processes that are reversible we can use

$$TdS = dU + \sum_i p_{X_i} dX_i \tag{3.3.33}$$

together with $\Delta S = 0$ for an isolated system.

3.4 The Thermodynamic Phase Space

Let us now confine our attention to reversible processes unless otherwise stated. It is somewhat instructive to rewrite the first law as

$$dU - TdS + \sum_i p_{X_i} dX_i = 0 \tag{3.4.1}$$

(where we assume there are n external parameters, X_i, so that there are $2n+3$ variables in all) because this form suggests enlarging our set of external parameters by including the entropy and viewing the temperature (actually, $-T$) as the "generalized force" conjugate to it. Alternatively, we could divide throughout by the temperature and express the first law as

$$dS - \frac{dU}{T} - \sum_i \frac{p_{X_i}}{T} dX_i = 0, \tag{3.4.2}$$

which suggests enlarging our set of external parameters by including the internal energy and viewing $-1/T$ as the "generalized force" conjugate to it. In fact we could rewrite the first law so that any of the $2n+3$ variables occupies the privileged position of U and S in the above examples, and the first law will *always* take the form

$$dq^0 - \sum_{i=1}^{n+1} p_i dq^i = 0 \tag{3.4.3}$$

in terms of $n+1$ q^i's and as many p_i's. Thus, in the first example, q^0 would be the internal energy, U, and in the second it would be the entropy, S. Note that the q^i may be intensive or extensive state variables, and the same holds for the p_i, although if q^k is intensive then p_k will be extensive and vice-versa. For example, the first law can be written as

$$d\widetilde{U} - TdS - \sum_i X_i dp_{X_i} = 0 \tag{3.4.4}$$

where $\widetilde{U} = U + \sum_i p_{X_i} X^i$. In each picture there will be one "thermodynamic potential" and a set of "fundamental variables" (q^i, p_i). Because q^0 is a function of state, it can only depend on the variables (q^i, p_i). Therefore (3.4.3) ensures that it can be naturally viewed as a function of the q^i's *only.* If we knew this function, *i.e.,* given

$$q^0 = \Phi(q^i) \tag{3.4.5}$$

we would immediately be able to derive $n+1$ equations of state,

$$p_i = \frac{\partial \Phi}{\partial q^i}, \tag{3.4.6}$$

interpreted as equations for the p_i. The p_i's would consequently satisfy the $n(n+1)/2$ integrability conditions

$$\frac{\partial p_i}{\partial q^j} = \frac{\partial^2 \Phi}{\partial q^j \partial q^i} = \frac{\partial^2 \Phi}{\partial q^i \partial q^j} = \frac{\partial p_j}{\partial q^i}. \tag{3.4.7}$$

This is the content of the first law. The $n+2$ equations in (3.4.5) and (3.4.6) therefore define an $n+1$ dimensional subspace in the thermodynamic phase space and physical processes may only occur on this subspace. For example, the thermodynamic phase space of an ideal gas consists of the five variables $\{U, S, V, T, p\}$, but the physical phase space is only two dimensional (since $n = 1$). Therefore any three of the state variables can always be expressed as functions of the other two.

It is not generally possible to determine $\Phi(q^i)$, although for some simple systems a knowledge of the equations of state can get us close. For example we know that for an ideal gas

$$p = \frac{NkT}{V} \tag{3.4.8}$$

so re-writing the first law in the form

$$dS = \frac{dU}{T} + Nk\frac{dV}{V} \tag{3.4.9}$$

we see that T can be viewed as an integrating factor. In fact, because dU/T is an exact differential, we must have $T = f(U)$. Thermodynamics cannot tell us more than this, but from the kinetic theory we already know that for the ideal gas

$$T = \frac{2U}{gNk} \tag{3.4.10}$$

where g represents the number of degrees of freedom of the molecules, so integrating gives

$$S = Nk\left[\frac{g}{2}\ln\left(\frac{U}{U_*}\right) + \ln\left(\frac{V}{V_*}\right)\right] \tag{3.4.11}$$

where U_* and V_* are arbitrary constants, depending possibly on N, which reflect our lack of knowledge about the actual value of the entropy. Of course we could now re-express the entropy in terms of any pair of the remaining phase space variables using the equation of state.[4]

The procedure is slightly more interesting for gases that satisfy the **Van der Waals** equation of state,

$$\left(p + \frac{aN^2}{V^2}\right)(V - Nb) = NkT, \tag{3.4.12}$$

---

[4] Problem: Write expressions for the entropy as a function of every pair of the four variables $\{U, V, p, T\}$.

which generalizes the ideal gas equation by taking into account the finite size of atoms and molecules as well as the weak electromagnetic interactions between them. The constant a represents the effect of an attractive interaction between the molecules if a is positive (and a replusion if a is negative) whereas the constant b represents the volume of a single molecule. That is why, for the ideal gas whose molecules are taken to be point-like and non-interacting both a and b are vanishing, which returns the ideal gas equation of state. The entropy is now

$$dS = \frac{NkdV}{V - Nb} + \frac{dU - \frac{aN^2}{V^2}dV}{T} \tag{3.4.13}$$

and, once again, T is an integrating factor that makes the last term an exact differential, so it must have the form

$$T = f\left(U + \frac{aN^2}{V}\right). \tag{3.4.14}$$

In the limit as the intermolecular forces become vanishing (equivalently as V approaches infinity) we should find that T approaches its relationship to U in the ideal gas limit. This means that

$$T = \frac{2}{gNk}\left(U + \frac{aN^2}{V}\right) \tag{3.4.15}$$

and we find[5]

$$S(U,V) = Nk\left[\ln\left(\frac{V - Nb}{V_* - Nb}\right) + \frac{g}{2}\ln\left(\frac{U + \frac{aN^2}{V}}{U_* + \frac{aN^2}{V_*}}\right)\right] \tag{3.4.16}$$

which, naturally, returns (3.4.11) in the limit as a and b become vanishing. The general equations for a gas involve two "arbitrary" constants, which we think of as describing a *class* of substances (fluids).

Maxwell's construction

It is interesting to examine the isotherms of the Van der Waals gas in greater detail. Expressing the equation of state in terms of the molecular volume (volume per molecule) $v = V/N$, as

$$p = \frac{kT}{v - b} - \frac{a}{v^2}, \tag{3.4.17}$$

we find that there is an isotherm, called the **critical isotherm** which admits an inflection point at a positive pressure and volume, p_c and v_c. To determine the inflection point, set

$$\left(\frac{\partial p}{\partial v}\right)_{T_c} = 0 = \left(\frac{\partial^2 p}{\partial v^2}\right)_{T_c} \tag{3.4.18}$$

---

[5] Problem: Determine $S = S(T,V)$, $S = S(T,p)$ and $S = S(p,V)$ for the Van-der-Waals gas.

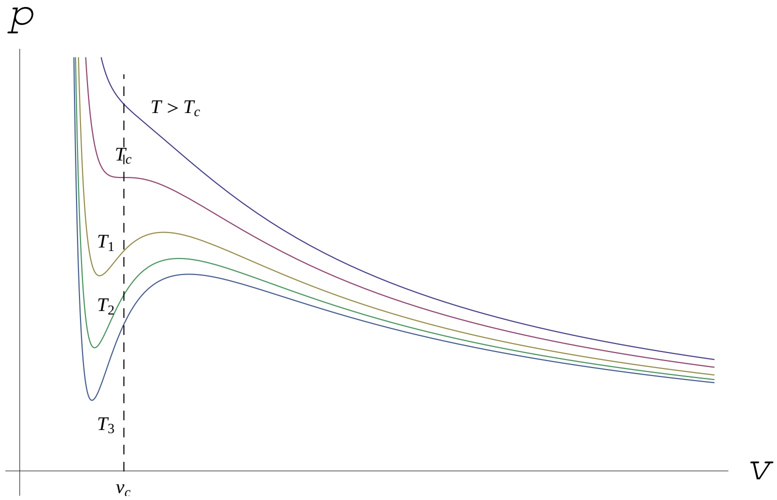

Figure 3.5: Isotherms of a Van der Waal's gas.

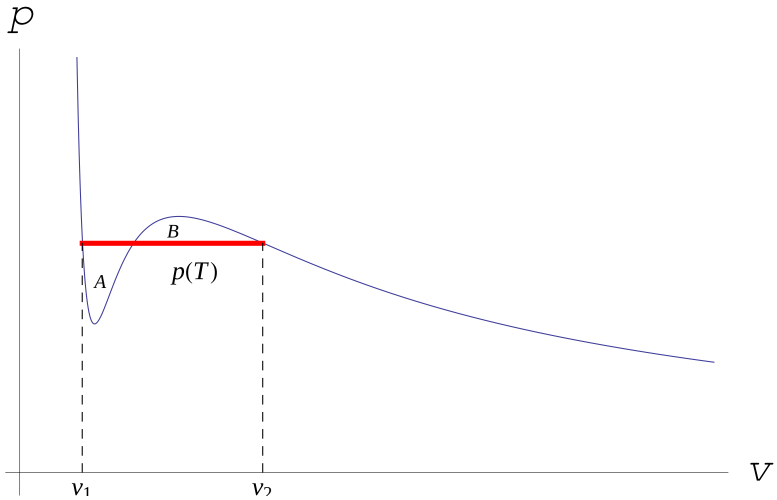

Figure 3.6: Maxwell's construction for the isotherms of a Van der Waal's gas.

and solve the set of three equations (the two above and the equation of state) for the pressure, volume and temperature to find

$$v_c = 3b, \quad p_c = \frac{a}{27b^2}, \quad kT_c = \frac{8a}{27b} \tag{3.4.19}$$

For isotherms above the critical temperature, the pressure decreases monotonically with volume but for isotherms below the critical temperature the pressure volume relationship is *not* monotonic, as shown in figure 3.5. These isotherms admit a region over which $\partial p/\partial v > 0$, which indicates that the pressure actually *increases* with increasing volume! This is unphysical behavior and signals a breakdown of the equation of state and the isotherms must be corrected. Maxwell suggested that the corrected behavior is obtained by drawing a horizontal line across the isotherm, as shown in figure 3.6, in such a way that the areas A and B in the figure are equal. This is equivalent to saying that the work done along the corrected isotherm is equal to that done along the uncorrected one,

$$p(T)(v_2 - v_1) = \int_{v_1,\mathrm{VdW}}^{v_2} p dv. \tag{3.4.20}$$

The corrected isotherm corresponds to a phase transition taking place at a fixed, temperature dependent pressure, $p = p(T)$, between volumes V_1 and V_2 as indicated in the figure. This is known as **Maxwell's construction**. In a later section we obtain an equation that determines $p(T)$ from purely thermodynamic considerations (the Clausius Clapeyron equation) and in the next chapter we will give a physical argument for the consistency of Maxwell's approach.

3.5 Integrability Conditions

In the previous section, we were able to determine the relationship between the internal energy and the temperature of a gas simply by noting that T serves as an integrating factor in the equation for S. In this section, we examine the integrability conditions in greater detail. Although we'll work with the five dimensional phase space (S, U, p, V, T), all that we learn below can be straightforwardly generalized to an arbitrary $2n + 3$ dimensional phase space and multiple equations of state. Since there is but one external parameter in our phase space we know that the relevant hypersurface is two dimensional. Viewing S as a function of U and V, *i.e.*, $S = S(U, V)$, the equation

$$dS = \frac{dU}{T} + \frac{p}{T} dV \tag{3.5.1}$$

requires that

$$\frac{\partial S}{\partial U} = \frac{1}{T}, \quad \frac{\partial S}{\partial V} = \frac{p}{T} \tag{3.5.2}$$

so that the integrability of S,

$$\frac{\partial^2 S}{\partial V \partial U} = \frac{\partial^2 S}{\partial U \partial V} \tag{3.5.3}$$

implies that

$$\left(\frac{\partial T}{\partial V}\right)_U = -T^2 \left[\frac{\partial}{\partial U}\left(\frac{p}{T}\right)\right]_V = p\left(\frac{\partial T}{\partial U}\right)_V - T\left(\frac{\partial p}{\partial U}\right)_V \tag{3.5.4}$$

where, in the last equation, we have explicitly labeled the variable being held constant with each derivative. This is our first integrability condition. It must hold for every thermodynamic system for which the first law can be given in the form (3.3.33), *i.e.,* for every system in which the work done by the system can be expressed as $đW = pdV$.[6]

This is not the only integrability condition possible. Although the entropy is naturally viewed as a function of the internal energy and the volume, nothing constrains us from thinking of it as a function of *any* pair of variables, eg., the volume and temperature. We would then think of the internal energy as a function of (V, T). The first law is written as

$$dS = \left(\frac{1}{T}\frac{\partial U}{\partial V} + \frac{p}{T}\right) dV + \frac{1}{T}\frac{\partial U}{\partial T} dT \tag{3.5.5}$$

which shows that

$$\begin{aligned} \frac{\partial S}{\partial V} &= \left(\frac{1}{T}\frac{\partial U}{\partial V} + \frac{p}{T}\right) \\ \frac{\partial S}{\partial T} &= \frac{1}{T}\frac{\partial U}{\partial T} \end{aligned} \tag{3.5.6}$$

Integrability of these equations,

$$\frac{\partial^2 S}{\partial T \partial V} = \frac{\partial^2 S}{\partial V \partial T} \tag{3.5.7}$$

then means that

$$-\frac{1}{T^2}\frac{\partial U}{\partial V} + \frac{1}{T}\frac{\partial^2 U}{\partial T \partial V} - \frac{p}{T^2} + \frac{1}{T}\frac{\partial p}{\partial T} = \frac{1}{T}\frac{\partial^2 U}{\partial V \partial T}. \tag{3.5.8}$$

Simplifying, we find

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \tag{3.5.9}$$

Instead, if we had taken $S = S(T, p)$ (take (T, p) as independent variables),

$$dS = \frac{1}{T}\left(\frac{\partial U}{\partial p} + p\frac{\partial V}{\partial p}\right) dp + \frac{1}{T}\left(\frac{\partial U}{\partial T} + p\frac{\partial V}{\partial T}\right) dT \tag{3.5.10}$$

---

[6] Problem: Generalize (3.5.4) to systems in which $đW = \sum_i p_i dX_i$. Note that in this case, $S = S(U, X_i)$.

which shows that

$$\begin{aligned}\frac{\partial S}{\partial p} &= \frac{1}{T}\left(\frac{\partial U}{\partial p}+p\frac{\partial V}{\partial p}\right)\\ \frac{\partial S}{\partial T} &= \frac{1}{T}\left(\frac{\partial U}{\partial T}+p\frac{\partial V}{\partial T}\right)\end{aligned} \tag{3.5.11}$$

Integrability then implies gives,

$$\left(\frac{\partial U}{\partial p}\right)_T = -p\left(\frac{\partial V}{\partial p}\right)_T - T\left(\frac{\partial V}{\partial T}\right)_p \tag{3.5.12}$$

Finally, if we consider $S = S(p, V)$ we find

$$dS = \frac{1}{T}\frac{\partial U}{\partial p}dp + \frac{1}{T}\left(\frac{\partial U}{\partial V}+p\right)dV, \tag{3.5.13}$$

which gives the integrability condition

$$T = \left[\left(\frac{\partial U}{\partial V}\right)_p + p\right]\left(\frac{\partial T}{\partial p}\right)_V - \left(\frac{\partial U}{\partial p}\right)_V\left(\frac{\partial T}{\partial V}\right)_p \tag{3.5.14}$$

The four integrability conditions (3.5.4), (3.5.9), (3.5.12) and (3.5.14) can be quite useful, as we will soon see.[7]

3.5.1 Internal energy of a Gas

The integrability conditions are different ways to express the fact that dS is an exact differential. For example, let's use (3.5.4) to show that the temperature of an ideal gas depends only on its internal energy. From the equation of state, $pV = NkT$, we see that

$$\left(\frac{\partial p}{\partial U}\right)_V = \frac{Nk}{V}\left(\frac{\partial T}{\partial U}\right)_V \tag{3.5.15}$$

so inserting this into the right hand side of (3.5.4) shows that $(\partial T/\partial V)_U = 0$ *i.e.*, $T = f(U)$ as we had before. On the other hand, for the Van-der-Waals gas

$$\left(\frac{\partial p}{\partial U}\right)_V = \frac{Nk}{V - Nb}\left(\frac{\partial T}{\partial U}\right)_V. \tag{3.5.16}$$

---

[7] Problem: Complete the proofs of (3.5.12) and (3.5.14). Obtain two more integrability conditions, taking the entropy as a function of the pairs (U, p) and (U, T).

Inserting this into the right hand side of (3.5.4) we find

$$\left(\frac{\partial T}{\partial V}\right)_U + \frac{aN^2}{V^2}\left(\frac{\partial T}{\partial U}\right)_V = 0 \tag{3.5.17}$$

The equations for the characteristic curves of this equation are

$$dV = \frac{V^2}{aN^2}\, dU, \quad T(U,V) = \text{const.} \tag{3.5.18}$$

and imply that

$$T(U,V) = f\left(U + \frac{aN^2}{V}\right) \tag{3.5.19}$$

as we guessed before.

We could just as well use (3.5.9) to arrive at the same conclusions. For an ideal gas, the equation of state allows us to express the pressure as

$$p = \frac{NkT}{V} \Rightarrow \left(\frac{\partial p}{\partial T}\right)_V = \frac{Nk}{V} \tag{3.5.20}$$

It follows from (3.5.9) that

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{NkT}{V} - p \equiv 0 \tag{3.5.21}$$

so $U = U(T)$. The situation is only mildly different for the Van-der-Waals gas, for now

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{Nk}{V - Nb} \tag{3.5.22}$$

and, plugging this into (3.5.9) gives

$$\left(\frac{\partial U}{\partial V}\right)_T = p + \frac{aN^2}{V^2} - p \Rightarrow U = -\frac{aN^2}{V} + g(T) \tag{3.5.23}$$

where g is an undetermined function only of the temperature. Inverting this relationship gives precisely (3.5.19).[8] Once again, because we know the internal energy of the ideal gas, we determine

$$g(T) = \frac{g}{2}NkT \tag{3.5.24}$$

where g is the number of degrees of freedom per molecule. Thus,

$$U(T,V) = -\frac{aN^2}{V} + \frac{g}{2}NkT \tag{3.5.25}$$

is exact for the internal energy of the Van-der-Waals gas.

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[8] Problem: Repeat these calculations with the integrability conditions in the form of (3.5.12) and (3.5.14) both for the ideal gas and the Van-der-Waals gas.

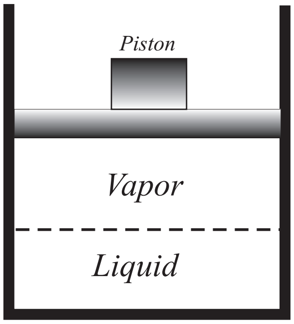

Figure 3.7: A liquid vapor system in equilibrium at a fixed temperature.

3.5.2 Phase Equilibrium

Consider a liquid inside a container that is closed on one end with a piston which may move freely up and down as in figure 3.7, making it possible to continuously change the volume and pressure inside the container. Let the base of the container be non-insulating, *i.e.,* able to transfer thermal energy across it and place it in contact with a reservoir of temperature T, allowing the liquid to achieve equilibrium with its vapor at T.

It's best to first understand this system microscopically. The molecules of the liquid have a certain amount of thermal energy, indeed some may acquire enough energy to escape the bonds that keep them attached to other molecules of the liquid. These molecules of positive total energy will attempt to leave the liquid, contributing to the vapor. However, the molecules in the vapor already present also have a certain amount of thermal energy by virtue of which they exert a (downward) pressure on the liquid. Assuming that they behave more or less like an ideal gas as a first approximation, this pressure will depend on the number density of molecules already present, according to the equation of state $p = nkT$ and will act to oppose the molecules that are trying to leave the liquid. The higher this vapor pressure the more energy a liquid molecule would have to acquire in order to escape into the vapor. Clearly, there will a point at which the probability that a liquid molecule has enough energy to pass into the vapor becomes negligibly small. When this happens the number density of molecules in the vapor remains constant (modulo small fluctuations) and therefore so does the pressure. Suppose we now increase the pressure slightly, holding the temperature fixed. The less energetic molecules in the vapor will condense and return to the liquid. As molecules leave the vapor, the vapor pressure drops, back to the level it was before we increased the pressure. On the other hand, if we decrease the pressure by lowering the weight on the piston, the most energetic molecules of the liquid will now be able to pass to the vapor phase, increasing the number density of molecules in the vapor phase and therefore also the vapor pressure, again to the same level it was before we decreased it. Thus the net effect is that the pressure always tries to stabilize itself. Of

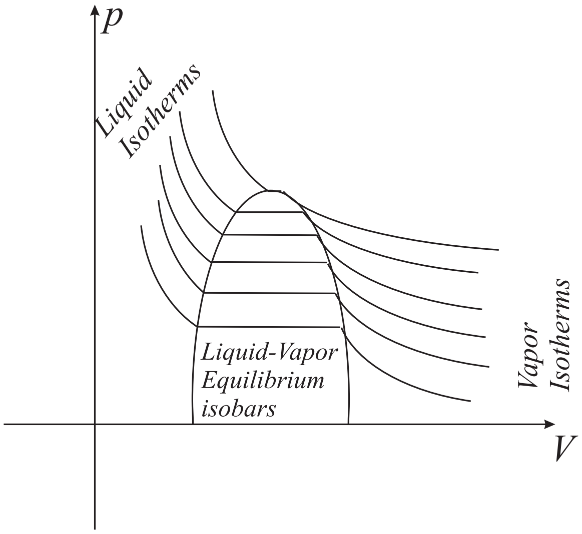

Figure 3.8: The liquid-gas isotherms

course, this can happen so long as there are both liquid and vapor phases present. On the extreme ends, if the pressure is too large all the vapor condenses to the liquid phase and the entire system behaves as a liquid, while if the pressure is too low all the liquid is transformed into vapor, after which the system behaves as a gas.

Experimentally, one finds the situation depicted in figure 3.8. Notice that there is an isotherm for which the region of constant pressure reduces to just one point. This is called the **critical point** and the temperature, volume and pressure are "critical". What we're after is the vapor pressure as a function of the temperature in the liquid-vapor equilibrium phase. Let m be the total mass of the system, m_l the mass of the liquid and m_v the mass of the vapor so that

$$m = m_l + m_v \tag{3.5.26}$$

Let the volume per unit mass (the **specific volume**) of the liquid be v_l and that of the vapor v_v (clearly, $v_v \gg v_l$). Also let the internal energy per unit mass be u_l and u_v respectively for the liquid and the vapor. Then, because U and V are extensive,

$$\begin{aligned} U &= m_l u_l + m_v u_v \\ V &= m_l v_l + m_v v_v \end{aligned} \tag{3.5.27}$$

are the total internal energy and the total volume respectively. Considering changes in U and V, and keeping in mind that the total mass is constant, *i.e.*, $dm = 0 \Rightarrow dm_l = -dm_v$

we get

$$dU = dm_v(u_v - u_l)$$

$$dV = dm_v(v_v - v_l) \tag{3.5.28}$$

so by the first law

$$đQ = dU + pdV = dm_v(u_v - u_l) + pdm_v(v_v - v_l) \tag{3.5.29}$$

and therefore

$$\frac{đQ}{dm_v} = (u_v - u_l) + p(v_v - v_l) = L \tag{3.5.30}$$

Experimentally, the right hand side is constant. It is precisely the latent heat of vaporization per unit mass, *i.e.,* the amount of energy required to be given to a unit mass of the liquid to cause it to change its state from liquid to vapor. Now, according to (3.5.9) (the independent variables are (T, V))

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \tag{3.5.31}$$

Clearly, p cannot depend on the volume in equilibrium (see the isotherms in figure 3.8), so $p = p(T)$ and the partial derivative is really a total derivative. Moreover,

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{u_v - u_l}{v_v - v_l} \tag{3.5.32}$$

so our integrability condition becomes

$$T\frac{dp}{dT} = \frac{u_v - u_l}{v_v - v_l} + p = \frac{(u_v - u_l) + p(v_v - v_l)}{v_v - v_l} \tag{3.5.33}$$

or

$$\frac{dp}{dT} = \frac{L}{T(v_v - v_l)} \approx \frac{L}{Tv_v} \tag{3.5.34}$$

since $v_v \gg v_l$. Notice the great beauty of this equation. It is a general relationship between measurable quantities, which we have found using only the first and second laws of thermodynamics (via the integrability condition (3.5.9)). Suppose that the vapor behaves as an ideal gas, then $pv_v = \overline{n}kT$, where $\overline{n}$ is the number of molecules per unit mass, *i.e.,* $\overline{n} = N_0/M$, where N_0 is Avogadro's number and M is the molecular mass in grams. Thus we can write

$$v_v = \frac{N_0kT}{pM} \Rightarrow \frac{dp}{dT} = \frac{MLp}{RT^2} \tag{3.5.35}$$

and this equation is easily integrated, provided L is independent of T, to give

$$p = p_0 e^{-\frac{ML}{N_0 kT}} \tag{3.5.36}$$

where p_0 is a constant that must be obtained experimentally. Notice that as T increases, the exponent also increases and the pressure increases. Vice-versa, when the temperature decreases, the pressure decreases as well. Equation (3.5.34) is called the **Clausius-Clapeyron equation** and all known substances in the two-phase region experimentally obey it.

3.5.3 Magnetic Systems

Each current loop inside a magnet is subject to an effective magnetic field, the magnetic field intensity $\vec{H}$. For a magnetic system, the work done must include not just the mechanical work pdV associated with changes in volume but also the magnetic work associated with changes in the magnetic intensity. We will now argue for an expression for the work done by small changes in H. For simplicity, we will consider a magnet oriented along the direction of the field, which we take to be in the positive $z-$direction (see figure 3.9). In the figure we have shown a typical current loop generating a magnetization in $z-$ direction, *i.e.,* the direction of the magnetic intensity vector, $\vec{H}$. If we imagine that the $\vec{H}$ changes along the $x-$ direction, the net force on the loop will be

$$\Delta F = (I)\frac{\partial H}{\partial x}\Delta x \Delta y = (I\Delta A)\frac{\partial H}{\partial x} = \Delta M \frac{\partial H}{\partial x} \tag{3.5.37}$$

where M is the magnetic moment of the loop. The force on the entire sample can be viewed as the superposition of these small forces on single current loops,

$$F = M\frac{\partial H}{\partial x} \tag{3.5.38}$$

so the work done on the sample in moving it a distance dx will be

$$đW = M\frac{\partial H}{\partial x}dx = MdH \tag{3.5.39}$$

and the first law of thermodynamics reads

$$TdS = dU + MdH. \tag{3.5.40}$$

where the magnetization used above is just the system's average magnetic moment.

The magnetic analogue of the ideal gas is the ideal paramagnet. The magnetic dipoles of a paramagnet do not interact with one another but only respond to an external magnetic field. The magnetic dipoles of a ferromagnet, on the other hand, interact not only with

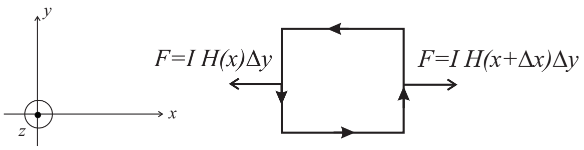

Figure 3.9: Work done on a magnetic system by a change in the magnetic field

the externally applied magnetic field but also with the average magnetic field of all the other magnetic dipoles within the system. Thus a ferromagnet can remain magnetized, *i.e.,* continue to possess a non-vanishing average magnetization, even in the absence of an external magnetic field. The ferromagnetic system can be thought of as the analogue of the Van der Waals gas. Let us write down the integrability conditions, drawn directly from (3.5.4), (3.5.9), (3.5.12) and (3.5.14),

$$\begin{aligned}
&\left(\frac{\partial T}{\partial H}\right)_U = M\left(\frac{\partial T}{\partial U}\right)_H - T\left(\frac{\partial M}{\partial U}\right)_H \\
&\left(\frac{\partial U}{\partial H}\right)_T = T\left(\frac{\partial M}{\partial T}\right)_H - M \\
&\left(\frac{\partial U}{\partial M}\right)_T = -M\left(\frac{\partial H}{\partial M}\right)_T - T\left(\frac{\partial H}{\partial T}\right)_M \\
&T = \left[\left(\frac{\partial U}{\partial H}\right)_M + M\right]\left(\frac{\partial T}{\partial M}\right)_H - \left(\frac{\partial U}{\partial M}\right)_H\left(\frac{\partial T}{\partial H}\right)_M
\end{aligned} \tag{3.5.41}$$

3.5.4 Paramagnetism

If the magnetic dipoles do not interact with one another, we may simply replace the magnetic field intensity by the external applied field, B. The equation of state relates the mean magnetic moment to the external magnetic field and the temperature, taking on a very simple form when the dipoles are spin $\frac{1}{2}$ particles,

$$M = N\mu \tanh\left(\frac{\mu B}{kT}\right) \tag{3.5.42}$$

where μ is the magnetic moment of the individual particles, the Bohr magneton,

$$\mu = \frac{e\hbar}{2m}, \tag{3.5.43}$$

N is the total number of paramagnetic particles and B is a constant external magnetic field. Notice that the magnetization is an odd function of B, as it should be. Further it is a bounded function, approaching the limits $\pm N\mu$, which represent the condition in which all the particles are either aligned or antialigned with the magnetic field. We now aim to use the integrability conditions in (3.5.41) with H replaced by B. By (3.5.42)

$$\left(\frac{\partial M}{\partial T}\right)_B = -\frac{N\mu^2 B}{kT^2}\,\mathrm{sech}^2\left(\frac{\mu B}{kT}\right) \tag{3.5.44}$$

so applying the second of the integrability conditions we find

$$U = -N\mu B\tanh\left(\frac{\mu B}{kT}\right) + \mathcal{U}(T) \tag{3.5.45}$$

and $\mathcal{U}(T)$ is a non-magnetic contribution to the internal energy. All the other integration conditions are now straightforwardly verified. Setting $\mathcal{U}(T) = 0$, we find the magnetic contribution to the heat capacity at constant B,

$$C_B = \left(\frac{\partial U}{\partial T}\right)_B = Nk\left(\frac{\mu B}{kT}\right)^2 \mathrm{sech}^2\left(\frac{\mu B}{kT}\right). \tag{3.5.46}$$

and eliminating T in favor of U according to

$$kT = -\frac{\mu B}{\tanh^{-1}\left(\frac{U}{N\mu B}\right)}, \tag{3.5.47}$$

we may express the entropy by

$$\begin{aligned}\frac{dS}{k} &= \frac{dU}{kT} + \frac{M}{kT}dB \\ &= -\frac{1}{\mu B}\tanh^{-1}\left(\frac{U}{N\mu B}\right)\left[dU - \frac{U}{B}dB\right] \\ &= -\frac{U}{\mu B}\tanh^{-1}\left(\frac{U}{N\mu B}\right) d\ln\frac{U}{B}\end{aligned} \tag{3.5.48}$$

But now this can be integrated directly and expressed as

$$S(U,B) = -\frac{kU}{\mu B}\tanh^{-1}\left(\frac{U}{N\mu B}\right) - \frac{N}{2}\ln\left(\frac{1}{4} - \frac{U^2}{4N^2\mu^2B^2}\right) + S_0 \tag{3.5.49}$$

where S_0 is an arbitrary, integration constant, chosen so that it is the entropy at zero temperature. This can be seen more directly when S is re-expressed in terms of the pair (T, B). We find

$$S(T,B) = Nk\left[\ln 2 + \ln\cosh\left(\frac{\mu B}{kT}\right) - \frac{\mu B}{kT}\tanh\left(\frac{\mu B}{kT}\right)\right] + S_0 \tag{3.5.50}$$

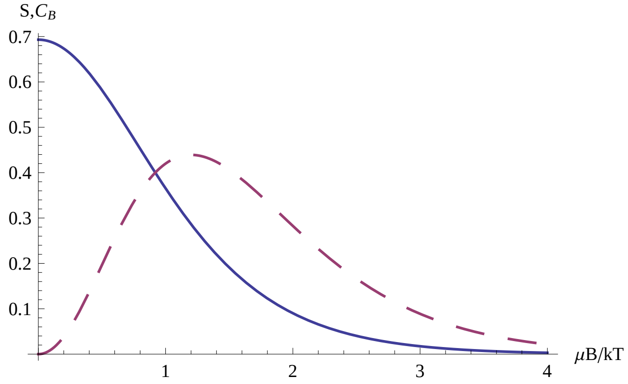

Figure 3.10: S (solid) and C_B (dashed) of the spin $\frac{1}{2}$ paramagnetic system.

whence it is clear that the magnetic part of S vanishes as $T \to 0$ if $S_0 = 0$.

At high temperatures, when $\mu B \ll kT$, we find

$$S(T,B) \approx Nk\left[\ln 2 - \frac{\mu^2 B^2}{2k^2T^2}\right] + S_0 \tag{3.5.51}$$

showing that the magnetic contribution is just $S \sim Nk\ln 2 = k\ln 2^N$ as $T \to \infty$. At very high temperatures the molecules become randomly oriented. In this disordered condition each elementary constituent is allowed only two states, *viz.,* either aligned or anti-aligned with the magnetic field, thus there are a total of 2^N states. The suggestion here is that the entropy is k times the natural logarithm of the number of states that are accessible to the system, provided that the integration constant is chosen so that it vanishes at zero temperature.

3.5.5 Ferromagnetism

In ferromagnetic materials the atoms possess an interaction between themselves, together with their interaction with an external magnetic field. The interaction is such as to lead to a decrease in the internal energy when the spins of neighboring atoms are oriented parallel to one another and an increase in energy when they are anitparallel. This favors spin alignment in the material, but the interaction energy is so small as to make the effect quite negligible at high temperatures. At low temperatures, however, cooperative behavior between the atoms can lead to a net magnetization of the material even in the absence of an external magnetic field. In the Weiss molecular, or mean, field approximation, each individual atom is taken to interact with an internal, mean molecular magnetic field, in addition to the external applied field if one is present. The molecular field is taken to be proportional to the mean magnetization (magnetic moment per unit volume) within the material, and one obtains an equation of state similar to the one we used for paramagnetic systems but with an additional contribution due to the magnetization itself *inside* the hyperbolic tangent. It has the form

$$M = N\mu \tanh\left(\frac{\mu B}{kT} + \frac{MT_c}{N\mu T}\right) \tag{3.5.52}$$

where M is the mean magnetic moment of the sample, B is an external magnetic field and T_c is a parameter that is determined by the specifics of the material and the strength of the spin-spin interaction. Equation (3.5.52) is a self-consistent equation for M, but not a very transparent one. First we note that in the absence of the external field, B, it has non-trivial solutions for M only if $T_c/T > 1$. When $T_c/T < 1$, the only solution of the equation of state is the trivial one, $M = 0$. Thus T_c represents a critical temperature, below which M may be non-vanishing even in the absence of an external magnetic field.

Solving the equation of state to express B in terms of M and T, we find

$$B = \frac{kT}{\mu}\tanh^{-1}\frac{M}{N\mu} - \frac{MkT_c}{N\mu^2} \tag{3.5.53}$$

and it follows that

$$\left(\frac{\partial B}{\partial T}\right)_M = \frac{k}{\mu}\tanh^{-1}\frac{M}{N\mu}$$

and

$$\left(\frac{\partial B}{\partial M}\right)_T = \frac{kT}{N\mu^2}\left[\frac{1}{1-\frac{M^2}{(N\mu)^2}} - \frac{T_c}{T}\right].$$

We can now integrate the third of the integrability conditions, which has the form

$$\left(\frac{\partial U}{\partial M}\right)_T = -\frac{MkT}{N\mu^2}\left[\frac{1}{1-\frac{M^2}{(N\mu)^2}} - \frac{T_c}{T}\right] - \frac{kT}{\mu}\tanh^{-1}\frac{M}{N\mu}, \tag{3.5.54}$$

to find that the internal energy is

$$U(N,m,T) = N\left[\frac{m^2kT_c}{2\mu^2} - \frac{mkT}{\mu}\tanh^{-1}\frac{m}{\mu}\right] + \mathcal{U}(T), \tag{3.5.55}$$

where we have expressed the result in terms of the magnetization per atom (the specific magnetization), $m = M/N$, so that the internal energy per atom is $u = U/N$. We may use this equation to eliminate the temperature in favor of $\{u, m\}$,

$$kT = -\frac{\mu[u - m^2kT_c/(2\mu^2)]}{m\tanh^{-1}(m/\mu)}. \tag{3.5.56}$$

and express B as a function of $\{u, m\}$,

$$B = -\frac{u}{m} - \frac{kT_c m}{2\mu^2}, \tag{3.5.57}$$

then, according to the first law, the specific entropy will be

$$Tds = du + mdB = du + m\left[\left(\frac{\partial B}{\partial u}\right)_m du + \left(\frac{\partial B}{\partial m}\right)_u dm\right] \tag{3.5.58}$$

and we determine that it depends only on the specific magnetization,

$$\frac{ds}{k} = -\left(\frac{1}{\mu}\tanh^{-1}\frac{m}{\mu}\right)dm \tag{3.5.59}$$

Integrating this equation gives the entropy,

$$S = Nk\left[\ln\cosh\tanh^{-1}\frac{m}{\mu} - \frac{m}{\mu}\tanh^{-1}\frac{m}{\mu}\right] + S_0, \tag{3.5.60}$$

where we have repeatedly used the equation of state and finally added the arbitrary constant, S_0. We have seen that, even in the absence of an external magnetic field, there are two non-zero minima for the specific magnetization so long as $T < T_c$. As such, we expect $m \to \pm\mu$ as $T \to 0$. If, as $m \to \mu$, we expand the expression for S in terms of $\delta = 1 - m/\mu$ (or $\delta = 1 + m/\mu$ if $m \to -\mu$), we find that S behaves as

$$S \to Nk\left[-\ln 2 + \frac{1}{2}\left(1 - \ln\frac{\delta}{2}\right)\delta + \mathcal{O}(\delta^2)\right] + S_0 \tag{3.5.61}$$

and vanishes as $\delta \to 0$ ($m \to \mu$) provided that $S_0 = Nk\ln 2$. On the other hand, because $m \to 0$ as $T \to \infty$, the entropy will approach S_0 or $Nk\ln 2$ in this limit. This is the result we obtained for paramagnetic systems and shows again that the entropy is indeed k times the natural logarithm of the number of accessible states. The cooperative behavior that exists between the ferromagnetic atoms by virtue of their mutual interactions is irrelevant in the limit of high temperature.

3.6 Macroscopic Motion of Systems in Equilibrium

We have so far been implicitly considering systems that are "at rest" relative to the laboratory frame, *i.e.,* systems that do not possess any **macroscopic motion**. Macroscopic motion is distinct from the microscopic motion, which is assiciated with the motion of molecules. To make this more precise, imagine that the system is made up of several *macroscopic* parts, which do not significantly interact with one another and which we label by a. Suppose that each part carries a momentum $\vec{p}_a$. If the system is macroscopically at rest then $\sum_a \vec{p}_a = 0$. If a system is in macroscopic motion then $\sum_a \vec{p}_a \neq 0$ and we will consider only the case when the system is mechanically closed so that the total linear momentum and the total angular momentum is conserved,

$$\sum_a \vec{p}_a = \text{const. and} \sum_a \vec{r}_a \times \vec{p}_a = \text{const.}, \tag{3.6.1}$$

where $\vec{r}_a$ is the position vector of the a^{th} part. Since the different parts of the system are assumed not to interact, the entropy of the system as a whole will be the sum of the entropies of its parts, $S = \sum_a S_a$ and the entropy of each part will be a function of the energy of that part *in its own rest frame*, E_a. Since its energy in the laboratory frame is related to E_a by

$$E'_a = E_a + \frac{\vec{p}_a^2}{2m_a} \tag{3.6.2}$$

we can say that

$$S_a = S_a\left(E'_a - \frac{\vec{p}_a^2}{2m_a}\right) \tag{3.6.3}$$

In equilibrium we must maximize the total entropy, S, for a given E'_a and subject to the two conditions in (3.6.1), so we apply the method of Lagrange multipliers and set the derivative with respect to $\vec{p}_a$ of

$$\sum_a [S_a + \vec{a}\cdot\vec{p}_a + \vec{b}\cdot(\vec{r}_a \times \vec{p}_a)] \tag{3.6.4}$$

to zero, for arbitrary constant vectors $\vec{a}$ and $\vec{b}$. This gives

$$\sum_a \left[-\frac{\vec{v}_a}{T} + \vec{a} + \vec{b}\times\vec{r}_a\right] = 0 \tag{3.6.5}$$

where we used

$$\frac{\partial S_a}{\partial \vec{p}_a} = \left(\frac{\partial S_a}{\partial E_a}\right)\left(\frac{\partial E_a}{\partial \vec{p}_a}\right) = \frac{1}{T}\left(-\frac{\vec{p}_a}{m_a}\right) = -\frac{\vec{v}_a}{T}. \tag{3.6.6}$$

Because the subsystems labeled by "a" are independent, we conclude that

$$-\frac{\vec{v}_a}{T} + \vec{a} + \vec{b}\times\vec{r}_a = 0 \tag{3.6.7}$$

for every subsystem, *i.e.,*

$$\vec{v}_a = \vec{u} + \vec{\Omega}\times\vec{r}_a \tag{3.6.8}$$

where $\vec{u} = T\vec{a}$ and $\vec{\Omega} = T\vec{b}$. Since $\vec{u}$ and $\vec{\Omega}$ are the same for all parts of the system, only translations of the system as a whole with constant linear velocity and/or rotations of the system as a whole with constant angular velocity are allowed in equilibrium.

Chapter 4

Thermodynamic Potentials

The introduction of a new state function, the entropy, provided us with the integrability conditions. These amounted to new consistency conditions between the state variables and we saw that, combined with the equation of state, these conditions can be used to good effect in describing thermodynamic systems. In this chapter we want to make the arguments leading to the integrability conditions more formal and more general. In the process we will introduce new functions of state, the so-called **Thermodynamic Potentials**. These new state functions will be defined in terms of the old ones and so will not be independent of them as, for example, the entropy is independent of the internal energy. Their usefulness lies in the ease with which they may describe particular thermodynamic systems and processes that occur frequently enough to be of general interest as well as in the deeper intuition they will provide for thermodynamics as a whole. We might get a better picture of where we're headed if we rexamine the integrability conditions (3.5.9), (3.5.12) and (3.5.14) from a slightly different point of view.

4.1 Legendre Transformations

Often in mathematics and physics it is desirable to express a function $f(x)$ as a different function whose argument is the derivative of $f(x)$ with respect to x rather than x itself. Suppose that we define

$$p = \frac{df}{dx} \tag{4.1.1}$$

and invert the relationship $p = f'(x)$ to get $x = x(p)$. Then the **Legendre Transform** of $f(x)$ is the function $f^\star(p)$ defined by

$$f^\star(p) = px - f(x) \tag{4.1.2}$$

We can readily check that $f^\star$ does not depend on x, since

$$\frac{df^\star}{dx} = p - \frac{df}{dx} \equiv 0 \tag{4.1.3}$$

by the definition of p. To actually calculate $f^\star(p)$ we should replace x by $x(p)$ everywhere in the definition (4.1.2) of $f^\star(p)$. Thus the Legendre transformation of $f(x)$ produces a new function in which the independent variable x is replaced by the new variable $p = df/dx$. As an example consider the function $f(x) = x^2$. Letting $p = f'(x) = 2x$ or $x = p/2$ we find that the Legendre transform of $f(x) = x^2$ is $f^\star(p) = p^2/4$. The same quadratic dependence was to be expected since the slope of tangents depends linearly on x. If instead we had the function $f(x) = e^x$, then $p = e^x \Rightarrow x = \ln p$ and we find the Legendre transform to be $f^\star(p) = p \ln p - p$, with $p \in (0, \infty)$. Applying the Legendre transform twice returns the original function. This is not difficult to verify. Suppose $f^\star(p)$ is the Legendre transformation of $f(x)$, then

$$\begin{aligned} f^\star(p) = px(p) - f(x(p)) \Rightarrow \frac{df^\star(p)}{dp} &= x(p) + p\frac{dx}{dp} - \frac{df}{dx}\frac{dx}{dp} \\ &= x(p) + p\frac{dx}{dp} - p\frac{dx}{dp} = x(p) \end{aligned} \tag{4.1.4}$$

where we used the equation defining p. Thus

$$f^{\star\star}(x) = xp(x) - f^\star(p(x)) = xp(x) - p(x)x + f(x) = f(x) \tag{4.1.5}$$

For example, for the Legendre transform of e^x we have $f^\star(p) = p \ln p - p$ and so we find

$$\frac{df^\star}{dp} = \ln p = x \Rightarrow p(x) = e^x \tag{4.1.6}$$

so that $f^{\star\star}(x) = xp(x) - f^\star(p(x)) = xe^x - xe^x + e^x = e^x = f(x)$.

When the functions we are dealing with are multivariate, the Legendre transform can be defined independently for as many of the independent variables as we choose, provided that the equations defining the new variables (in terms of derivatives of the function) can be inverted. Imagine that we have a function $f(x_i)$ and we define

$$p_a = \frac{\partial f}{\partial x_a} \tag{4.1.7}$$

for some subset of the variables x_i. The required Legendre transformation would then be

$$\sum_a p_a x_a - f(x_i) \tag{4.1.8}$$

but, by the inverse function theorem, the relations can be inverted to eliminate the x_a in favor of the p_a if and only if

$$\det\left|\frac{\partial p_a}{\partial x_b}\right| = \det\left|\frac{\partial^2 f}{\partial x_a \partial x_b}\right| \neq 0 \tag{4.1.9}$$

The matrix $W_{ab} = \partial p_a/\partial x_b$ is called the **Hessian**. We will only consider cases with non-vanishing $\det|W_{ab}|$. For example, we could not find a double Legendre transformation of the function $f(x,y) = x^2 + y$ since the Hessian

$$W = \begin{pmatrix} 2 & 0 \\ 0 & 0 \end{pmatrix} \tag{4.1.10}$$

is is not invertible, but we could find the double Legendre transformation for the function $f(x,y) = x^2 + xy$, because for this function $|W_{ab}| = -1$.

As examples closer to home, consider the entropy function which, according to the first law, is naturally thought of as a function of the internal energy and the volume, $S = S(U,V)$. The first law also implies that

$$\frac{\partial S}{\partial U} = \frac{1}{T}, \quad \frac{\partial S}{\partial V} = \frac{p}{T} \tag{4.1.11}$$

Suppose we wish to replace the internal energy U by the temperature T. We could perform a Legendre transformation of S by setting

$$S_1^\star = \frac{U}{T} - S \tag{4.1.12}$$

Evidently, $S_1^\star = S_1^\star(T,V)$ because, using the first law,

$$dS_1^\star = d\left(\frac{U}{T}\right) - dS = \frac{dU}{T} - \frac{U}{T^2}dT - \frac{dU}{T} - \frac{p}{T}dV = -\frac{U}{T^2}dT - \frac{p}{T}dV \tag{4.1.13}$$

and therefore

$$\frac{\partial S_1^\star}{\partial T} = -\frac{U}{T^2}, \quad \frac{\partial S_1^\star}{\partial V} = -\frac{p}{T} \tag{4.1.14}$$

It is straightforward to show then that the integrability condition for $S_1^\star$ is just (3.5.9).[1] Again, if we wanted to replace U with T *and* V with p/T, we could do so by making the double Legendre transformation[2]

$$S_2^\star = \frac{U}{T} + \frac{pV}{T} - S \tag{4.1.15}$$

---

[1] Problem: Show this by simplifying

$$\frac{\partial^2 S_1^\star}{\partial V \partial T} = \frac{\partial^2 S_1^\star}{\partial T \partial V}$$

[2] Problem: What condition ensures invertibility in this case? Verify that it holds for an ideal gas.

Checking its dependence as before we see that

$$\begin{aligned} dS_2^\star &= \frac{dU}{T} - \frac{U}{T^2}dT + \frac{p}{T}dV + \frac{V}{T}dp - \frac{pV}{T^2}dT - \frac{dU}{T} - \frac{p}{T}dV \\ &= -\left(\frac{U+pV}{T^2}\right)dT + \frac{V}{T}dp \end{aligned} \tag{4.1.16}$$

so $S_2^\star$ is a function of (T, p) and

$$\frac{\partial S_2^\star}{\partial T} = -\frac{U+pV}{T^2}, \quad \frac{\partial S_2^\star}{\partial p} = \frac{V}{T} \tag{4.1.17}$$

Again, one can show that the integrability condition for $S_2^\star$ is precisely (3.5.12).[3]

4.2 Maxwell Relations

If the first law is rewritten in the form

$$dU = TdS - pdV, \tag{4.2.1}$$

we see that U is naturally viewed as a function of (S, V) and

$$\frac{\partial U}{\partial S} = T, \quad \frac{\partial U}{\partial V} = -p \tag{4.2.2}$$

Integrability of U then requires that

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \tag{4.2.3}$$

We could define the new function, H, by using a Legendre transformation to trade V for p,

$$-H(S,p) = V\frac{\partial U}{\partial V} - U \Rightarrow H = U + pV \tag{4.2.4}$$

The function H is called the **Enthalpy**. It is the first of three new thermodynamic potentials that we will examine in this section and is naturally a function of (S, p),

$$dH = dU + pdV + Vdp = TdS + Vdp \tag{4.2.5}$$

This gives the relations

$$\frac{\partial H}{\partial S} = T, \quad \frac{\partial H}{\partial p} = V \tag{4.2.6}$$

---

[3] Problem: Show this explicitly.

and the integrability conditions

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p \tag{4.2.7}$$

Again, according to (4.2.2), we could also choose to trade S for T by a Legendre transformation, defining

$$-F(T,V) = \frac{\partial U}{\partial S} S - U \Rightarrow F = U - TS \tag{4.2.8}$$

The function F, called the **Helmholz Free Energy**, is our second thermodynamic potential, and satisfies

$$dF = dU - TdS - SdT = -SdT - pdV. \tag{4.2.9}$$

It follows that

$$\frac{\partial F}{\partial T} = -S, \quad \frac{\partial F}{\partial V} = -p, \tag{4.2.10}$$

so integrability of F requires that

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V. \tag{4.2.11}$$

Finally, let's perform a double Legendre transformation, which is possible only so long as

$$\left\| \begin{matrix} \left(\frac{\partial T}{\partial S}\right)_V & -\left(\frac{\partial p}{\partial S}\right)_V \\ \left(\frac{\partial T}{\partial V}\right)_S & -\left(\frac{\partial p}{\partial V}\right)_S \end{matrix} \right\| \neq 0, \tag{4.2.12}$$

to get the last of the three new thermodynamic potentials that we will introduce, the **Gibbs Free Energy**

$$-G(T,p) = \left(\frac{\partial U}{\partial V}\right)_S V + \left(\frac{\partial U}{\partial S}\right)_V S - U \;\Rightarrow\; G = U - TS + pV, \tag{4.2.13}$$

which satisfies

$$dG = dU - TdS - SdT + pdV + Vdp = -SdT + Vdp. \tag{4.2.14}$$

Integrability of the Gibbs free energy will then require

$$-\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p \tag{4.2.15}$$

Relations (4.2.3),(4.2.7),(4.2.11) and (4.2.15) are examples of the **Maxwell relations** of Thermodynamics. In our discussion above, each thermodynamic function depended on two variables, but in general they may depend on several. In that case there will be more than one Maxwell relation per thermodynamic potential. This follows from the fact that they are statements about integrability. If the thermodynamic potential Φ is an analytic function of several variables, call these Z_i, then

$$\frac{\partial}{\partial Z_i}\left(\frac{\partial \Phi}{\partial Z_j}\right) \equiv \frac{\partial}{\partial Z_j}\left(\frac{\partial \Phi}{\partial Z_i}\right) \tag{4.2.16}$$

and so there are $n(n-1)/2$ Maxwell relations per thermodynamic function, where n is the number of natural variables for that potential. We will soon see that they can be potent problem solving tools in Thermodynamics.

4.2.1 Heat Capacities

In Chapter 2, we had obtained a simple relation between the heat capacity of an ideal gas and constant volume and its heat capacity at constant pressure. This relationship relied heavily on the equation of state, its simplicity resulting from the simple form that the ideal gas equation of state has. We would like to obtain a relationship between the heat capacities for an arbitrary thermodynamic system, regardless of the equation of state.

Let's begin by noting that since

$$đQ = TdS \tag{4.2.17}$$

then considering $S = S(p, T)$, we find

$$đQ = T\left(\frac{\partial S}{\partial T}\right)_p dT + T\left(\frac{\partial S}{\partial p}\right)_T dp \tag{4.2.18}$$

showing that

$$C_p = \left(\frac{đQ}{dT}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p \tag{4.2.19}$$

and

$$đQ = C_p dT + T\left(\frac{\partial S}{\partial p}\right)_T dp \tag{4.2.20}$$

But, now if we think of $p = p(V, T)$ then

$$đQ = C_p dT + T\left(\frac{\partial S}{\partial p}\right)_T \left[\left(\frac{\partial p}{\partial V}\right)_T dV + \left(\frac{\partial p}{\partial T}\right)_V dT\right] \tag{4.2.21}$$

so the heat capacity at constant volume will be

$$\left(\frac{đQ}{dT}\right)_V = C_V = C_p + T\left(\frac{\partial S}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V \tag{4.2.22}$$

and so we end up with the analogue of (2.2.10),

$$C_p - C_V = -T\left(\frac{\partial S}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V \tag{4.2.23}$$

The right hand side has a derivative of the entropy, which is not a quantity easily measured. However, thanks to the Maxwell's equation (4.2.15), we could trade the derivative of S for a derivative of V, to write this relation in the more useful form

$$C_p - C_V = T\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_V . \tag{4.2.24}$$

Experimentally, the quantity

$$\gamma = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \tag{4.2.25}$$

is easily measured and changes slowly with temperature in most cases, and is called the **coefficient of volume expansion**. So we may write the difference in heat capacities in terms of the coefficient of volume expansion as

$$C_p - C_V = \gamma T V \left(\frac{\partial p}{\partial T}\right)_V . \tag{4.2.26}$$

The derivative of p that appears on the right hand side is easy to measure, but still we'll trade it for volume derivatives which are most often used as descriptors of the physical properties of thermodynamic systems. To bring it to final form, let's think of $V = V(p,T)$, so

$$dV = \left(\frac{\partial V}{\partial p}\right)_T dp + \left(\frac{\partial V}{\partial T}\right)_p dT = 0 \tag{4.2.27}$$

(for a constant volume process) and therefore

$$\left(\frac{\partial p}{\partial T}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T} \tag{4.2.28}$$

If we divide both numerator and denominator by V, we will recognize the numerator as the coefficient of volume expansion. The denominator is also easily measured and its opposite is called the **coefficient of isothermal compressibility**,

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T . \tag{4.2.29}$$

Finally, we have

$$C_p - C_V = \frac{\alpha^2}{\kappa} T V \tag{4.2.30}$$

For the ideal gas, with $pV = NkT$,

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{Nk}{pV} = \frac{1}{T} \tag{4.2.31}$$

whereas

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = \frac{NkT}{p^2 V} = \frac{1}{p} \tag{4.2.32}$$

Plugging these into (4.2.30) we find (2.2.10). To find the analogue for the Van-der-Waals gas, we use the equation of state (3.4.12) to obtain

$$\begin{aligned} \alpha &= \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{Nk}{\frac{NkTV}{V-Nb} - \frac{2aN^2}{V^2}(V-Nb)} \\ \kappa &= -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = \frac{V-Nb}{\frac{NkTV}{V-Nb} - \frac{2aN^2}{V^2}(V-Nb)} \end{aligned} \tag{4.2.33}$$

giving

$$C_p - C_V = \frac{(Nk)^2 TV}{(V-Nb)\left(\frac{NkTV}{V-Nb} - \frac{2aN^2}{V^2}(V-Nb)\right)}, \tag{4.2.34}$$

which depends on both the volume and temperature, but reduces to (2.2.10) in the limit of very large volume, or as a and b vanish.

The auxilliary functions U, H, F and G that were introduced in the previous section are four out of five thermodynamic potentials. Each leads to an integrability condition, a Maxwell relation, by virtue of the fact that it is a state function. Each acquires a special meaning for particular thermodynamic processes, so it's worth having a summary of results at our disposal, for future use:

$$\begin{array}{lll} \text{The Internal Energy:} & U(S,V) & \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \\ \text{The Enthalpy:} & H(S,p) = U + pV & \left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p \\ \text{The Helmholz Free Energy:} & F(T,V) = U - TS & \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \\ \text{The Gibbs Free Energy:} & G(T,p) = U - TS + pV & -\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p \end{array} \tag{4.2.35}$$

An important fact to keep in mind is that *all* the thermodynamic potentials are extensive quantities. By this we mean that if a thermodynamic potential Φ is given in terms of some extensive variables $\vec{X}$ (apart, possibly, from some intensive ones), then

$$\Phi(\ldots, \alpha\vec{X}) = \alpha\Phi(\ldots, \vec{X}) \tag{4.2.36}$$

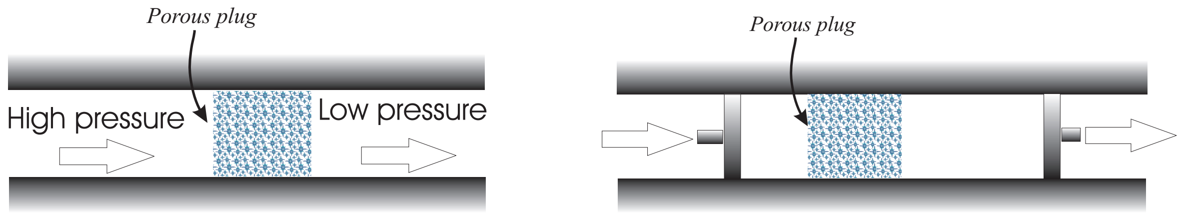

Figure 4.1: The Joule-Thompson process.

where ... refer to the intensive variables on which Φ may depend. Our purpose in the following sections is to explore their usefulness and scope. Since we already have a good idea of what the internal energy signifies via the first law of thermodynamics we begin with the enthalpy.

4.3 The Enthalpy

The relation $dH = TdS + Vdp$ tells us that during a reversible isobaric process ($dp = 0$) the change in enthalpy is just the amount of energy that is transferred to a system by heat, $dH = TdS = đQ$. We can see that this is true for an irreversible process as well, since

$$đQ = dU + pdV = d(U + pV) - Vdp = dH - Vdp = dH \tag{4.3.1}$$

where the last equality holds only if the process is isobaric. Most chemical reactions occur at constant pressure rather than at constant volume (for isovolumetric processes, $đQ = dU$) and for them dH would represent the energy absorbed by the reactants and products as heat. If the enthalpy decreases it means that the reaction is exothermic (releases energy by heat) and if it increases the reaction is endothermic (absorbs energy by heat).

If we think of $H = H(T,p)$ (even though S and not T is a natural variable for H), the first law of thermodynamics says that

$$C_p = \left(\frac{đQ}{dT}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p \tag{4.3.2}$$

and therefore that

$$H(T,p) = \int_{p,i}^{f} C_p(T,p)\ dT + \mathcal{H}(p) \tag{4.3.3}$$

where the suffix p indicates that the integral is to be carried out holding p fixed.

We can obtain expressions for the enthalpy in certain simple cases. For an ideal gas, whose internal energy is $U = gkT/2$, we have

$$H(T) = \frac{g}{2}kT + pV = \left(\frac{g}{2}+1\right)NkT = C_pT \tag{4.3.4}$$

and for the Van der Waals gas

$$H(T,V) = -\frac{aN^2}{V} + \frac{g}{2}NkT + p(T,V)V = -\frac{2aN^2}{V} + \frac{g}{2}NkT + \frac{NkTV}{V-Nb} \tag{4.3.5}$$

where we use (3.5.25) for the internal energy in the first step and the equation of state (3.4.12) in the last.

4.3.1 The Joule-Thompson (throttling) process

A very important application of the enthalpy is the **Joule-Thompson** or **throttling** process. Here a gas is allowed to flow adiabatically and steadily from a region of constant high pressure to a region of constant low pressure through a porous plug as shown on the left of figure 4.1. Since the flow occurs adiabatically, then

$$đQ = 0 = dU + đW. \tag{4.3.6}$$

To calculate the work that is done in passing from one side of the porous plug to the other, it is convenient to imagine that a volume V_h from the high pressure region is moved to occupy a volume V_l in the low pressure region by the action of two pistons as shown on the right of figure 4.1 (generally a steady flow and constant pressures are maintained by pumps). For instance, to start with the piston on the right would be pressed against the plug ($V_l = 0$) and a certain volume V_h of the gas would lie between the piston on the left and the porous plug. The pistons are then moved together quasi-statically to the right in such a way that the pressures in each region are kept constant and, by the end of this process, a volume V_h has passed from the left to the right of the porous plug. It is then easy to see that the work done by the gas in the high pressure region is $-p_hV_h$ and in the low pressure region it is p_lV_l. It follows that the total work done by the gas is

$$\Delta W = -p_hV_h + p_lV_l \tag{4.3.7}$$

and the total change in internal energy, because the gas was initially in the high pressure region and ends up in the low pressure region is

$$\Delta U = U_l - U_h \tag{4.3.8}$$

so by the first law (there is no energy transfer by heat)

$$U_l - U_h - p_hV_h + p_lV_l = 0 \Rightarrow H_l = U_l + p_lV_l = U_h + p_hV_h = H_h \tag{4.3.9}$$

and the process is isenthalpic (*i.e.,* the enthalpy of the gas remains unchanged). We would like to know if there is a change in temperature as the gas expands. Let's consider the situation microscopically first. If the molecules exert an attractive force on one another then the effect of increasing the intermolecular distance as they pass from the high pressure region to the low pressure region is to increase the intermolecular potential energy. Since energy is conserved, this would cause the kinetic energy of each molecule to correspondigly decrease causing a drop in the temperature. There is another opposing effect, however. During collisions, kinetic energy is temporarily converted into potential energy. If the intermolecular collision rate decreases then on the average less energy is stored as potential energy and the average molecular kinetic energy will correspondingly increase. This would cause a rise in the temperature. Below a certain temperature we expect the first effect to dominate. Above this temperature the latter effect should dominate. The temperature at which the behavior of the gas changes from one to the other is called the **inversion temperature**. Our objective is to determine $(\partial T/\partial p)_H$, which is called the **Joule-Thompson coefficient**, $\mu_{\rm JT}$. Inversion will occur when $\mu_{\rm JT}$ vanishes.

Now we have seen that $dH = TdS + Vdp$. If we think of $S = S(p,T)$ then

$$dH = T\left(\frac{\partial S}{\partial T}\right)_p dT + \left[T\left(\frac{\partial S}{\partial p}\right)_T + V\right]dp \tag{4.3.10}$$

But evidently since

$$\left(\frac{\partial H}{\partial T}\right)_p = C_p = T\left(\frac{\partial S}{\partial T}\right)_p \tag{4.3.11}$$

and since H itself is constant during the Joule-Thompson process,

$$0 = C_p dT + \left[T\left(\frac{\partial S}{\partial p}\right)_T + V\right]dp \tag{4.3.12}$$

Replace the derivative of S with respect to p using the Maxwell relation in (4.2.15), we have

$$C_p dT = \left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right]dp \tag{4.3.13}$$

The derivative of V that appears above is related to the coefficient of volume expansion, γ by

$$\gamma = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p, \tag{4.3.14}$$

therefore

$$\mu_{\rm JT} = \left(\frac{\partial T}{\partial p}\right)_H = \frac{V}{C_p}(\gamma T - 1) \tag{4.3.15}$$

Only when $\mu_{\rm JT} > 0$ will the gas cool upon expansion. When $\mu_{\rm JT} < 0$ the gas will actually warm during expansion.

For the ideal gas, the coefficient of volume expansion is just $\gamma = 1/T$, therefore $\mu_{\rm JT} = 0$. This is to be expected because neither mechanism for a change of temperature is available to the ideal gas: (i) there are no molecular interactions, so there is no loss of kinetic energy in favor of potential energy and (ii) the molecules are pointlike and there are no collisions, so no kinetic energy is never temporarily stored as potential energy during collisions.

The situation is more complicated with a Van-der-Waals gas, for which

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{Nk}{p - \frac{aN^2}{V^2} + \frac{2N^2ab}{V^3}} = \frac{Nk}{\frac{NkT}{V-Nb} - \frac{2aN^2}{V^2} + \frac{2N^2ab}{V^3}} \tag{4.3.16}$$

We can insert this into the expression for the Joule-Thompson coefficient, (4.3.15), to get

$$\mu_{\rm JT} = \frac{1}{C_p}\left[\frac{NkT}{\frac{NkT}{V-Nb} - \frac{2aN^2}{V^2} + \frac{2N^2ab}{V^3}} - V\right] \tag{4.3.17}$$

First let's calculate C_p. According to (4.3.5),

$$C_p = \frac{g}{2}Nk + \frac{NkT}{V-Nb}\left(\frac{\partial V}{\partial T}\right)_p = \frac{g}{2}Nk + \frac{NkT}{V-Nb}\frac{Nk}{\frac{NkT}{V-Nb} - \frac{2aN^2}{V^2} + \frac{2N^2ab}{V^3}} \tag{4.3.18}$$

Notice that as V approaches infinity, $C_p \to (g+2)Nk/2$ (as we expect) but

$$\lim_{V\to\infty} \mu_{\rm JT} = \frac{2}{(g+2)k}\left[\frac{2a}{kT} - b\right] \tag{4.3.19}$$

In this limit the Van-der-Waals should behave like an ideal gas, but we see that the Joule-Thompson coefficient does *not* approach zero. The inversion temperature is determined by both a and b as $T_c = 2a/kb$ and at low temperatures ($T < T_c$) the coefficient is positive (the gas cools upon expansion) but at high temperatures ($T > T_c$) the coefficient is negative and the gas would warm on expanding. As you have probably guessed by now, the Joule-Thompson effect is used in refrigeration.

4.4 The Helmholz Free Energy

For the Helmholz free energy, we had obtained $dF = -SdT - pdV$, showing that for an isothermal process $pdV = -dF$, *i.e.,* the *decrease* in free energy is the work done by the system. This holds for reversible processes, only. To see what would happen during an irreversible process we must return to the first law,

$$TdS \geq đQ = dU + pdV \quad \Rightarrow \quad d(TS) - SdT \geq dU + pdV$$

$$\Rightarrow \quad dF = d(U - TS) \leq -SdT - pdV \tag{4.4.1}$$

from which we see that during an isothermal process (only)

$$pdV \leq -dF \tag{4.4.2}$$

Thus the decrease in the Helmholz free energy is really an upper bound for the amount of work extracted from the system (done by the system). This is what gives this thermodynamic function its name, the "free energy". Only if the process is reversible is it possible to extract an amount of work equal to the decrease in free energy. In this sense the free energy plays the role of the energy in mechanical systems, but it should be remembered that in mechanical systems the equality always holds. During a process in which no work is done either by or on the system, say an isovolumetric process, $dF \leq 0$ and we conclude that for isothermal systems involving no exchange of energy with the environment by mechanical work, the free energy *may never increase.* It follows that mechanically isolated systems operating at constant temperature achieve equilibrium at the minimum of the free energy.

Using the expression (3.4.11) and the ideal gas equation of state it is not difficult to find that

$$F(T,V) = \frac{g}{2}NkT\left[1 - \ln\left(\frac{T}{T_*}\right) - \frac{2}{g}\ln\left(\frac{V}{V_*}\right)\right] \tag{4.4.3}$$

and, for the Van-der-Waals gas, using (3.4.16),

$$F(T,V) = \frac{g}{2}NkT\left[1 - \ln\left(\frac{T}{T_*}\right) - \frac{2}{g}\ln\left(\frac{V - Nb}{V_* - Nb}\right)\right] \tag{4.4.4}$$

Armed with a knowledge of the meaning of the Helmolz free energy, we can now address the following natural question. We know that every isotherm involves work. If the isothermal process results in an expansion of the system then work is done by the system on the environment and, vice-versa, if there is a reduction of the volume of the system work is done on the system by the environment. What is the upper limit on the amout of work that is done during an isothermal process as a function of the temperature, but for the same net expansion?

4.4.1 The Van 't Hoff Equation

For definiteness, let's consider two isothermal expansions at temperatures that differ by dT. Call these AB and $A'B'$ as in figure 4.2. Join the isotherms by isovolumetric processes at either end as shown in the figure. If W and W' are the maximum amounts of work for processes AB and $A'B'$ respectively, then

$$W = F(A) - F(B)$$

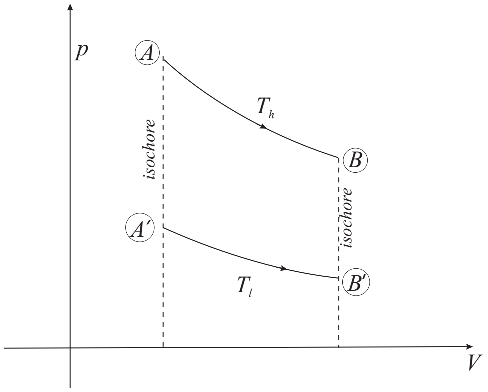

Figure 4.2: The Van 't Hoff isochores

$$W' = F(A') - F(B') \tag{4.4.5}$$

The difference in the works done by the two isotherms is therefore

$$dW = W' - W = [F(A') - F(A)] - [F(B') - F(B)] = dF(A) - dF(B) \tag{4.4.6}$$

But, $F = U - TS$, and we can go from A to A' via the isochore on the left and from B to B' via the isochore on the right. No work is done along the isochores, so at A

$$dF(A) = -S(A)dT = \frac{dT}{T}[F(A) - U(A)] \tag{4.4.7}$$

and likewise at B

$$dF(B) = -S(B)dT = \frac{dT}{T}[F(B) - U(B)] \tag{4.4.8}$$

It follows that

$$dW = \frac{dT}{T}\{[F(A) - F(B)] - [U(A) - U(B)]\} \tag{4.4.9}$$

and, therefore

$$dW = \frac{dT}{T}\{W + \Delta U_{AB}\}, \tag{4.4.10}$$

where $\Delta U_{AB} = U_B - U_A$, or

$$\frac{dW}{dT} - \frac{W}{T} = \frac{\Delta U_{AB}(T)}{T} \tag{4.4.11}$$

This is called the **Van 't Hoff equation**. It has Bernoulli's form and can be formally integrated,

$$W(T) = T\left[\int \frac{\Delta U_{AB}(T)}{T^2}\, dT + \alpha\right] \tag{4.4.12}$$

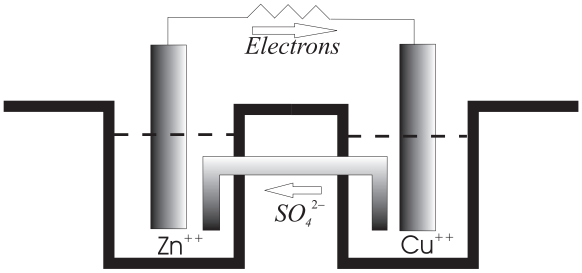

Figure 4.3: An Electrochemical Cell

where α is independent of T but may depend on the other parameters of the system. Since W in the Van 't Hoff equation actually represents the work done along an isotherm, let's rename it ΔW and note that the Van 't Hoff equation can be put into the form

$$T\frac{d\Delta W}{dT} = \Delta W + \Delta U_{AB} \tag{4.4.13}$$

which suggests that

$$\Delta Q = T\frac{d\Delta W}{dT} \tag{4.4.14}$$

is to be interpreted as the heat absorbed or given out by the system during the process.

For the ideal gas, no change in the internal energy occurs along any isotherm, so we find

$$W = \alpha T, \tag{4.4.15}$$

which could also be obtained from a direct integration of the work. This gives $\alpha = Nk\ln(V_B/V_A)$. The work done along an isotherm will generally depend on the form of the internal energy. For the Van-der-Waals gas, the internal energy changes as one goes from A to B, but only by the constant

$$\Delta U_{AB} = -aN^2\left[\frac{1}{V_B} - \frac{1}{V_A}\right] \tag{4.4.16}$$

and we see that

$$W = \alpha T - \Delta U_{AB}. \tag{4.4.17}$$

(If $a > 0$, the change in potential energy is positive when $V_B > V_A$. This is to be expected because the molecular potential energy rises as the intermolecular separation increases, consequently the work done decreases.)

4.4.2 The Reversible Electrochemical Cell

Although we have, by and large, considered external work to have the form $đW = pdV$, the concept of mechanical work is not limited to changes in volume, as we have already seen with magnetic systems. We can also consider processes that do external work electrically. An **electrochemical cell** is a device used for generating an electromotive force (e.m.f.) via chemical reactions, as shown in figure 4.3. In general the cell consists of two chambers, each of which is made up of an electrode and an electrolyte. Ions in the electrolyte from one chamber lose electrons to their electrode, which then pass to the other electrode by means of an external circuit, allowing ions in the electrolyte from the other chamber to gain electrons. The flow of negative charge back to the first chamber is maintained via a "salt bridge" connecting the electrolytes, whose function is to selectively permit the flow of negative ions from the latter chamber to the first. Each chamber has a characteristic potential, depending on its composition. In the figure, the chamber on the left consists of a Zinc (Zn) electrode immersed in a aqueous solution of Zinc Sulphate ($ZnSO_4$), whereas the chamber on the right consists of a Copper (Cu) electrode immersed in a solution of Copper Sulphate ($CuSO_4$). Zn atoms in the electrode on the left tend to cede electrons to the Cu ions in the electrolyte on the right, the reaction being

$$\mathrm{Zn} + \mathrm{Cu}^{++} \rightarrow \mathrm{Zn}^{++} + \mathrm{Cu}. \tag{4.4.18}$$

As the electrons flow from the Zn electrode to the Cu electrode by way of the external circuit, the Zn atoms lose electrons and become positive ions, which go into the aqueous solution. The Zinc electrode loses mass. On the other hand, the electrons gained by the Cu electrode allow it to convert Cu ions from the solution to uncharged Cu atoms which deposit on the electrode. The Cu electrode gains mass. The two chambers are connected by a salt bridge which permits the movement of sulphate ions from the right cell to the left cell and prevents the movement of the metal ions. This is generally accomplished by separating the electrolytes by a porous membrane (or other mechanism) that provides for the selective movement of the negative ions in the electrolyte from right to left.

Consider a cell which functions reversibly.[4] Let $\mathcal{E}(T)$ be the e.m.f. across the cell, then the work done by the cell in moving a very small charge, δq, across from the positive terminal to the negative terminal (we take δq to be positive, for convenience but in fact electrons are flowing from the negative terminal to the positive one) is $W = \delta q \mathcal{E}(T)$. We assume that the work is done isovolumetrically, so there is no contribution to the work from changes in volume.

There is also a change of internal energy, ΔU, which must be negative because the cell converts chemical energy to electrical energy and, by the Van 't Hoff equation, we know

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[4] A reversible cell can always be brought back to its initial state by simply allowing an equal amount of charge to flow in the reverse direction.

that

$$\frac{dW}{dT} - \frac{W}{T} = \frac{\Delta U}{T}. \tag{4.4.19}$$

Now the change in internal energy must be proportional to the charge being moved across the cell and it is more convenient to work with the change in internal energy per unit of charge moved, defined by $u(T) = -\Delta U/\delta q$. Substituting for W and ΔU, and dividing throughout by δq gives

$$\frac{d\mathcal{E}}{dT} - \frac{\mathcal{E}}{T} = -\frac{u(T)}{T}, \tag{4.4.20}$$

from which we obtain the e.m.f. as a function of temperature

$$\mathcal{E}(T) = T\left[-\int \frac{u(T)}{T^2} dT + \mathcal{C}\right]. \tag{4.4.21}$$

Because the work done to move a charge Δq at temperature T is $\Delta W = \Delta q \mathcal{E}(T)$, it follows from (4.4.14) that

$$\Delta Q = \Delta q T \frac{d\mathcal{E}}{dT} \tag{4.4.22}$$

is the heat absorbed or given out to the environment during the transfer of charge. This is the heat of the chemical reaction and it may be positive or negative depending on the behavior of $u(T)$.

4.4.3 The Law of Mass Action

The Law of Mass Action is a statement concerning the equilibrium concentrations of the gases in a mixture, for example the system consisting of hydrogen, H_2, oxygen, O_2, and water, H_2O, and the reaction

$$2\mathrm{H}_2 + \mathrm{O}_2 \rightleftharpoons 2\mathrm{H}_2\mathrm{O} \tag{4.4.23}$$

where two molecules of hydrogen combine with one of oxygen to yield two molecules of water. In general we can consider a reaction

$$n_1\mathrm{A}_1 + n_2\mathrm{A}_2 + \ldots + n_3\mathrm{A}_3 \rightleftharpoons m_1\mathrm{B}_1 + m_2\mathrm{B}_2 + \ldots + m_s\mathrm{B}_s \tag{4.4.24}$$

where "A_r" represent the reagents, "B_s" the products, n_r the number of moles of the reagent A_r and m_s the number of moles of the product B_s. If we define the **concentration**, c, of each gas in the mixture as the number of moles per unit volume of the gas present, the law of mass action states that *in equilibrium*

$$\frac{c_{\mathrm{A}_1}^{n_1} c_{\mathrm{A}_2}^{n_2} \ldots c_{\mathrm{A}_r}^{n_r}}{c_{\mathrm{B}_1}^{m_1} c_{\mathrm{B}_2}^{m_2} \ldots c_{\mathrm{B}_s}^{m_s}} = K(T) \tag{4.4.25}$$

where $K(T)$ is a function only of the equilibrium temperature T, called the equilibrium constant of the reaction. We shall determine $K(T)$.

Consider an isothermal mixture of gases in a container of volume V. When the concentrations of the gases change as a consequence of the chemical reaction, the free energy $F = U - TS$ will also change. We know that

$$dF \leq -đW \tag{4.4.26}$$

and if the volume is held fixed no work is done so $dF \leq 0$, *i.e.,* F must be a minimum. Making use of the fact that the Helmholz free energy is an extensive quantity, we can write

$$F = \sum_i F_i = \sum_i n_i(u_i - Ts_i) = V \sum_i c_i(u_i - Ts_i) \tag{4.4.27}$$

where n_i represents the number of moles of the individual chemicals, u_i is the internal energy per mole and s_i is the entropy per mole respectively. We have set $n_i = c_i V$. Now we can use (4.4.3) to express each F_i as

$$F_i = F_i(T, V) = V c_i[\mathcal{C}_{V_i} T + W_i - T(\mathcal{C}_{V_i} \ln T + R \ln \overline{V}_i + a)] \tag{4.4.28}$$

where $\overline{V}_i$ is the molar volume (the volume occupied by a single mole of species i), $\mathcal{C}_{V_i}$ is the molar heat capacity at constant volume of species i, "a" is the entropy constant, $R = N_0 k$ is the ideal gas constant and W_i is a constant which represents the internal energy left in the gas at absolute zero *i.e.,* we take $u_i = \mathcal{C}_{V_i} T + W_i$.[5] Inserting $\overline{V} = c_i^{-1}$ we have

$$F_i = F_i(T, V) = V c_i[\mathcal{C}_{V_i} T + W_i - T(\mathcal{C}_{V_i} \ln T - R \ln c_i + a_i)] \tag{4.4.29}$$

and so

$$\begin{aligned} F &= V \sum_{i=1}^{r} c_{A_i}[\mathcal{C}_{V_{A_i}} T + W_{A_i} - T(\mathcal{C}_{V_{A_i}} \ln T - R \ln c_{A_i} + a)] \\ &+ V \sum_{i=1}^{s} c_{B_i}[\mathcal{C}_{V_{B_i}} T + W_{B_i} - T(\mathcal{C}_{V_{B_i}} \ln T - R \ln c_{B_i} + b_i)] \end{aligned} \tag{4.4.30}$$

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[5] This zero point energy W_i has not been included in (4.4.3) because we obtained the relation between the absolute temperature and the internal energy from the kinetic theory, in which the molecules are treated as non-interacting particles. It is nevertheless good to include it. From the point of view of thermodynamics alone, if we only assume that the internal energy is independent of the temperature then simply integrating the defining equation

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V \Rightarrow U = C_V T + W(V)$$

where W is a constant of the integration.

In an isothermal reaction at constant volume, only the concentrations may change. Since the free energy is minimum at equilibrium ($\delta F = 0$),

$$V\left\{\sum_{i=1}^{r} \delta c_{A_i}[(\mathcal{C}_{V_{A_i}} T \ldots) + RT] + \sum_{i=1}^{s} \delta c_{B_i}[(\mathcal{C}_{V_{B_i}} T \ldots) + RT]\right\} = 0. \tag{4.4.31}$$

Of course, the term RT that one gets in the above expression, coming from the derivative of the log of the concentration, can safely be absorbed into the arbitrary constant, but we will leave it in for the present. If n_{A_i} moles of the reagents react to form n_{B_i} moles of the products, the concentration of the reagents decreases according to $\delta c_{A_i} \sim -n_{A_i}$ and the concentration of the products increases according to $\delta c_{B_i} \sim m_{B_i}$. We therefore have

$$V\left\{-\sum_{i=1}^{r} n_{A_i}[(\mathcal{C}_{V_{A_i}} T \ldots) + RT] + \sum_{i=1}^{s} m_{B_i}[(\mathcal{C}_{V_{B_i}} T \ldots) + RT]\right\} = 0 \tag{4.4.32}$$

It's useful to write this out completely

$$\begin{aligned} &-\sum_{i=1}^{r} n_{A_i}[\mathcal{C}_{V_{A_i}} T + W_{A_i} - T(\mathcal{C}_{V_{A_i}} \ln T - R \ln c_{A_i} + a_i) + RT] \\ &+\sum_{i=1}^{s} n_{B_i}[\mathcal{C}_{V_{B_i}} T + W_{B_i} - T(\mathcal{C}_{V_{B_i}} \ln T - R \ln c_{B_i} + b_i) + RT] = 0 \end{aligned} \tag{4.4.33}$$

and separate out the parts that involve the concentrations. We then find that the equilibrium condition can be expressed as

$$\begin{aligned} &-\sum_{i=1}^{r} n_{A_i}[\mathcal{C}_{V_{A_i}} T + W_{A_i} - T(\mathcal{C}_{V_{A_i}} \ln T + a_i) + RT] \\ &\qquad +\sum_{i=1}^{s} n_{B_i}[\mathcal{C}_{V_{B_i}} T + W_{B_i} - T(\mathcal{C}_{V_{B_i}} \ln T + b_i) + RT] \\ &\qquad\qquad = RT\left[\sum_{i=1}^{r} \ln c_{A_i}^{n_i} - \sum_{i=1}^{s} \ln c_{B_i}^{m_i}\right] = RT \ln \frac{\prod_{i=1}^{r} c_{A_i}^{n_i}}{\prod_{i=1}^{s} c_{B_i}^{m_i}}, \end{aligned} \tag{4.4.34}$$

which can be exponentiated to get precisely (4.4.25) with

$$\begin{aligned} K(T) &= T^{\frac{1}{R}(\sum_{i=1}^{r} n_i \mathcal{C}_{V_{A_i}} - \sum_{i=1}^{s} m_i \mathcal{C}_{V_{B_i}})} \times \\ &\exp\left[\frac{1}{R}\left(\sum_{i=1}^{s} m_i (C_{V_{B_i}} + \frac{W_{B_i}}{T} + R + b_i) - \sum_{i=1}^{r} n_i (C_{V_{A_i}} + \frac{W_{A_i}}{T} + R + a_i)\right)\right] \end{aligned} \tag{4.4.35}$$

and completes our proof of the law of mass action.

The heat of a reaction at constant volume is the energy absorbed or released as heat during the reaction, assumed to occur at constant volume. If heat is released, the reaction is exothermic. If heat is absorbed, it is endothermic. We can calculate the heat of a reaction at constant volume as follows: if Q represents the energy absorbed (Q will be negative if it is released) by heat then according to the first law of thermodynamics

$$Q = \Delta U \tag{4.4.36}$$

because no work is done at constant volume. But we have

$$U = V\left[\sum_{i=1}^{r} c_{A_i}(\mathcal{C}_{V_{A_i}}T + W_{A_i}) + \sum_{i=1}^{s} c_{B_i}(\mathcal{C}_{V_{B_i}}T + W_{B_i})\right] \tag{4.4.37}$$

and therefore

$$\begin{aligned} Q = \Delta U &= V\left[\sum_{i=1}^{r} \Delta c_{A_i}(\mathcal{C}_{V_{A_i}}T + W_{A_i}) + \sum_{i=1}^{s} \Delta c_{B_i}(\mathcal{C}_{V_{B_i}}T + W_{B_i})\right] \\ &= V\left[-\sum_{i=1}^{r} n_{A_i}(\mathcal{C}_{V_{A_i}}T + W_{A_i}) + \sum_{i=1}^{s} m_{A_i}(\mathcal{C}_{V_{B_i}}T + W_{B_i})\right]. \end{aligned} \tag{4.4.38}$$

Now the natural logarithm of (4.4.35),

$$\begin{aligned} \ln K(T) &= \frac{1}{R}\left(\sum_{i=1}^{s} m_i\left[\mathcal{C}_{V_{B_i}} + \frac{W_{B_i}}{T} + R + b_i\right]\right. \\ &\qquad \left. - \sum_{i=1}^{r} n_i\left[\mathcal{C}_{V_{A_i}} + \frac{W_{A_i}}{T} + R + a_i\right]\right) \\ &\qquad\qquad + \frac{1}{R}\left(\sum_{i=1}^{r} n_i\mathcal{C}_{V_{A_i}} - \sum_{i=1}^{s} m_i\mathcal{C}_{V_{B_i}}\right)\ln T \end{aligned} \tag{4.4.39}$$

has the T derivative

$$\begin{aligned} \frac{d}{dT}\ln K(T) &= -\frac{1}{RT^2}\left(\sum_{i=1}^{s} m_i W_{B_i} - \sum_{i=1}^{r} n_i W_{A_i}\right) \\ &\qquad + \frac{1}{RT^2}\left(\sum_{i=1}^{r} n_i\mathcal{C}_{V_{A_i}}T - \sum_{i=1}^{s} m_i\mathcal{C}_{V_{B_i}}T\right) \\ &= \frac{1}{RT^2}\left(\sum_{i=1}^{r} n_i[\mathcal{C}_{V_{A_i}}T + W_{A_i}] - \sum_{i=1}^{s} m_i[\mathcal{C}_{V_{B_i}}T + W_{B_i}]\right) \end{aligned} \tag{4.4.40}$$

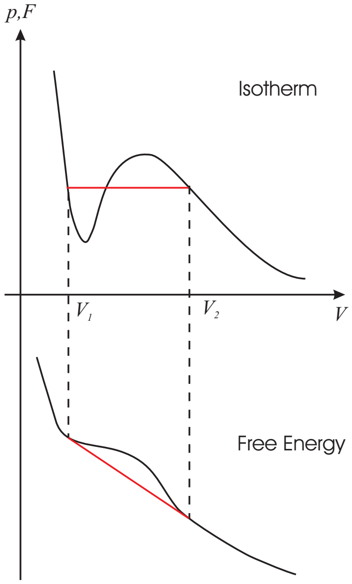

Figure 4.4: The Free Energy and Maxwell's Construction

which, when compared to the our expression for Q shows that

$$\frac{d}{dT}\ln K(T) = -\frac{Q}{RT^2}. \tag{4.4.41}$$

Thus, if the reaction is endothermic (energy is absorbed as heat) then $Q > 0$ and its equilibrium constant is an decreasing function of the temperature. On the contrary, if the reaction is exothermic (energy is released as heat) then $Q < 0$ and its equilibrium constant is an increasing function of the temperature.

4.4.4 Maxwell's construction revisited

Finally we will apply the Helmholz free energy to discuss the reasoning behind Maxwell's reconstruction of the Van der Waals isotherms. The rate of change in the free energy of a gas along an isotherm is given by $dF/dv = -p(v)$, and therefore its concavity is determined by the rate of change of pressure with volume,

$$\frac{d^2F}{dv^2} = -\frac{dp}{dv} \tag{4.4.42}$$

It follows that the free energy is concave up ($d^2F/dV^2 > 0$) so long as the pressure decreases with the volume ($dp/dv < 0$) and, vice-versa, it is concave down ($d^2F/dv^2 < 0$) when the pressure increases with the volume ($dp/dv < 0$). The former situation occurs everywhere except between the local minimum and local maximum of the isotherm, during which $dp/dv > 0$, therefore it becomes possible to draw a common tangent line such that it touches the left dip at V_1 and the right dip at V_2. Because the tangent lies *below* the free energy curve, molecules prefer to be in two coexisting phases (gas and liquid) between V_1 and V_2. The work done in the process will be $W = p(T)(V_2 - V_1)$ and must equal the net change in the free energy, which depends only on the initial and final states, therefore

$$p(T)(V_2 - V_1) = -(F_2 - F_1) = \int_{V_1,\mathrm{VdW}}^{V_2} p dV. \tag{4.4.43}$$

The left hand side is the area under the horizontal construction (in red) and the right hand side is the work done along the Van der Waal isotherm. The two areas are equal, which is precisely Maxwell's condition.

4.5 The Gibbs Free Energy

The Gibbs free energy is naturally a function of the variables (T, p) because $dG = -SdT + Vdp$. In processes during which both the pressure and the temperature remain constant, such as during some phase transitions (for example, boiling) the Gibbs free energy stays constant. This holds for a reversible process, but it needs to be modified for irreversible processes. Thus, beginning with the first law,

$$TdS \geq đQ = dU + pdV \Rightarrow d(U - TS + pV) - Vdp - SdT \leq 0 \tag{4.5.1}$$

or, for processes that are both isobaric and isothermal, $dG \leq 0$. Equilibrium in systems for which both the temperature and pressure remain constant is determined by the minimum of the Gibbs free enery.

We could easily obtain expressions for G for gases, using our knowledge of the internal energy. For the ideal gas,

$$G(T, V) = \frac{g}{2} NkT \left[1 - \ln\left(\frac{T}{T_*}\right) - \frac{2}{g}\left\{\ln\left(\frac{V}{V_*}\right) - 1\right\}\right] \tag{4.5.2}$$

and for the Van-der-Waals gas

$$G(T, V) = \frac{g}{2} NkT \left[1 - \ln\left(\frac{T}{T_*}\right) - \frac{2}{g}\ln\left(\frac{V - Nb}{V_* - Nb}\right)\right] + V\left[-\frac{aN^2}{V^2} + \frac{NkT}{V - Nb}\right] \tag{4.5.3}$$

Expressions in terms of other pairs of independent variables can be obtained by using the appropriate equations of state.

The most direct justification for Maxwell's construction comes by examining the phase transition from the point of view of the Gibbs free energy because, since the phase transition occurs at a fixed temperature and pressure, the Gibbs free energy cannot change. Then

$$0 = \int_L^R dG = \int_L^R V dp = \int_L^R [d(pV) - pdV] = p(T)(V_2 - V_1) - \int_{V_1,\mathrm{VdW}}^{V_2} pdV, \qquad (4.5.4)$$

where $L(R)$ represent the left and right edges of the constant pressure (horizontal) construction. The first term on the right is the area under the horizontal construction between V_1 and V_2. The second is the work done along the Van der Waal isotherm. The areas must be equal and Maxwell's condition follows.

4.5.1 The Clausius-Clapeyron equation

Let us revisit the Clausius-Clapeyron equation, viewing the equilibrium isotherms through the lens of the Gibbs free energy. Recall that the system in consideration is a liquid in equilibrium with its vapor at some temperature T and the $p-V$ diagram is shown in figure 3.8. During the liquid-vapor equilibrium phase both the temperature and the pressure remain constant, therefore the equilibrium is determined by the minimum of the Gibbs free energy. Let us continue to use the notation of section (3.4.2). Since the Gibbs free energy is extensive, we analyze the system in terms of the Gibbs free energy *per unit mass*. For the liquid and the gas these are, respectively,

$$\mathfrak{g}_l = u_l - Ts_l + pv_l$$

$$\mathfrak{g}_v = u_v - Ts_v + pv_v \qquad (4.5.5)$$

in obvious notation. Let the mass of liquid be m_l and that of vapor be m_v, then certainly $m_l + m_v$ is constant and any change will be such that $dm_l = -dm_v$. The total Gibbs free energy of the system is

$$G = m_l\mathfrak{g}_l + m_v\mathfrak{g}_v \qquad (4.5.6)$$

Imagine that a small transformation occurs reversibly in such a way that dm_l of the liquid transforms into vapor (dm_l can be positive or negative). The corresponding change in the Gibbs free energy is then

$$dG = dm_l(\mathfrak{g}_l - \mathfrak{g}_v) \qquad (4.5.7)$$

but, since the system is in equilibrium, $dG = 0 \Rightarrow \mathfrak{g}_l = \mathfrak{g}_v$. Thus

$$(u_v - u_l) - T(s_v - s_l) + p(v_v - v_l) = 0 \Rightarrow$$

$$d(u_v - u_l) - dT(s_v - s_l) - Td(s_v - s_l) + dp(v_v - v_l) + pd(v_v - v_l) = 0 \quad (4.5.8)$$

Now, using the first law, $Tds = du + pdv$, we find that

$$\frac{dp}{dT} = \frac{s_v - s_l}{v_v - v_l} \tag{4.5.9}$$

But, $s_v - s_l$ is the change in entropy when one gram of the liquid changes to vapor at the temperature T, therefore

$$s_v - s_l = \frac{L}{T} \tag{4.5.10}$$

where L is the latent heat of vaporization and so

$$\frac{dp}{dT} = \frac{L}{T(v_v - v_l)} \tag{4.5.11}$$

4.5.2 The Gibbs Phase Rule

In the previous example, we had considered a liquid and its vapor in equilibrium, *i.e.,* two phases of a substance. All the properties of each phase depend exclusively on the temperature, the pressure and the chemical composition of the phase.

What exactly is a phase? A phase is a homogeneous mixture, in a definite physical state, of all possible chemical compounds that can be formed from the chemical elements present. Its thermodynamic properties will depend on T, p and the relative concentrations of all the elements. Clearly, the number of components of a phase may be larger or smaller than the actual number of elements present. For example, if the chemical elements present in a gaseous phase are Hydrogen and Oxygen we can expect three components, *viz.,* molecular Hydrogen, H_2, molecular Oxygen, O_2, water H_2O and perhaps rarer combinations.

Consider a system composed of p phases and n components. There are clearly a large number of potential variables describing this system, but not all of them are independent. The question is: how many of them can be independently chosen? Put in another way, what are the number of independent variables of the system? The answer is given by the Gibbs phase Rule.

Let m_{ik} be the mass of the i^{th} phase ($i \in \{1, 2, \ldots, p\}$ and k^{th} component ($k \in \{1, 2, \ldots, n\}$. Form a $p \times n$ matrix $\widehat{m}$ of these masses. Because the Gibbs free energy is extensive, its value for the system will be

$$G = \sum_i G_i \tag{4.5.12}$$

where G_i is the free energy for each phase. Each function G_i can depend on T, p and the masses of each component in the i^{th} phase,

$$G_i = G_i(T, p, m_{i1}, m_{i2}, \ldots, m_{in}) \tag{4.5.13}$$

Now the masses are extensive and so is each G_i, so if we simply scaled all the masses by the same factor the net effect would be to scale G_i by the same factor, *i.e.,*

$$G_i(T, p, \alpha m_{i1}, \alpha m_{i2}, \ldots, \alpha m_{in}) = \alpha G_i(T, p, m_{i1}, m_{i2}, \ldots, m_{in}) \tag{4.5.14}$$

Because of this scaling property

$$\frac{\partial}{\partial(\alpha m_{ik})} G_i(p, T, \alpha m_{i1}, \ldots, \alpha m_{in}) = \frac{\partial}{\partial m_{ik}} G_i(T, p, m_{i1}, m_{i2}, \ldots, m_{in}) \tag{4.5.15}$$

so $\partial G_i/\partial m_{ik}$ depends only on the ratios of the m_{ik}. For each phase there are $(n-1)$ such ratios. There are p phases, so $p(n-1)$ such ratios in all and the total number of variables required to describe the system is then, including the pressure and the temperature,

$$\overline{v} = 2 + p(n-1) \tag{4.5.16}$$

but there are constraints. Consider a transformation in which dm_{ik} (of the k^{th} component in the i^{th} phase) transforms to the j^{th} phase and there is no other change, then

$$dG = dG_i + dG_j = \frac{\partial G_i}{\partial m_{ik}} dm_{ik} + \frac{\partial G_j}{\partial m_{jk}} dm_{jk} = 0 \tag{4.5.17}$$

because if the phases are in equilibrium the total Gibbs free energy is at a minimum. Since $dm_{ik} = -dm_{jk}$,

$$\frac{\partial G_i}{\partial m_{ik}} = \frac{\partial G_j}{\partial m_{jk}} \tag{4.5.18}$$

These are a total of $n(p-1)$ equations relating the variables of the system. Taking into account these constraints, the total number of variables required to describe the system should be

$$v = 2 + p(n-1) - n(p-1) = n - p + 2 \tag{4.5.19}$$

where we have subtracted the $n(p-1)$ equilibrium conditions. v is called the degree of variability of the system. This is a truly remarkable relation. Consider some examples.

- For a system consisting of one phase and one chemically well-defined substance, $v = 2$.
- For a system of two distinct, chemically well defined gases, $v = 3$.
- For a system of one chemically well defined substance and two phases (the liquid vapor system we have just examined), $v = 1$. This system has only one degree of freedom in equilibrium which we could choose to be the temperature. Thus there must be an equation relating the pressure to the temperature; this is the Clausius-Clapeyron equation.

- Finally, consider water at its triple point; we have one chemically well defined substance and three phases, so the system has *no* degrees of freedom. It can exist only at a fixed temperature and pressure. This is of course precisely what we mean by the triple point.

Chapter 5

Variable Contents

In much of our work this far we have implicitly assumed that the contents of the thermodynamic system being considered were fixed, *i.e.,* the number of molecules of any given kind present in the system was always taken to be constant. However, we soon saw that there are interesting systems for which it would simply be incorrect to assume that the total number of molecules of any particular kind is fixed. There are many examples of such systems. For instance, if we think of a system consisting of a mixture of ice and water as composed of two systems in thermal contact with one another, one (A) being the ice and the other (B) being the water then, depending on the pressure and temperature of the mixture, the quantity of ice and water will change in time. Neither the system A nor the system B can be assumed to contain a fixed amount of matter. Again, imagine two chambers separated by a porous medium through which the molecules of some gas which fills one of the chambers can flow. The number of molecules of gas in neither chamber will remain fixed in time. Another example arises during chemical reactions in which the mass of the reagents in the chemical mixture will change in time, as will the mass of the products. Charging capacitors are still other examples of such systems since the number of electrons in a charging capacitor, or in a conductor into which electrons are flowing from some external source is varying in time. The special cases we examined were the liquid-vapor equilibrium conditions, the law of mass action and the Gibbs phase rule. In these cases, making use of the extensive property of the thermodynamic potentials, we built them up from their values per unit mass, which allowed us to indirectly account for possible changes in in the number of any one kind of molecule. This procedure is, in fact, unnecessary and it is often a very inconvenient way to set up a thermodynamic system.

Indeed, in practice one never actually measures or directly controls the precise number of molecules of any given type in a thermodynamic system but rather infers it indirectly by probing the system, just as one infers the value of its internal energy. Therefore it is more consistent with the principles of thermodynamics to treat the numbers of particles of every species as thermodynamic variables. The set of numbers, $\{N_s\}$, of molecules of species labeled by s, specifies the **composition** of the mixture. In the previous chapters we simply assumed that these numbers were all constant. In this chapter we generalize the laws of thermodynamics to take into account situations in which the composition may vary.

5.1 The Chemical Potential

Our first question concerns the possible form that the first law should take for a system with variable contents. We have seen earlier that the entropy is rightly viewed as a function of the internal energy and the extensive, external parameters of the system. Thus we had, for the real or ideal gas $S = S(U, V)$. The composition of a system is a set of externally specified extensive parameters, the number of molecules of each species present. Thus, we now write $S = S(U, V, N_1, N_2, \ldots N_s, \ldots)$, where N_s represents the numbers of molecules species j. Taking the differential of S for a small change,

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V,N_s} dU + \left(\frac{\partial S}{\partial V}\right)_{U,N_s} dV + \sum_s \left(\frac{\partial S}{\partial N_s}\right)_{U,V,N_r,r\neq s} dN_s \tag{5.1.1}$$

We see immediately that when the N_s are fixed we must identify

$$\begin{aligned}\left(\frac{\partial S}{\partial U}\right)_{V,N_s} &= \frac{1}{T}\\ \left(\frac{\partial S}{\partial V}\right)_{U,N_s} &= \frac{p}{T}.\end{aligned} \tag{5.1.2}$$

If we now call

$$\left(\frac{\partial S}{\partial N_s}\right)_{U,V,N_r,r\neq s} = -\frac{\mu_s}{T}, \tag{5.1.3}$$

then the first law, combined with the second, will read

$$TdS = dU + pdV - \sum_s \mu_s dN_s \geq 0. \tag{5.1.4}$$

The quantity μ_s is called the **chemical potential** of species s. To understand its significance, consider two systems A and B in contact with one another in such a way that they are able to spontaneously exchange particles between themselves but otherwise interact weakly. These systems could be coexisting phases of matter, such as water and ice in our earlier example. The total entropy of $A + B$ is the sum of the individual entropies

$$S = S_A + S_B \tag{5.1.5}$$

Now imagine that the combined system $A+B$ is mechanically and thermally isolated (but each system is not isolated from the other), then the total internal energy, volume and particle number are conserved,

$$\begin{aligned} U_A + U_B &= U^{(0)} \\ V_A + V_B &= V^{(0)} \\ N_{A,s} + N_{B,s} &= N_s^{(0)} \end{aligned} \tag{5.1.6}$$

and it follows that $dU_A = -dU_B$, etc., so that the law of entropy increase would read

$$dS = \left(\frac{1}{T_A} - \frac{1}{T_B}\right) dU_A + \left(\frac{p_A}{T_A} - \frac{p_B}{T_B}\right) dV_A - \sum_s \left(\frac{\mu_{A,s}}{T_A} - \frac{\mu_{B,s}}{T_B}\right) dN_{A,s} \geq 0. \tag{5.1.7}$$

Therefore, in equilibrium, $T_A = T_B$, $p_A = p_B$ and $\mu_{A,s} = \mu_{B,s}$ for each species, s. The first and second conditions represent thermal and mechanical equilibrium respectively. If the systems are already in mechanical and thermal equilibrium, but possibly exchanging particles, then $T_A = T_B$, $p_A = p_B$ and

$$-\sum_s (\mu_{A,s} - \mu_{B,s}) dN_{A,s} \geq 0. \tag{5.1.8}$$

If there is just one species then system A *gains* particles, $dN_A > 0$, if and only if $\mu_A \leq \mu_B$ and, vice-versa, if A *loses* particles, $dN_A < 0$ then $\mu_A \geq \mu_B$. The chemical potential is so seen to determine the direction of particle flow. Particles flow spontaneously from higher chemical potential to lower chemical potential in systems which are in thermal and mechanical equilibrium.

5.2 Integrability Conditions

Now take another look at the thermodynamic functions we studied in the previous chapters and extend their range. Rewriting the first law in the form

$$dU = TdS - pdV + \sum_s \mu_s dN_s, \tag{5.2.1}$$

we recognize that

$$\left(\frac{\partial U}{\partial S}\right)_{V,N_s} = T, \quad \left(\frac{\partial U}{\partial V}\right)_{S,N_s} = -p, \quad \left(\frac{\partial U}{\partial N_s}\right)_{S,V,N_r,r\neq s} = \mu_s \tag{5.2.2}$$

First, define the enthalpy etc. in the usual way. For example, $H = U + pV$ so that

$$dH = TdS - pdV + \sum_s \mu_s dN_s + dpV + Vdp = TdS + Vdp + \sum_s \mu_s dN_s \tag{5.2.3}$$

which is now naturally a function of (S, p, N_s). Likewise

$$\begin{aligned} F = U - TS &\Rightarrow dF = -SdT - pdV + \sum_s \mu_s dN_s, \\ G = U + pV - TS &\Rightarrow dG = -SdT + Vdp + \sum_s \mu_s dN_s \end{aligned} \tag{5.2.4}$$

and thus we arrive at an enlarged set of Maxwell relations. We get the same Maxwell relations we had before as well as eight additional relations, two for each function. From the integrability of the internal energy in (5.2.2) we find

$$\begin{aligned} \left(\frac{\partial T}{\partial N_s}\right)_{V,S,N_r,r\neq s} &= \left(\frac{\partial \mu_s}{\partial S}\right)_{V,N_s} \\ \left(\frac{\partial p}{\partial N_s}\right)_{V,S,N_r,r\neq s} &= \left(\frac{\partial \mu_s}{\partial V}\right)_{S,N_s} \end{aligned} \tag{5.2.5}$$

whereas from the integrability condition on H,

$$\left(\frac{\partial H}{\partial S}\right)_{p,N_s} = T, \quad \left(\frac{\partial H}{\partial p}\right)_{S,N_s} = V, \quad \left(\frac{\partial H}{\partial N_s}\right)_{S,p,N_r,r\neq s} = \mu_s \tag{5.2.6}$$

we find

$$\begin{aligned} \left(\frac{\partial T}{\partial N_s}\right)_{p,S,N_r,r\neq s} &= \left(\frac{\partial \mu_s}{\partial S}\right)_{p,N_s} \\ \left(\frac{\partial V}{\partial N_s}\right)_{p,S,N_r,r\neq s} &= \left(\frac{\partial \mu_s}{\partial p}\right)_{S,N_s} \end{aligned} \tag{5.2.7}$$

and likewise, the integrability conditions for the other two potentials,

$$\begin{aligned} &\left(\frac{\partial F}{\partial T}\right)_{V,N_s} = -S, \quad \left(\frac{\partial F}{\partial V}\right)_{T,N_s} = -p, \quad \left(\frac{\partial F}{\partial N_s}\right)_{T,V,N_r,r\neq s} = \mu_s \\ &\left(\frac{\partial G}{\partial T}\right)_{p,N_s} = -S, \quad \left(\frac{\partial G}{\partial p}\right)_{T,N_s} = +V, \quad \left(\frac{\partial G}{\partial N_s}\right)_{T,p,N_r,r\neq s} = \mu_s, \end{aligned} \tag{5.2.8}$$

gives

$$\left(\frac{\partial S}{\partial N_s}\right)_{V,T,N_r,r\neq s} = -\left(\frac{\partial \mu_s}{\partial T}\right)_{V,N_s}$$

$$\begin{aligned}
\left(\frac{\partial p}{\partial N_s}\right)_{V,T,N_r,r\neq s} &= -\left(\frac{\partial \mu_s}{\partial V}\right)_{T,N_s} \\
\left(\frac{\partial S}{\partial N_s}\right)_{p,T,N_r,r\neq s} &= -\left(\frac{\partial \mu_s}{\partial T}\right)_{p,N_s} \\
\left(\frac{\partial V}{\partial N_s}\right)_{p,T,N_r,r\neq s} &= +\left(\frac{\partial \mu_s}{\partial p}\right)_{T,N_s}
\end{aligned} \tag{5.2.9}$$

These expressions can be quite useful as we see below.

5.3 Chemical Potential of an ideal gas

As an example of the use of the integrability conditions we now determine the chemical potential of an ideal gas as a function of $\{U, V, N\}$. Consider only one species for convenience and use the integrability conditions arising from the form

$$dS = \frac{dU}{T} + \frac{p}{T}dV - \frac{\mu}{T}dN \tag{5.3.1}$$

which are[1]

$$\begin{aligned}
\left(\frac{\partial T}{\partial V}\right)_{U,N} &= -T\left(\frac{\partial p}{\partial U}\right)_{V,N} + p\left(\frac{\partial T}{\partial U}\right)_{V,N} \\
\left(\frac{\partial T}{\partial N}\right)_{U,V} &= T\left(\frac{\partial \mu}{\partial U}\right)_{V,N} - \mu\left(\frac{\partial T}{\partial U}\right)_{V,N} \\
T\left(\frac{\partial p}{\partial N}\right)_{U,V} - p\left(\frac{\partial T}{\partial N}\right)_{U,V} &= -T\left(\frac{\partial \mu}{\partial V}\right)_{U,N} + \mu\left(\frac{\partial T}{\partial V}\right)_{U,N}
\end{aligned} \tag{5.3.2}$$

As before, using the equation of state, $p = NkT/V$, tells us that the left hand side of the first condition is identically zero, *i.e.*, $T = T(U, N)$. Inserting this into the third equation and once again using the equation of state we find that

$$\left(\frac{\partial \mu}{\partial V}\right)_{U,N} = -\frac{kT}{V} \Rightarrow \mu(U, V, N) = -kT\ln\frac{V}{V_0} + \gamma(U, N) \tag{5.3.3}$$

where γ is yet to be determined. It is not possible to make further progress without exploiting our knowledge from the kinetic theory:

$$T = \frac{2U}{gNk} \Rightarrow \left(\frac{\partial T}{\partial U}\right)_{V,N} = \frac{2}{gNk}, \quad \left(\frac{\partial T}{\partial N}\right)_{U,V} = -\frac{2U}{gN^2k} \tag{5.3.4}$$

---

[1] Problem: Work these out.

Inserting this into the second of the integrability conditions gives

$$-\frac{2U}{gN^2k} = \frac{2U}{gNk}\left(\frac{\partial\mu}{\partial U}\right)_{V,N} - \frac{2\mu}{gNk} \tag{5.3.5}$$

But since

$$\left(\frac{\partial\mu}{\partial U}\right)_{V,N} = -\frac{2}{gN}\ln\frac{V}{V_0} + \left(\frac{\partial\gamma}{\partial U}\right)_{V,N} \tag{5.3.6}$$

we get a rather simple Bernoulli equation for $\gamma(U, N)$,

$$\left(\frac{\partial\gamma}{\partial U}\right)_{V,N} - \frac{\gamma}{U} = -\frac{1}{N} \tag{5.3.7}$$

whose solution can be given as

$$\gamma(U, N) = -\frac{U}{N}\ln\frac{U}{U_0} - U\lambda(N) \tag{5.3.8}$$

where $\lambda(N)$ remains undetermined. Therefore we have found $\mu(U, V, N)$ up to one arbitrary function of N,

$$\mu(U, V, N) = -\frac{2U}{gN}\left[\frac{g}{2}\ln\frac{U}{U_0} + \ln\frac{V}{V_0} + \frac{gN}{2}\lambda(N)\right] \tag{5.3.9}$$

Note that U_0 and V_0 are constants of the integration and cannot be further determined within the context of thermodynamics. Neither U_0 nor V_0 may depend on N because it has been used as a thermodynamic variable in this approach. This contrasts with the expressions we derived for the entropy of an ideal gas in (3.4.11).

5.4 Applications of the Equilibrium Conditions

When no chemical reactions occur, the equilibrium conditions together with the integrability conditions of the previous sections can be applied with good effect to a variety of situations.

5.4.1 The Clausius-Clapeyron Equation

Let us briefly return to the Clausius-Clapeyron equation to see how it may be simply obtained from the requirement that in equilibrium

$$\mu_v = \mu_l \tag{5.4.1}$$

where μ_v and μ_l are the chemical potentials of the water respectively in the vapor and liquid phases. Letting lower case letters represent the thermodynamic quantities per molecule, we can write the Gibbs free energy as

$$G = N_v(u_v + pv_v - Ts_v) + N_l(u_l + pv_l - Ts_l) \tag{5.4.2}$$

so that the chemical potentials in each case turn out to be

$$\mu_v = \left(\frac{\partial G}{\partial N_v}\right)_{p,T}, \quad \mu_l = \left(\frac{\partial G}{\partial N_l}\right)_{p,T} \tag{5.4.3}$$

and therefore

$$u_v + pv_v - Ts_v = u_l + pv_l - Ts_l \tag{5.4.4}$$

Differentiating once we find

$$-s_v dT + v_v dp = -s_l dT + v_l dp \Rightarrow \frac{dp}{dT} = \frac{s_v - s_l}{v_v - v_l} \tag{5.4.5}$$

This of course is precisely (4.5.9).

5.4.2 Thermodynamics of Adsorption

Sometimes the surfaces of certain solids bind significant numbers of molecules of the ambient gas (or liquid) to their surfaces. This phenomenon is called **adsorption**. It is different from absorption in which the molecules are simply dispersed within the absorbing medium. In adsorption, the molecules although adhering to the surface of the solid are more or less free in the directions parallel to the solid surface. The adsorbed substance is called the **adsorbate** and the solid upon whose surface the molecules are adsorbed is called the **adsorbent**. Adsorption can be a very useful process: it is a vital part of catalysis; it can also be used in a separation process, for example, to remove low concentration pollutants in a fluid stream, or in a storage process in which molecules are trapped by adsorption for future release. In the case of adsorption of gaseous molecules the number of adsorbed molecules depends on the temperature of the system and the gas pressure. For a fixed temperature fewer molecules are adsorbed at low pressures. On the other hand, for a fixed pressure fewer molecules are adsorbed at high temperatures.

Adsorption is a consequence of the fact that the adsorbate molecules acquire a small, negative binding energy when they come close enough to molecules on the surface of the adsorbent. Another way of saying this is that the adsorbate molecules experience a small, short range attractive force to the solid surface. This force does not, however, cause the adsorbate molecules to stick to the adsorbent molecules. As a result, the the gas goes from three dimensional to effectively two dimensional near the surface of the adsorbent. This significantly changes the behavior of the gas, though the change does not occur abruptly. It was originally Gibbs who realized that it is precisely this fact that can be exploited to obtain an equilibrium thermodynamic description of the phenomenon without delving into its microscopic details. Thus, for the purposes of a thermodynamic description of the process it is sufficient to treat the system as a two dimensional gas phase in equilibrium with its three dimensional phase.

The spreading pressure is not directly accessible to experiment and must be calculated. So how many degrees of freedom are required to describe this system? There is one chemically well defined substance in two phases so, according to the phase rule, (4.5.19), $v = 1$. However, the fact that the pressure is not directly measurable modifies the Gibbs phase rule so that the number of degrees of freedom is actually two.

As we did for the Clausius-Clapeyron equation, we will describe this system in equilibrium by requiring

$$\mu_a = \mu_v \tag{5.4.6}$$

where μ_a and μ_v are the chemical potentials of the gas in the adsorbed state and in the normal three dimensional state. Again, we know from earlier work that

$$\mu_a = u_a + \mathcal{P}\mathcal{A}_a - Ts_a, \quad \mu_v = u_v + pv_v - Ts_v \tag{5.4.7}$$

where we introduced the *areal pressure*, $\mathcal{P}$, and the surface area, $\mathcal{A}_a$, occupied by the adsorbed gas per molecule. The difference with the case of the Clausius-Clapeyron equation is that the pressure $\mathcal{P}$ remains in principle unknown. Differentiating the relation $\mu_a = \mu_v$ as before

$$-s_a dT + \mathcal{A}_a d\mathcal{P} = -s_v dT + v_v dp \tag{5.4.8}$$

Along a fixed isotherm,

$$\mathcal{A}_a d\mathcal{P} = v_v dp \tag{5.4.9}$$

and applying the ideal gas equation of state, $pv_v = kT$, to eliminate v_v, we find

$$d\ln p = \frac{\mathcal{A}_a d\mathcal{P}}{kT} \tag{5.4.10}$$

Furthermore, we will take the equation of state in the adsorbed state to be of the form

$$\mathcal{P}\mathcal{A}_a = zkT \tag{5.4.11}$$

where z is called the **compressibility factor** for the adsorbate, then along an isotherm

$$d\mathcal{P}\mathcal{A}_a = kT(dz - zd\ln\mathcal{A}_a) \tag{5.4.12}$$

For an ideal two dimensional gas, the compressibility factor would be precisely one. However, for real gases the compressibility factor will generally depend on the pressure and the temperature, increasing with pressure and decreasing with temperature. At high pressures molecules are colliding more often and at low temperatures they are moving less rapidly. This allows intermolecular forces to have a significant effect. If N_a represents the number of adsorbed molecules and A the adsorbent surface area, then substituting $\mathcal{A}_a = A/N_a$ and $d\mathcal{A}_a = -A/N_a^2 dN_a$ gives

$$d\ln p = dz + z\frac{dN_a}{N_a} \tag{5.4.13}$$

Subtracting dN_a/N_a from both sides

$$d\ln\frac{p}{N_a} = dz + (z-1)\frac{dN_a}{N_a} \tag{5.4.14}$$

Now, when $p \to 0$ and $N_a \to 0$ we expect $z \to 1$. Likewise the number of molecules is N_a when the pressure is p. Thus, integrating both sides of this equation

$$\ln\frac{p}{N_a} - \ln \lim_{N_a, p \to 0}\frac{p}{N_a} = \int_0^{N_a}(z-1)\frac{dN_a}{N_a} + z - 1 \tag{5.4.15}$$

Suppose that the limiting value of p/N_a above is k_H,[2] then

$$\ln\frac{p}{k_H N_a} = \int_0^{N_a}(z-1)\frac{dN_a}{N_a} + z - 1 \tag{5.4.16}$$

and

$$k_H N_a = p\exp\left[\int_0^{N_a}(1-z)\frac{dN_a}{N_a} + 1 - z\right] \tag{5.4.17}$$

If z is approximately constant in a given range of p, T and N_a, and if $\ln N_a \gg 1$ then we may further approximate the above expression by

$$N_a = \frac{p}{k_H}N_a^{1-z} \Rightarrow N_a = \left(\frac{p}{k_H}\right)^{1/z} \overset{\text{def}}{=} \chi\, p^{1/z} \tag{5.4.18}$$

It appears from the above that the number of adsorbed molecules may grow indefinitely as the pressure is increased without bound. In reality this is not so because z also grows as p is increased. This reflects the observation that the number of adsorbed molecules has an asymptotic maximum as p increases. Likewise, as the temperature increases z changes to reflect the observation that the quantity of adsorbed molecules rises more slowly with increasing p.

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[2] The constant k_H is known as Henry's constant for adsorption. In general, Henry's law can be written as

$$p = k_H c$$

where c is the concentration of the gas in the affected portion of the gas and p refers to the partial pressure of the unaffected portion of the gas. For example, in the case of adsorption, c refers to the concentration of the adsorbed portion of gas on the surface and p to the pressure of the three dimensional gas above the adsorbed layer; in the case of a solution c would refer to the concentration of the solute in the solution and p to the partial pressure of the solute in the gas above the solution.

5.4.3 Equilibrium in Chemical Reactions

The chemical potential is of great importance in the study of the chemical equilibrium between species when chemical reactions may occur in a mixture of various types of molecules. In fact, consider a general chemical reaction of the form

$$n_1\mathrm{A}_1 + n_2\mathrm{A}_2 + ...n_r\mathrm{A}_r \rightarrow m_1\mathrm{B}_1 + m_2\mathrm{B}_2 + ...m_s\mathrm{B}_s, \tag{5.4.19}$$

occurring in an isolated mixture of chemicals labeled by the A's and B's. We can consider the entire mixture as consisting of several sub-systems, each consisting of one species of molecule. Assume that the sub-systems are in thermal and mechanical equilibrium with each other, but not necessarily in chemical equilibrium. During any process that the system undergoes, the total entropy will either increase or stay the same; therefore

$$-\sum_s \mu_s dN_s \geq 0, \tag{5.4.20}$$

where s is used to label the chemical species. If the reaction proceeds to the right, we lose n_j moles of species A_j (for $j \in \{1, 2, ..., r\}$) and gain m_k moles of B_k (for $k \in \{1, 2, ..., s\}$) and vice versa if the reaction proceeds to the left. Assuming thermal and mechanical equilibrium between the species, the above condition requires that

$$\begin{aligned} &\Rightarrow -\sum_{j=1}^{r} \mu_{A_j} dN_{A_j} - \sum_{k=1}^{s} \mu_{B_k} dN_{B_k} \geq 0 \\ &\Rightarrow \sum_{j=1}^{r} \mu_{A_j} n_{A_j} \geq \sum_{k=1}^{s} \mu_{B_k} m_{B_k} \end{aligned} \tag{5.4.21}$$

where we have used the fact that

$$\begin{aligned} dN_{A_j} &= -n_{A_j} \\ dN_{B_k} &= +m_{B_k} \end{aligned} \tag{5.4.22}$$

which follows from our condition that the equation proceeds to the *right* so that n_{A_j} moles of A_j are *lost* and m_{B_k} moles of B_k are *gained* by the system. Equation (5.14) can be expressed by saying that *the total chemical potential of the reagents must be greater than the total chemical potential of the products if the reaction proceeds to the right.* The chemical potential therefore determines the direction in which a chemical reaction occurs and hence receives its name.

5.4.4 Mass Action Revisited

The equation (5.4.21) gives us the condition for the reaction to proceed to the right. The analogous condition

$$\sum_{j=1}^{r} \mu_{A_j} n_{A_j} \leq \sum_{k=1}^{s} \mu_{B_k} m_{A_k} \tag{5.4.23}$$

is the condition for the reaction to proceed to the left. In equilibrium, the forward rate must equal the backward rate, so

$$\sum_{j=1}^{r} \mu_{A_j} n_{A_j} - \sum_{k=1}^{s} \mu_{B_k} m_{A_k} = 0 \tag{5.4.24}$$

Now suppose that we wish to describe a gaseous reaction occurring at a constant volume and temperature and suppose that under the conditions the chemicals behave approximately as ideal gases. Then the most direct way to obtain the chemical potential under these conditions is via the Helmholz free energy since

$$\left(\frac{\partial F}{\partial N_s}\right)_{T,V,N_r,r\neq s} = \mu_s. \tag{5.4.25}$$

With

$$F = \left[\sum_j N_{A_j}(u_{A_j} - Ts_{A_j}) + \sum_k N_{B_k}(u_{B_k} - Ts_{A_k})\right] \tag{5.4.26}$$

where u and s are the internal energies and entropies per particle respectively. We see that the equilibrium condition reduces to

$$\sum_j n_{A_j}(u_{A_j} - Ts_{A_j}) - \sum_k n_{B_k}(u_{B_k} - Ts_{B_k}) = 0 \tag{5.4.27}$$

and writing the expression out *in extenso* using expressions we had earlier for the internal energy and entropy of ideal gases we have, after multiplying throughout by Avogadro's number

$$\begin{aligned} &\sum_j n_{A_j}[\mathcal{C}_{V_{A_j}} T + W_{A_j} - T(\mathcal{C}_{V_{A_j}} \ln T + R \ln v_{A_j} + a_j)] \\ &\qquad \sum_k n_{B_k}[\mathcal{C}_{V_{B_k}} T + W_{B_k} - T(\mathcal{C}_{V_{B_k}} \ln T + R \ln v_{B_k} + b_j)] = 0 \end{aligned} \tag{5.4.28}$$

where v is the specific volume, *i.e.,* in terms of the concentration, $c = n/N$, we can express $v = V/N = 1/(N_0 c)$. Thus

$$\ln v_{A_j} + a_j = -\ln c_{A_j} + a'_j \tag{5.4.29}$$

and we have

$$\sum_j n_{A_j}[\mathcal{C}_{V_{A_j}}T + W_{A_j} - T(\mathcal{C}_{V_{A_j}}\ln T - R\ln c_{A_j} + a'_j)]$$
$$\sum_k n_{B_k}[\mathcal{C}_{V_{B_k}}T + W_{B_k} - T(\mathcal{C}_{V_{B_k}}\ln T + R\ln c_{B_k} + b'_j)] = 0 \quad (5.4.30)$$

which is identical with (4.4.33), given that the constants a'_j and b'_j are arbitrary and we can identify a'_i with $a_i + R$ and b'_i with $b_i + R$.

5.5 New Thermodynamic Potentials

We may now extend the range of thermodynamic potentials by a further Legendre transformation, introducing the new functions

$$\begin{aligned}
\Phi_U &= U - \sum_s \mu_s N_s \Rightarrow d\Phi_U \leq TdS - pdV - \sum_s N_s d\mu_s,\\
\Phi_H &= H - \sum_s \mu_s N_s \Rightarrow d\Phi_H \leq TdS + Vdp - \sum_s N_s d\mu_s,\\
\Phi_F &= F - \sum_s \mu_s N_s \Rightarrow d\Phi_F \leq -SdT - pdV - \sum_s N_s d\mu_s,\\
\Phi_G &= G - \sum_s \mu_s N_s \Rightarrow d\Phi_G \leq -SdT + Vdp - \sum_s N_s d\mu_s, \qquad (5.5.1)
\end{aligned}$$

where the equality holds only during quasi static processes. These yield more Maxwell relations.[3] Of the generalized potentials above, the most important is Φ_F and was called by Gibbs the **grand potential**. The role of the grand potential is similar to that of F, *i.e.,* it is the maximum amount of energy available to do external work for a system in contact with both a heat and a particle reservoir.[4]

Consider a homogeneous system, *i.e.,* one that has a single or uniform phase. Notice that with the introduction of the chemical potential, we can imagine building up a homogeneous system by adding material while always keeping the intensive variables fixed. Then the above relations are trivially integrated to give

$$\begin{aligned}
\Phi_U &= TS - pV \Rightarrow U = TS - pV + \sum_s \mu_s N_s\\
\Phi_H &= TS \Rightarrow H = TS + \sum_s \mu_s N_s
\end{aligned}$$

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[3] Problem: Determine all the new Maxwell relations.

[4] Problem: Prove this.

$$\begin{aligned}\Phi_F &= -pV \Rightarrow F = -pV + \sum_s \mu_s N_s \\ \Phi_G &= 0 \Rightarrow G = \sum_s \mu_s N_s \end{aligned} \tag{5.5.2}$$

so that in a homogeneous system the chemical potential may be thought of as the partial Gibbs free energy. In such a system then we have the the following relationship between changes in the chemical potential and the other intensive variables of the system,

$$\sum_s N_s d\mu_s = -SdT + Vdp. \tag{5.5.3}$$

This is known as the **Gibbs-Duhem** relationship. It shows that in a homogeneous system the intensive variables are not really independent. When pressure and temperature vary only $n-1$ of n species of substances present (in each phase) have independent chemical potentials.

If we use the integrated form of the first law, as given by the first equation in (5.5.2) together with the equation of state and the relationship between the temperature and the internal energy, $T = T(U)$, then we find that for an ideal gas

$$\begin{aligned} S &= \frac{U}{T} + \frac{pV}{T} - \frac{\mu N}{T} \\ \Rightarrow \qquad \mu &= -\frac{T}{N}\left[S - \frac{U}{T} - \frac{pV}{T}\right] \end{aligned} \tag{5.5.4}$$

and therefore

$$\mu = -kT\left[\frac{S}{Nk} - \left(\frac{g}{2}+1\right)\right], \tag{5.5.5}$$

but it remains undetermined to the extent that S in (3.4.11) is undetermined. It should be compared with the result obtained in (5.3.9) from the integrability conditions.

Chapter 6

The Third Law

6.1 Introduction

We have finally arrived at the third and final law of Thermodynamics. Its objective is to complete the definition of entropy, although this in and of itself does not turn out to be so useful in the end. Recall that the second law only gives the *change* in the entropy [according to (3.3.20)] when a macroscopic system undergoes a thermodynamic process that takes it from some initial state to some final state, but it has nothing to say about the actual value of the entropy in any state even though, as a function of state, the entropy must have a definite value in every state. However, if it were possible to specify the entropy in any one state then (3.3.20) would allow us to determine its value in any other state. This is what the third law attempts to do. The statement of the third law, according to **Planck** is the following:

The entropy of every system at zero temperature is zero.

It follows that the entropy of any system in any state, A, can be defined as

$$S(A) = \int_{T=0}^{A} \frac{đQ}{T} \tag{6.1.1}$$

What is the meaning of this law? It does not have a basis either in classical thermodynamics or in classical statistical mechanics, but in quantum statistical mechanics. To understand it, let us take a small foray into statistical mechanics, in which the the entropy of an isolated system is defined, following Boltzmann, as

$$S(U, N, V, \ldots) = k \ln \Omega(U, N, V, \ldots) \tag{6.1.2}$$

where $\Omega(U, N, V, \ldots)$ is the **number of microstates** compatible with a given macrostate described by the parameters $U, N, V, \ldots$. Planck's statement of the third law implies that at zero temperature every isolated thermodynamic system has *just one state* available to it. This is the state of lowest energy, or the **ground state** of the system.

6.2 The number of microstates

6.2.1 Classical Microstates

Recall that the initial conditions required to solve Newton's equation are the positions and momenta of each particle. A classical microstate of any system would consist of the positions, $\vec{q}_i$, and momenta, $\vec{p}_i$, of all of its constituents, *i.e.,* a typical microstate would be represented by the set

$$\{\vec{q}_1, \vec{q}_2, \ldots, \vec{q}_N, \vec{p}_1, \vec{p}_2, \ldots, \vec{p}_N\}. \tag{6.2.1}$$

If each constituent has g degrees of freedom, the microstate has $2gN$ "phase space" variables, *viz.,* gN coordinates and gN momenta. Of course there will be a certain number of conserved integrals of the motion, which we must subtract from the $2gN$ phase space degrees of freedom. Moreover, when the system is subject to some external constraints, not all positions or momenta would be realized by the constituents, but only those that obey the external constraints. In other words, not all possible points in the $2gN$ dimensional phase space are allowed by the constraints. The constraints and conserved quantities will determine a $2f$ dimensional hypersurface in phase space on which the system is allowed to evolve and each point of this hypersurface would correspond to a microstate of the system.

We now assume that all the allowed microstates are equally likely to occur and we're interested in counting them. This is like saying that we want to count the "number of points" in the hypersurface defined by the constraints and conservation laws. However, the coordinates and momenta can take on any real value and the set of real numbers is dense, therefore the number of possible classical microstates of a system are *ab initio* uncountable. This unpleasant situation can be corrected by "coarse graining" phase space, *i.e.,* dividing phase space into cells of fixed area, agreeing that states that have momentum between $\vec{p}$ and $\vec{p} + \delta\vec{p}$ and position between $\vec{q}$ and $\vec{q} + \delta\vec{q}$ cannot be distinguished. These "indistinguishable" states may all be specified by a single representative point $(\vec{q}, \vec{p})$ within a cell of area

$$\delta^f \vec{p} \delta^f \vec{q} = \delta\vec{q}_1 \delta\vec{q}_2 ... \delta\vec{q}_f \delta\vec{p}_1 \delta\vec{p}_2 ... \delta\vec{p}_f = h_o^f, (\text{constant.}) \tag{6.2.2}$$

as shown in figure (7.3). In this way the microstates become countable. Clearly, the description becomes more accurate as we take the area of each cell to approach zero. Although we will not be able to take that limit, we will assume that h_o is "macroscopically small" but "microscopically large". What this means is that we assume that *any* macroscopic volume in phase-space includes a very large number of fundamental cells of volume h_o^f while each cell itself holds a large number of points all of which represent a

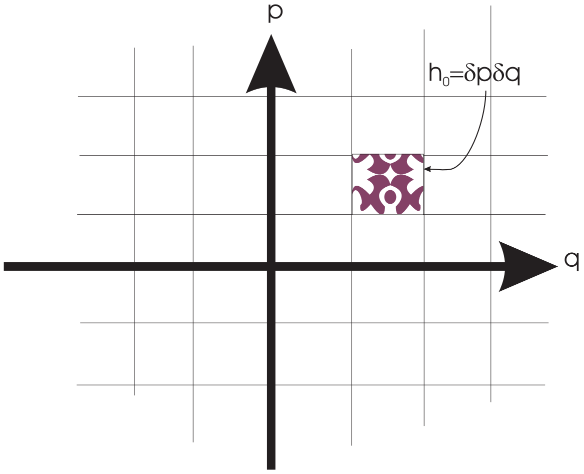

Figure 6.1: Coarse graining classical phase space

single microstate. This is the "continuum" approximation. To find the total number of microstates, we must then sum over all the cells that lie within the region of phase space that is defined by our external constraints, in principle taking the limit as $h_o \to 0$ in the end if possible. Thus

$$\Omega(U, N, V, \ldots) = \sum_{\text{cells}} \ldots \to \lim_{h_o \to 0} \frac{1}{h_o^f} \int_{\mathcal{R}} d^f \vec{q}\, d^f \vec{p} \tag{6.2.3}$$

where $\mathcal{R}$ is some region of the phase-space defined by $U, N, V, \ldots$ Let us consider some examples.

The simplest example is that of a gas of N non-interacting particles in a box. Suppose that, besides the number of particles, we also know the total internal energy of the system, U. Because the energy of the system is simply the kinetic energy of the particles,

$$U = \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m_i} \tag{6.2.4}$$

Assume, for simplicity that we have a system of identical particles, of mass m, then we could write the equation as

$$\sum_i \vec{p}_i^2 = 2mU \tag{6.2.5}$$

which is the equation of a $3N$ dimensional sphere of radius $\sqrt{2mU}$. The number of states of the system can now be written as

$$\Omega(U,N) = \frac{1}{h_o^{3N}} \int_V d^{3N}\vec{r} \int d^{3N}\vec{p}\, \delta\left(\sum_{i=1}^{N} \vec{p}_i^2 - 2mU\right) \tag{6.2.6}$$

The $\delta-$ function enforces the energy condition, which requires that all the momenta live on the surface of a $3N-1$ dimensional sphere. Its surface area is[1]

$$A_{3N-1} = \frac{2\pi^{(3N-1)/2}}{\Gamma[(3N-1)/2]}(2mU)^{(3N-1)/2} \sim B_N(m)U^{3N/2-1} \tag{6.2.7}$$

Further, each particle may occupy any point in the enclosed volume, V, so the number of states available to this gas is

$$\Omega(U,N,V) \sim \frac{1}{h_o^{3N}} B_N(m) V^N U^{3N/2} \tag{6.2.8}$$

---

[1] We had obtained the result from the volume of a $N-1$ dimensional sphere in momentum space of radius $\sqrt{2mE}$, where m is the mass of each particle. Now the volume of a $d-1$ dimensional sphere of radius R is $R^{d-1}\Omega_{d-1}$, where Ω_{d-1} is the solid angle in $d-1$ dimensions. To calculate this solid angle, let us evaluate the integral

$$I = \int_{-\infty}^{\infty} dx_1 dx_2 .... dx_d e^{-r^2}$$

where $r^2 = x_1^2 + x_2^2 + ... + x_d^2$ in two different ways. First we simply write the integral as

$$\int dx_1 dx_2 .... dx_d e^{-r^2} = \prod_i \int_{-\infty}^{\infty} dx_i e^{-x_i^2} = (\pi)^{\frac{d}{2}}$$

Next, let us evaluate the same integral using spherical coordinates, in which

$$d\text{Vol}_d = r^{d-1} dr d\Omega_{d-1} \Rightarrow I = \Omega_{d-1} \int_0^{\infty} dr r^{d-1} e^{-r^2} =$$

If we define $r^2 = t$,

$$I = \frac{1}{2}\Omega_{d-1} \int dt t^{\frac{d}{2}-1} e^{-t} = \Gamma\left(\frac{d}{2}\right)$$

where $\Gamma(x)$ is the "Gamma" function, which analytically continues the "factorial" function from the original domain of the natural numbers to the complex numbers:

$$\Gamma(n+1) = n!, \quad n \in \mathbb{N}.$$

Comparing this value of the integral with the previous, we find

$$\Omega_{d-1} = \frac{2\pi^{\frac{d}{2}}}{\Gamma\left(\frac{d}{2}\right)}$$

where we have set $3N/2 - 1 \approx 3N/2N$ because N is assumed to be very large. According to Boltzmann, the entropy of this system is given by (6.1.2),

$$S = Nk \ln \frac{U^{3/2} V B_N^{1/N}(m)}{h_o^{3N}}. \tag{6.2.9}$$

Notice that as $T \to 0$ (or $U \to 0$) this expression does not yield zero, so the classical entropy does *not* obey Planck's statement of the third law. On the contrary, the number of states seems to approach negative infinity, which is definitely a problem and signals the inappropriateness of applying classical mechanics concepts at very low temperatures. However, it does yield the equation of state for an ideal gas,

$$\frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_U = \frac{Nk}{V} \Rightarrow pV = NkT \tag{6.2.10}$$

and reproduces the relation between the internal energy and the temperature for the ideal gas,

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_V = \frac{3Nk}{2U} \Rightarrow U = \frac{3}{2}NkT \tag{6.2.11}$$

giving the heat capacity of an ideal gas as $C_V = 3Nk/2$.

Consider also a system of identical, non-interacting harmonic oscillators. Einstein proposed that such a collection of oscillators models a solid. If we know the total energy of the oscillators then

$$U = \sum_i \left(\frac{\vec{p}_i^2}{2m} + \frac{1}{2}k\vec{q}_i^2\right) \Rightarrow 2mU = \sum_i \left(\vec{p}_i^2 + \vec{\xi}_i^2\right) \tag{6.2.12}$$

where we define $\vec{\xi} = mk\vec{q}$. Now we have a $6N - 1$ dimensional sphere, so by the same arguments we made before

$$\Omega(U, N) = \widetilde{B}_N(m) U^{3N} \tag{6.2.13}$$

where $\widetilde{B}(m)$ contains all the dimensional factors pertaining to the surface area of a $6N-1$ dimensional sphere of radius $\sqrt{2mU}$. Notice that for this idealized solid the entropy is simply a function of the internal energy,

$$S = k \ln \Omega = 3Nk[\ln U + \ln \widetilde{B}_N(m)] \tag{6.2.14}$$

and

$$\frac{1}{T} = \frac{\partial S}{\partial U} = \frac{3Nk}{U} \Rightarrow U = 3NkT \tag{6.2.15}$$

and gives the heat capacity $C_V = 3Nk$.[2] The entropy is ill behaved in the $T = 0$ limit, once again showing that classical mechanics concepts break down in this regime.

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[2] The system has two degrees of freedom per oscillator. This is because a harmonic oscillator stores energy in two ways: as kinetic energy and as potential energy. Thus the result agrees with the prediction of the equipartition theorem.

6.2.2 Quantum microstates

The quantum states of particles are usually defined by a small set of quantum numbers which may or may not have a discrete spectrum. Thus counting the number of quantum microstates of a macroscopic system must proceed in a way that is compatible with the principles of quantum mechanics, as the following examples will illustrate. A more detailed analysis will be deferred until later.

A simple example is that of a paramagnetic system consisting of N non-interacting spin-$\frac{1}{2}$ particles, each possessing a magnetic moment $\vec{\mu}$, placed in an external magnetic field. Each particle has one of two possible orientations, parallel or antiparallel to the external magnetic field. A particle that is parallel to the magnetic field has energy $E_- = -\mu B$ and one that is antiparallel to the field has energy $E_+ = \mu B$. The internal energy of the N particles will be depend on the orientations of the particles: if m particles are oriented parallel to the field and n particles are oriented antiparallel to it $(n + m = N)$, the internal energy will be $(n - m)\mu B$. How many states are there in which n out of N particles are oriented antiparallel to the magnetic field. Assuming that the particles are identical but distinguishable, the answer is

$$\Omega(n, m) = \frac{N!}{n!(N-n)!} \tag{6.2.16}$$

But since $(2n - N)\mu B = U$, we could replace n in the above expression by

$$n = \frac{1}{2}\left(N + \frac{U}{\mu B}\right) \tag{6.2.17}$$

and find

$$\Omega(U, N) = \frac{N!}{\left[\frac{1}{2}\left(N + \frac{U}{\mu B}\right)\right]!\left[\frac{1}{2}\left(N - \frac{U}{\mu B}\right)\right]!} \tag{6.2.18}$$

One can use **Stirling's formula**[3] to simplify this expression assuming that N and $N \pm U/\mu B \gg 1$,

$$\begin{aligned} S = k \Bigg[& N \ln N - N - \frac{1}{2}\left(N + \frac{U}{\mu B}\right)\ln\frac{1}{2}\left(N + \frac{U}{\mu B}\right) + \frac{1}{2}\left(N + \frac{U}{\mu B}\right) \\ & - \frac{1}{2}\left(N - \frac{U}{\mu B}\right)\ln\frac{1}{2}\left(N - \frac{U}{\mu B}\right) + \frac{1}{2}\left(N - \frac{U}{\mu B}\right)\Bigg] \end{aligned} \tag{6.2.20}$$

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[3] Stirling's formula: For any $A \gg 1$

$$\ln A! \approx A \ln A - A. \tag{6.2.19}$$

This expression can be simplified to

$$S = Nk\left[\ln N - \frac{1}{2}\ln\frac{1}{4}\left(N^2 - \frac{U^2}{\mu^2 B^2}\right) - \frac{U}{2\mu NB}\ln\frac{\left(N + \frac{U}{\mu B}\right)}{\left(N - \frac{U}{\mu B}\right)}\right] \tag{6.2.21}$$

and, taking a derivative with respect to U, one can easily show that

$$U = -N\mu B\tanh\left(\frac{\mu B}{kT}\right) \tag{6.2.22}$$

which is the result we obtained before, where we were given the equation of state. What is noteworthy about these expressions is the fact that as T approaches zero the internal energy approaches $-N\mu B$, which says that *all* the spin $\frac{1}{2}$ particles align themselves antiparallel to the external magnetic field, as a consequene of which there is *just one state*. We can check that the entropy approaches zero in this limit.

Another interesting system is the Einstein model of a solid, which consists of a set of ideal, non-interacting harmonic oscillators. A quantum harmonic oscillator has discrete energy levels given by

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega \tag{6.2.23}$$

where n is an integer which counts the number of “quanta” of energy exciting the oscillator and $\hbar\omega/2$ represents its ground state energy. Suppose that we know the total energy of N oscillators. This energy may be achieved in many different ways by the system and each way corresponds to a particular distribution of the available quanta among the oscillators. Each distribution of the quanta among the oscillators is a microstate and we want to count the number of microstates, so we imagine that the quanta and the oscillators are distributed along a line with the rule that every oscillator is excited by the quanta immediately to its left. Since every quantum must be associated with one oscillator the last object must be an oscilator and we can rearrange only $N-1$ of the N oscillators. Suppose that there are Q quanta distributed among the oscillators, *i.e.,*

$$U = \left(Q + \frac{N}{2}\right)\hbar\omega \Rightarrow Q = \frac{U}{\hbar\omega} - \frac{N}{2} \tag{6.2.24}$$

then the number of possible arrangements of Q objects of one type (quanta) and $N-1$ objects of another type (the oscillators) gives the total number of states having energy U,

$$\Omega(Q, N) = \frac{(N+Q-1)!}{Q!(N-1)!} \tag{6.2.25}$$

and so

$$S(U,N) = k[(Q+N-1)\ln(Q+N-1) - Q\ln Q - (N-1)\ln(N-1)]$$

$$\approx \quad k\left[\left(\frac{U}{\hbar\omega}+\frac{N}{2}\right)\ln\left(\frac{U}{\hbar\omega}+\frac{N}{2}\right)-\left(\frac{U}{\hbar\omega}-\frac{N}{2}\right)\ln\left(\frac{U}{\hbar\omega}-\frac{N}{2}\right)-N\ln N\right] \tag{6.2.26}$$

upon applying Stirling's formula and setting $N-1\approx N$. Now rearranging terms we find that

$$S(U,N)\approx k\left[\frac{N}{2}\ln\left(\frac{U^2}{\hbar^2\omega^2}-\frac{N^2}{4}\right)+\frac{U}{\hbar\omega}\ln\frac{\left(\frac{U}{\hbar\omega}+\frac{N}{2}\right)}{\left(\frac{U}{\hbar\omega}-\frac{N}{2}\right)}-N\ln N\right] \tag{6.2.27}$$

which means that

$$U=\frac{N\hbar\omega}{2}\coth\left(\frac{\hbar\omega}{2kT}\right). \tag{6.2.28}$$

Now we notice that

$$U\overset{T\to\infty}{\approx}NkT,\quad U\overset{T\to 0}{\approx}\frac{1}{2}N\hbar\omega \tag{6.2.29}$$

The first limit is expected for one dimensional oscillators. The low temperature limit says that as $T\to 0$ all the oscillators tend to be their ground states. As a consequence, as $T\to 0$ there is, once again, just one microstate available to the system and again it is not difficult to check that S approaches zero in this limit.[4]

Now although the examples of quantum microstates presented above have zero entropy in the limit as T approaches zero, this is not necessarily always the case. If, for example, the quantum mechanical ground state of the constituents is degenerate the number of states available to the system will be larger than one. The resulting non-zero entropy at $T=0$ is then called the **residual entropy** of the system. If the ground state has a $p-$fold degeneracy then at $T=0$ there will be p^N available states for the system and the residual entropy will be $S_{\text{res}}=Nk\ln p$. An example is Carbon Monoxide which has a two fold degenerate ground state, so its residual entropy is $Nk\ln 2$.

6.3 Nernst's Statement

The third law of thermodynamics was originally postulated by the chemist Walther Nernst between 1906 and 1912 and is sometimes referred to as Nernst's "theorem". Although we called the previous statement the "Planck" statement, it was first proposed by Nernst, who required that:

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[4] Problem: Show that

$$\lim_{T\to 0}S(U,N)=0$$

where U is given as a function of T by (6.2.28).

At $T = 0$ all substances have the same value of the entropy.

Planck then recognized that this value could be chosen to be zero. However this statement is too strong because the ground states of all substances cannot be required to possess the same degeneracy. Thus both statements must be modified and a more appropriate statement of the third law would be:

At $T = 0$ the specific entropy (entropy per particle) is a constant, independent of all the extensive properties of the system.

Later, in 1917, Nernst proposed another form of the law, today known as the **unattainability statement** of the Third Law, but which we will refer to as **Nernst's statement**

It is impossible by any procedure, no matter how idealised, to reduce any system to the absolute zero of temperature in a finite number of operations.

This statement is not equivalent to the previous statement(s). There are thermodynamic systems (black holes, for example) that obey Nernst's statement of the third law but not Planck's.

6.4 Applications

Consider the implications of the thermodynamic definition of entropy

$$S(T) = \int_0^T \frac{đQ}{T} = \int_0^T \frac{C(T)dT}{T}, \tag{6.4.1}$$

where $C(T)$ is the heat capacity of the system. We have determined that the heat capacities, C_V and C_p of an ideal gas are constant and since one can always cook up two quasi-static processes, one isovolumetric and another isobaric, to get from any thermodynamic state to any other we immediately see that the integral is ill defined at $T = 0$ unless $C(T)$ approaches zero "fast enough" as T approaches zero. What is "fast enough"? For the integral to converge, $C(T)$ should behave as some positive power of T near absolute zero. Thus the third law says that the classical theory of heat capacities breaks down at low temperatures and requires a more complete theory which yields a $C(T) \sim T^\nu$, near $T = 0$, where $\nu > 0$.

6.4.1 Heat Capacities

We have seen in a few examples that the quantum theory satisfies this criterion for a "more complete theory". Why can we ignore quantum effects at high temperatures but not at low

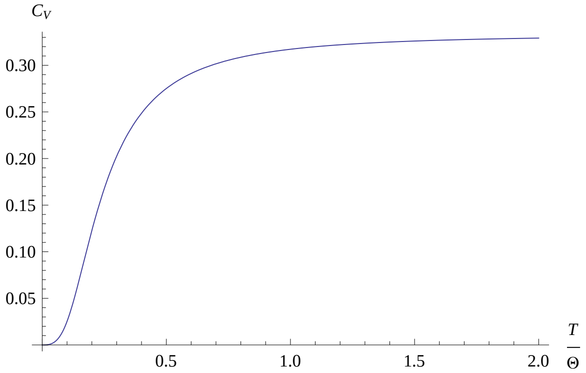

Figure 6.2: Heat capacity of a solid as a function of the Temperature

temperatures, and what might these effects be? Quantum effects in a macroscopic system can usually be neglected when the wave-functions of the constituents do not overlap, so there is no quantum interference. For an ideal gas this is the condition that the mean distance between the molecules is greater than twice the mean wavelengths of the particles. Applying de Broglie's hypothesis, $\lambda = h/p$, this requirement translates to

$$\frac{h}{mv_{\rm rms}} \ll n^{-1/3} \tag{6.4.2}$$

Using the ideal gas equation of state and expressing the rms speed in terms of the temperature we find

$$\frac{h}{\sqrt{3mkT}} \ll \left(\frac{kT}{p}\right)^{1/3} \tag{6.4.3}$$

(the left hand side is called the **thermal de Broglie wavelength** of the molecules) so that

$$p \ll \frac{(3m)^{3/2}(kT)^{5/2}}{h^3} \tag{6.4.4}$$

which gives a lower bound for the temperature below which quantum effects become unavoidable. The lower bound decreases with increasing particle mass, and it is indeed quite low for ordinary molecules at standard pressure. However, it is high for an electron gas at standard pressure ($\approx$ 1405 K), so free electrons in a metal will behave quantum mechanically at STP. At temperatures below the lower bound, the heat capacity of an ideal gas will depend on the **statistics** obeyed by its molecules, a purely quantum effect. While this will be discussed in detail later, let us mention that although we have implicitly assumed that all the molecules are **identical** in the sense that they have the same physical properties, we have not taken into account that *if* they have the same physical properties they must also be **indistinguishable**. Indistinguishability requires us to modify our counting of microstates for classical systems and quantum systems and it will play a particularly special role in quantum systems. To understand its implications, consider the wave function of two particles, labeled "1" and "2". Suppose one of these particles is in state "$|\alpha\rangle$" and the other is in state "$|\beta\rangle$". If the particles are distinguishable then the two states

$$\psi_{12}^{\alpha\beta} = \psi_1^\alpha \psi_2^\beta \tag{6.4.5}$$

and

$$\psi_{21}^{\alpha\beta} = \psi_2^\alpha \psi_1^\beta, \tag{6.4.6}$$

which are obtained from the one another by interchanging "1" and "2", are distinct states because the first represents a situation in which "1" is in state $|\alpha\rangle$ and "2" is in state $|\beta\rangle$ while the second represents the situation in which "2" is in state $|\alpha\rangle$ and "1" is in state $|\beta\rangle$. However, if they are indistinguishable then it is impossible to tell which particle is in which particular state, so the wave function for the two particles should be given by a linear combination of states in which "1" is in "$|\alpha\rangle$" and "2" in "$|\beta\rangle$" and "2" is in "$|\alpha\rangle$" and "1" in "$|\beta\rangle$". We can only have one of the two following possibilities:

$$\psi_{12}^{\alpha\beta} = \frac{1}{\sqrt{2}}[\psi_1^\alpha \psi_2^\beta \pm \psi_2^\alpha \psi_1^\beta] \tag{6.4.7}$$

The wave function with the negative sign will then vanish if the states $|\alpha\rangle$ and $|\beta\rangle$ are the same, whereas the wave function with the positive sign will be enhanced. Thus, either no two particles may exist in the same quantum state or the particles "prefer" to exist in the same state and these are the only two possibilities. This leads, in the first case, to a **Fermi** gas and in the second to a **Bose** gas. The particles of a Fermi gas are described by a completely antisymmetric wave function while those of a Bose gas are described by a completely symmetric wave function.

The heat capacity of a Bose gas below a certain critical temperature, T_c, which depends on the fundamental constants, the molecular parameters and the number density of particles, behaves as

$$C_V \sim Nk\left(\frac{T}{T_c}\right)^{3/2} \tag{6.4.8}$$

and rises above its classical value. At the critical temperature there is a $\lambda-$shaped cusp in C_V and above the critical temperature C_V falls to its clasical value. There is no cusp in C_V for Fermi gases. Their specific heat rises smoothly from zero to the classical value, behaving near $T = 0$ as

$$C_V \sim \frac{\pi^2}{2}\frac{T}{T_F}\left[1 - \frac{3\pi^2}{10}\left(\frac{T}{T_F}\right)^2 + \ldots\right] \tag{6.4.9}$$

where T_F is the "Fermi Temperature" and kT_F is the Fermi energy, the highest energy quantum state that may be accessed by a particle of the system at absolute zero.

Apart from taking the quantum theory into account, one must also be careful to account for all degrees of freedom. We see how important this is, for example, in the description of solids. In the previous section we obtained the internal energy of our simplified solid as a function of the temperature in (6.2.28). Taking a derivative with respect to the temperature we find

$$C_V = \frac{N\hbar^2\omega^2}{4kT^2}\text{csch}^2\left(\frac{\hbar\omega}{2kT}\right), \tag{6.4.10}$$

which approaches Nk at high temperatures ($kT \gg \hbar\omega$) and at very low temperatures approximates to

$$C_V \approx \frac{N\hbar^2\omega^2}{kT^2}e^{-\hbar\omega/kT}. \tag{6.4.11}$$

This was the model originally proposed by Einstein, who suggested that the frequency ω had to be determined experimentally for each solid. However, although C_V in (6.4.10) does have the correct high temperature behavior and vanishes faster even than any positive power of T near absolute zero, its low temperature behavior does not agree experiment. The model was refined by Peter Debye in 1912. He pointed out that the problem lies in assuming that all the oscillators have the same frequency. Atomic vibrations in crystalline solids give rise to lattice vibrations which propagate through the solid. These waves, called **phonons**, propagate with well defined wavelengths and frequencies called **normal modes**. In determining the specific heat of such solids, the lattice vibrations must also be counted because they also cost the system some energy. Taking into account the lattice vibrations, Debye showed that the constant volume heat capacity of a crystalline solid behaves as

$$C_V(T) = 9Nk\left(\frac{T}{\Theta}\right)^3\int_0^{\Theta/T} dx\ x^4\text{csch}^2 x \tag{6.4.12}$$

where Θ is the so-called Debye temperature. At low temperatures, $T \ll \Theta$, the heat capacity is dominated by the phonons: the upper limit in the integral can be taken to be effectively infinite and the heat capacity will behave as T^3. At high temperatures, $T \gg \Theta$, x must be small and we can replace csch$x$ by $1/x$ to find that the heat capacity is constant. The change from its cubic behavior near absolute zero to its classical, constant value at high temperatures occurs smoothly as shown in figure 6.2.

6.4.2 Sublimation

Some substances pass directly from the solid phase to the gas phase in a process known as **sublimation**. Sublimation occurs at a fixed temperature, as does any phase transformation, and there is a latent heat, L, associated with the process. Since there is no ambiguity in the definition of the entropy associated with a particular state, we know that

$$S_{\text{vapor}} - S_{\text{solid}} = \frac{ML}{T} \tag{6.4.13}$$

where T is the temperature of sublimation. We can compute the entropy of the vapor at high temperatures as follows. Starting with the number of states in (6.2.9) and using (6.2.11) we can estimate the entropy as a function at high temperatures via

$$S = k \ln \frac{\Omega}{N!} \tag{6.4.14}$$

where we divided the number of states calculated before by the number of interchanges between particles to account for indistinguishability, since every interchange of two particles will lead to the same state. We easily find

$$S_{\text{vapor}} = \frac{g}{2} Nk \ln \left[\frac{2\pi m k e^{\gamma} T}{h_o^2} \left(\frac{V}{N} \right)^{2/g} \right] \tag{6.4.15}$$

where m is the molecular mass, g the number of degrees of freedom per molecule and γ is the ratio of specific heats, $\gamma = C_p/C_V$. We have used the expression for the number of states that is derived from classical statistical mechanics, which is only good at high temperatures. That is acceptable provided we also take into account the indistinguishability of the gas particles and any possible degeneracy they may have in the ground state. We have already done the first by dividing the number of states by $N!$. To account for a possible degeneracy of the ground state, let us also add

$$gNk \ln \omega_v \tag{6.4.16}$$

where ω represents the said degeneracy. Thus we get

$$S_{\text{vapor}} = \frac{g}{2} Nk \ln \left[\frac{2\pi m k e^{\gamma} \omega_v^2 T}{h_o^2} \left(\frac{V}{N} \right)^{2/g} \right] \tag{6.4.17}$$

On the other hand, the entropy of a solid at high temperatures in three dimensions is given by the formula in (6.2.14)

$$S_{\text{solid}} = 3Nk \ln \left[\frac{\omega_s T}{\Theta} \right] \tag{6.4.18}$$

where we introduced ω_s to account for the degeneracy per degree of freedom just as we did for the ideal gas.

For definiteness, we'll now assume that the molecules are monatomic and point like, having only translational degress of freedom. Then we have, for the gas

$$S_{\text{vapor}} = \frac{3}{2} Nk \ln \left[\frac{2\pi m k e^{5/3} \omega_v^2 T}{h_o^2} \left(\frac{V}{N} \right)^{2/3} \right] \tag{6.4.19}$$

and putting it together with the entropy for the solid, we find that (6.4.13) reads

$$Nk \left[-\frac{1}{2} \ln T - \ln p + \frac{3}{2} \ln \left(\frac{\omega_v^2 \sigma^2 \Theta^2}{\omega_s^2} \right) \right] = \frac{ML}{T} \tag{6.4.20}$$

where

$$\sigma^2 = \frac{2\pi m k^{5/3} e^{5/3}}{h_0^2}.$$

Therefore

$$p = \left(\frac{\omega_v \sigma \Theta}{\omega_s} \right)^3 \frac{1}{\sqrt{T}} e^{-\frac{ML}{NkT}} \tag{6.4.21}$$

This solution should be compared with (3.5.36), since it describes essentially the same phenomenon. There is an extra factor of $T^{-1/2}$ in the expression here, which originates in the difference between the number of degrees of freedom of the solid and vapor phases. From a thermodynamic point of view we must think of (6.4.21) as a solution of the Clausius-Clapeyron equation in which there is a temperature dependence of the latent heat of vaporization. Notice also that the constant p_0 in (3.5.36) has here been determined by the third law.

6.4.3 Allotropic Forms

Some elements can exist in the same phase but different forms, called **allotropes** of that element. Two allotropes differ from each other in the manner in which the atoms bind to one another, *i.e.,* in their crystal structures, just as **isomers** are chemical compounds whose molecules bind to one another differently although they share the same chemical formula. Carbon atoms, for example, have three different allotropes, *viz.,* (i) diamond, (ii) graphite and (iii) fullerenes. In diamond, the carbon atoms are bound in a tetraherdral lattice, in graphite they are bound together in sheets of a hexagonal lattice and in fullerenes they are bonded in spherical, tubular or ellipsoidal formations.

We will consider the case of tin, which can exist in two forms: white tin and grey tin. White tin is unstable below a certain temperature, T_0, and grey tin is unstable above T_0. However, the transformation from white to grey tin is very slow below T_0 and it is possible to work with white tin even at very low temperatures. Now as $T \to 0$ the entropy of white tin should approach a constant, which counts the number of degrees of freedom associated with its ground state. The same statement is true of grey tin. These degrees of freedom count the number of possible orientations of their nuclear spins, but since they are the same nuclei and we deal with the same number of nuclei in each case we can conclude that the entropy as $T \to 0$ must be the same for both. Thus the entropy of each at the temperature T_0 will be

$$S_{\rm wt} = S(0) + \int_0^{T_0} \frac{C_{\rm wt}(T')}{T'} dT' \tag{6.4.22}$$

and likewise

$$S_{\rm gt} = S(0) + \int_0^{T_0} \frac{C_{\rm gt}(T')}{T'} dT' \tag{6.4.23}$$

where we have used the *same* value S_0 for the entropy at T_0 for both forms. Now imagine taking a sample of grey tin and transforming it quasi-statically at T_0 to white tin (which is stable above T_0). We will need to suppy an amount of energy Q_0 to the grey tin for this purpose and entropy of the resulting sample of white tin will be

$$S_{\rm wt} = S(0) + \int_0^{T_0} \frac{C_{\rm gt}(T')}{T'} dT' + \frac{Q_0}{T_0} \tag{6.4.24}$$

But S can only depend on the state and therefore comparing (6.4.24) with (6.4.22) we find that

$$\frac{Q_0}{T_0} = \int_0^{T_0} \frac{C_{\rm wt}(T')}{T'} dT' - \int_0^{T_0} \frac{C_{\rm gt}(T')}{T'} dT' \tag{6.4.25}$$

from which we can determine the latent heat of the transformation. In fact, by using the experimental specific heat measurements and performing the integrations numerically one can compare the theoretical result for Q_0 with the experimental result. One finds that they compare very favorably.

Chapter 7

Foundations of Equilibrium Statistcal Mechanics

7.1 Brief Review of Thermodynamics

Thermodynamics is a completely self-contained, phenomenological theory of matter. It is concerned with the properties of a macroscopic system (a system that is extremely large on the molecular scale and consisting of about 10^{24} molecules in equilibrium with the environment. Matter in equilibrium is defined by its equilibrium macrostate, which is a set of variables that adequately describe all the *measurable* properties of the system. These "macroscopic" or "thermodynamic" variables need not be the mechanical variables of the system but they are, eventually, related to them. Equilibrium macrostates do not change significantly with time. Thermodynamics is also concerned with processes that take a macroscopic system from some initial equilibrium state to a finalequilibrium state, but generally it has little to say about the system during the process itself, unless the process happens to take place very "slowly" compared to the characteristic relaxation time scale of the system. Transformations between equilibrium states come about by relaxing one or more external constraints, thereby letting the system evolve and achieve a new equilibrium state. If the constraints are relaxed slowly, in the sense mentioned, then the system effectively stays in equilibrium at all times and the process is said to be quasi-static. On the other hand, if the constraints are relaxed suddenly, so that the transformation occurs rapidly compared with the relaxation time of the system, the system is out of equilibrium during the transformation process and the process is not quasi-static. In this case, while thermodynamics is unable to describe the process itself, it is able to give us some general conditions under which one equilibrium state may evolve into another. It is based upon four fundamental laws, which we briefly review below.

1. **Zeroeth Law:** The law introduces a new variable, called the Temperature. It says that there exists a variable of the macroscopic state (a state variable) called the Temperature, which determines thermal equilibrium between two systems. Two thermodynamics systems having the same temperature will not exchange energy by thermal interactions on the average if their temperatures are the same.

2. **First Law:** The law introduces a new variable, called the internal energy. It says that there exists a function of state called the internal energy and asserts that the total energy is conserved:
$$đQ = dU + đW \tag{7.1.1}$$
where $đQ$ is the heat exchanged between the system and its environment the system, and $đW$ is the work done by (on) the system on (by) the environment, with the sign conventions:
$$\begin{aligned} &đQ > 0 \quad \text{if heat is absorbed by the system} \\ &đW > 0 \quad \text{if work is done by the system} \end{aligned} \tag{7.1.2}$$
and negative (or zero) otherwise.

   Neither $đQ$ nor $đW$ are "exact differentials", which means that their integrals depend on the precise process taking the system from the initial to the final state. This is why we represent these differential by $đ$ instead of the usual d. However, U being a function of state, dU is indeed an exact differential (its integral depends only on the initial and final states of the process). The experimental justification for the 1st law is Joule's experiment which demonstrates the equivalence between heat and energy.

3. **Second Law:** In as much as the first law is concerned only with the overall conservation of energy in the universe, it does not tell when a given process may or may not occur. Consider the example of a lake on a hot summer's day: it has never been observed to suddenly give up all its heat to the atmosphere around it and freeze. Even though this process in principle obeys the 1st law of thermodynamics, somehow nature forbids it from actually happening. The second law deals with the problem of determining when a given process may or may not occur. It introduces a new function of state, called the entropy, S, defined such that the *change* in entropy from initial some state i to some final state, f is given by
$$\Delta_{if}S = S_f - S_i = \int_{i,(\text{q.s.})}^{f} \frac{đQ}{T} \tag{7.1.3}$$

where the subscript "(q.s.)" refers to *any* quasi-static process taking the system from an initial state to a final state. A given thermodynamic process can occur if and only if

$$\Delta_{if} S \geq 0 \tag{7.1.4}$$

for the corresponding closed or isolated system. It can be shown that the integral in (7.1.3) depends only on the initial and final states, therefore entropy is a function of state and dS is and exact differential. A **reversible** process is one in which $\Delta S = 0$; if $\Delta S > 0$, the process is **irreversible**. A reversible process is quasi-static but the converse is not necessarily true.

Equation (7.1.3) gives only the change in entropy during a process, therefore the second law does not serve as a complete definition of entropy. It gives only changes in entropy between initial and final states.

4. **Third Law:** This law completes the thermodynamic definition of entropy by stating its canonical value at a given temperature. It states that the entropy of any system at $T = 0$ is just k times the natural logarithm of the degeneracy of its ground state:

$$S(T = 0) = S_0 \tag{7.1.5}$$

so that the entropy function in any state f can be calculated directly from (7.1.3) as

$$S(f) = S(T = 0) + \int_{T=0,(\text{q.s.})}^{f} \frac{\text{đ}Q}{T} \tag{7.1.6}$$

We will now be interested in the molecular foundations of thermodynamics. Specifically, we will ask ourselves the following question: if mechanics (classical or quantum) provides the fundamental description of the dynamics of particles, atoms and molecules, and if macroscopic systems are indeed built up of these particles, then is it possible to recover a description of macroscopic systems starting with the microscopic dynamics? We want to obtain the macroscopic dynamics *from* the microscopic dynamics. With the ensuing theory we will be able to analyze the natural fluctuations about equilibrium and, putting it side by side with thermodynamics, we will have a comprehensive mathematical theory that is capable of describing the stability or instability of macroscopic systems. In everything that follows we assume, unless otherwise stated, that the center of mass of the macroscopic system under consideration is at rest in the laboratory frame and that the individual atoms or molecules are not energetic enough to be relativistic. That is, when we speak of mechanics we will mean Newtonian mechanics or Schroedinger's quantum mechanics.

7.2 Equilibrium Statistical Mechanics

Why do we need something as limited as thermodynamics when we have at our disposal all the tools for a complete mechanical description of any system? We can answer this question by asking precisely what such a detailed description would entail.

- First of all we need to know the initial state of the system. If we are working within classical mechanics this means that we must know the initial positions and momenta of each and every particle within the system. This "state" would be defined by a set of variables of the form

  $$\{S\} = \{\vec{r}_1, \vec{r}_2 .... \vec{r}_N; \vec{p}_1, \vec{p}_2 .... \vec{p}_N\} \tag{7.2.1}$$

  where N is the number of particles, all obtained (experimentally) at the initial time, say $t = 0$. One can easily count the number of variables in this set: there are $6N$ of them, three positions and three momenta for each particle. Now consider that a mole of any material would contain 6.02×10^{23} molecules, so we would need to measure roughly 3.6×10^{24} variables to determine completely the initial classical state.[1] To know the quantum state, on the other hand, we would need to know the Schroedinger wave function at some initial time (t_o), which involves f quantum numbers, where f is the number of degrees of the system.

- We would need to know the detailed interactions between all the particles of the system. Thus, for a system of N particles, we should know all the interaction potentials of the form $U_{ij}, \forall i \neq j \in \{1, 2, ..., N\}$. There are $N(N-1)/2$ distinct pairs of N particles, so therefore there are that approximately 10^{48} interaction potentials to be determined for every mole of any material.

- Lastly we need to solve the equations of motion (Newton's equations in a classical treatment, or Schroedinger's equation in a quantum), subject to satisfactory boundary conditions. These are generally f *coupled* equations, because of the interactions between the particles.

It should need no convincing that **all three** steps in the list above are impossible to carry out in practice. It is impossible to know the precise initial state, very difficult to model all the intermolecular interactions and again practically impossible to solve $\sim$

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[1] In this example, $f = 3N$ is the number of degrees of freedom of the system. A degree of freedom is roughly a way in which the system can store energy. The number of degrees of freedom is the number of independent ways in which the system can store energy. Thus, for example, for an ideal gas of point-like molecules, each molecule can move in three independent directions, storing kinetic energy. Therefore each molecule has 3 independent ways to store energy, or three degrees of freedom. The gas of N molecules would have $f = 3N$ degrees of freedom

10^{24} coupled equations even with our fastest computers. However, let us consider what such a description would give us if it were possible: in principle it would predict the precise trajectories of each particle in the system, something that we could not hope to measure in the laboratory anyway. Happily, therefore, a precise mechanical or quantum mechanical description is too detailed to be of any practical use. Nonetheless, we can measure *certain* properties of a macroscopic system. For example, its energy, temperature, pressure, volume, etc. This is a relatively small set compared with the huge set of variables required to measure the microscopic state of the system, indeed it is only a small part of the total detailed information that is, in principle, available. We must keep in mind that the choice of this small subset of thermodynamic variables depends on the nature of the system and the kind of experiments being performed. We shall call the variables that are measured and controlled in the laboratory the "macroscopic variables". A macroscopic variable is said to be **extensive** if it depends on the total amount of substance in the system and **intensive** if it does not.

We would like to give the "macroscopic" variables some mechanical meaning, however. We would also be interested in attempting a more detailed description of macroscopic systems than is afforded by thermodynamics, though not as detailed as a purely mechanical treatment would afford. This is the objective of Statistical Mechanics: we seek a description of the equilibrium properties of macroscopic systems by applying the laws of mechanics and combining them with general statistical principles, thus "deriving" thermodynamics from more fundamental laws and giving mechanical meaning to the thermodynamic variables. Mechanics provides the general physical framework, such as the laws of conservation, and statistics replaces the rigorous detail that mechanics requires by general, reasonable, statistical assumptions whose validity can only be measured by experiment. Naturally, the questions we may ask of the resulting theory will be far less detailed than those we might ask of pure mechanics, but that is the price we must pay for avoiding the impossible task (and useless detail) of a purely mechanical treatment. It should be noted finally that statistical mechanics has nothing whatever to say about the actual approach to equilibrium, or even if the equilibrium is reached. One assumes that, if we wait long enough, an equilibrium state is achieved and goes from there.

7.3 Formulation of the Statistical Problem

The state of the system is a set of values of all the variables one needs to describe that system at any given time. These are of two kinds, depending on the kind of description we are after:

- A **macrostate** of a system is a set of values of all its macroscopic variables, *i.e.,* variables that are actually measured in an experiment, such as the total energy, the pressure, the volume, the temperature, etc.

- A **microstate** of a system is a set of values of the microscopic variables required for a complete [quantum] mechanical description of the system. These are the positions and momenta of each particle in the system (for a classical description) or the quantum state of the system as a whole.

Generally speaking, a given macrostate will correspond to a huge number of allowable microstates. For example, if a macrostate is described only by the total energy and total number of particles of the system, there are a large number of ways in which this energy may be distributed between the particles to give the same total energy. Each of the ways corresponds to a given microstate. Let's see how this works in some simple systems.

7.3.1 Quantum Systems

We begin with quantum systems. A microstate of a system is completely given once its wavefunction is known and the wavefunction is specified by f "quantum numbers", where f is the number of degrees of freedom of the system,

$$\psi = \psi_{\alpha_1,\alpha_2,\alpha_3\ldots,\alpha_f}(t, x_1, \ldots x_N) \tag{7.3.1}$$

where we assume N particles.

1. A single spin $\frac{1}{2}$ particle: It's quantum state is specified by giving the value of one component of the spin, say s_z, which can take values $\pm 1/2$. The quantum microstates are therefore represented by the set $\{s_z\}$, and there are two of them.

2. N relatively fixed, non-interacting, spin $\frac{1}{2}$ particles: here the quantum state is specified by giving N quantum numbers (one component of the spin of each particle)

   $$\{S\} = \{s_{1z}, s_{2z}, \ldots s_{Nz}\} \tag{7.3.2}$$

   There are now therefore 2^N possible distinct microstates.

3. A single harmonic oscillator: Its quantum state is determined by the "energy" quantum number, $\{n\}$, where $E_n = (n + 1/2)\hbar\omega$. There are a countably infinite number of possible quantum states.

4. N non-interacting harmonic oscillators: The quantum state is defined by N integers, the excitation levels of each of the oscillators,

   $$\{S\} = \{n_1, n_2, n_3, \ldots n_N\} \tag{7.3.3}$$

   each of which is the "energy" quantum number of some oscillator. Again there are a countably infinite number of possible quantum states.

Figure 7.1: The spin $\frac{1}{2}$ particles

More information than just the number of particles in the system is generally available. For example, suppose we know the total energy as well.

1. Consider, first, the case of N non-interacting spin $\frac{1}{2}$ particles in a magnetic field, which we'll orient along the z axis. If the particles do not interact appreciably with each other, but only with the magnetic field, the energy of the system will depend on the orientation of the spins of each particle according to

   $$E = -\sum_n \vec{\mu}_n \cdot \vec{B} = -\sum_n \mu_{n z} B \tag{7.3.4}$$

   where $\vec{\mu} = g_s|e|\vec{s}/2m$ is the magnetic moment of each particle, g_s is its spin g-factor ($g_s = 2$). Each particle with spin up contributes $-\mu_z B$ to the total energy of the system and each particle with spin down contributes $+\mu_z B$ to the total energy. Clearly therefore the total energy will be

   $$E = (n - m)\mu_z B \tag{7.3.5}$$

   where n is the number of particles with spin down and m is the number with spin up. Moreover, we know that $N = (m + n)$. Now suppose we know only the total energy of the system, say E, and the total number of particles, N. These are fixed and the set $\{E, N\}$ constitutes the macrostate of the system. Knowing E and N allows us to determine the total number of spin up particles and the total number of spin down particles, but not their arrangement (see figure (7.1). Each arrangement will correspond to a given microstate! Thus to calculate the number of microstates corresponding to one macrostate of fixed energy and particle number, we need only to calculate the number of distinct arrangements of n particles of one kind and m particles of another kind. The n particles are identical and so are the m particles. Therefore, the number of microstates is just

   $$\Omega(n, m) = \frac{(m+n)!}{m!n!} = \frac{N!}{m!n!} \tag{7.3.6}$$

   with

   $$n = \frac{1}{2}\left(N + \frac{E}{\mu_z B}\right), \quad m = \frac{1}{2}\left(N - \frac{E}{\mu_z B}\right) \tag{7.3.7}$$

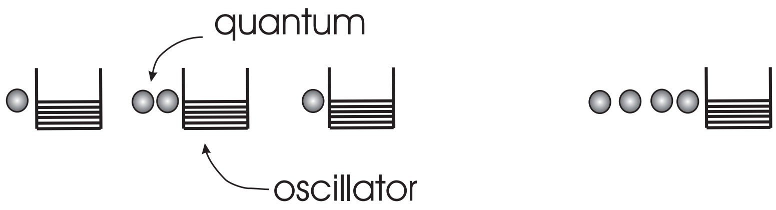

Figure 7.2: The Oscillator Problem

For a system of three spin $\frac{1}{2}$ particles with total energy $-\mu_z B$, $n = 1$ and $m = 2$, so that the number of possible microstates is just 3. If, instead we had 50 spin $\frac{1}{2}$ particles and, knowing the total energy, we determined that 40 of them are spin up and 10 are spin down, there would be $\sim 10^{10}$ microstates corresponding to this single macrostate.

2. Again, consider N non-interacting harmonic oscillators. Each oscillator has a minimum energy (the ground state energy), $E = \hbar\omega/2$, so the minimum energy of the N oscillators would be $N\hbar\omega/2$. If the macrostate is given by $\{E, N\}$, its total energy E must be greater than or equal to $N\hbar\omega/2$ and $E - N\hbar\omega/2 = Q\hbar\omega$ where Q is some (non-negative) integer because the energy of each oscillator can go up only by an integer multiple of $\hbar\omega$. Now the question is: how many microstates of the system correspond to any given macrostate $\{E, N\}$? Each microstate corresponds to a particular distribution of the Q quanta between the N oscillators, so the question can be reformulated as follows: in how many ways can N integers be added to get another integer Q? This is a particular so-called "partition" of Q. A more pictorial way of formulating the problem would be: in how many ways can Q identical objects (the quanta) be distributed into N (identical) "boxes" (the oscillators) with no limit on the number of objects that can be put into each box (see figure (7.2; the rule is that every quantum is attached to the oscillator immediately to its right)? Notice that each quantum must end up in an oscillator, so clearly the last object of the distribution must be an oscillator – we have no freedom about this. Therefore the problem is rephrased as follows: In how many ways can we arrange Q identical objects of one type and $N - 1$ (because the last object must be an oscillator) identical objects of another. The answer is:

$$\Omega = \frac{(N-1+Q)!}{(N-1)!Q!} \tag{7.3.8}$$

which is the number of microscopic states available subject to the constraints of fixed energy and oscillator number given by the macrostate $\{E, N\}$.

> For example, of there were only one quantum, it would have to go into some oscillator and there are N possibilities (put $Q = 1$ in the above formula) corresponding to the number of ways in which the quantum is distributed between the oscillators. On the other hand if there were $N = 100$ oscillators and $Q = 4$ quanta then there are 4,424,275 possible microstates corresponding to this macrostate! Here we have only a hundred oscillators and fifty quanta. In a normal solid, which can be thought of as a collection of oscillators (the molecules of the solid): each mole has on the order of 10^{23} oscillators, so there are generally a huge number of microstates that correspond to any given macrostate of fixed energy and size.

In these examples, we have seen that fixing the macroscopic parameters by the application of some external constraints is only a very loose control over a system, *i.e.,* the system can be in a huge number of distinct microstates, all subject to the constraints. Indeed, this is precisely what allows us to do statistics so successfully.

7.3.2 Classical Systems

Classical microstates have a very different description. Recall that the initial conditions required to solve Newton's equation are the positions and momenta of each particle. Thus, in order to fully describe the classical microstate of a system of particles, we need to specify all the coordinates and momenta (tangents to the trajectories) of the particles of the system. For example, if the system has f degrees of freedom, we must specify $2f$ "phase space" variables: f coordinates and f momenta. Now the coordinates and momenta can take on any real value and the set of real numbers is dense, therefore the number of possible classical microstates of a system are *ab initio* uncountably infinite. This unpleasant situation can be corrected by "coarse graining" phase space, *i.e.,* divide phase space into cells of fixed area, agreeing that the state of the system is to be specified by saying that its momentum lies between $\vec{p}$ and $\vec{p} + \delta\vec{p}$ and its position between $\vec{q}$ and $\vec{q} + \delta\vec{q}$ where the representative point $(\vec{q}, \vec{p})$ is within a cell of area

$$\delta^f \vec{p}\delta^f \vec{q} = \delta\vec{q}_1\delta\vec{q}_2...\delta\vec{q}_f\delta\vec{p}_1\delta\vec{p}_2...\delta\vec{p}_f = h_o^f, \text{(constant.)} \tag{7.3.9}$$

as shown in figure (7.3). The microstates thus defined are then all countable. Clearly, the description becomes more accurate as we take the area of each cell to approach zero. Although we will not be able to take that limit, we will assume that h_o is "macroscopically small" but "microscopically large". What this means is that we assume that *any* macroscopic volume in phase-space includes a very large number of fundamental cells of volume h_o^f, while each cell itself contains a very large number of points. This is the "continuum" approximation.

Very often we will need to sum over all microstates. For example, if we want to find average values of mechanical variables we will need to sum over values of the variables

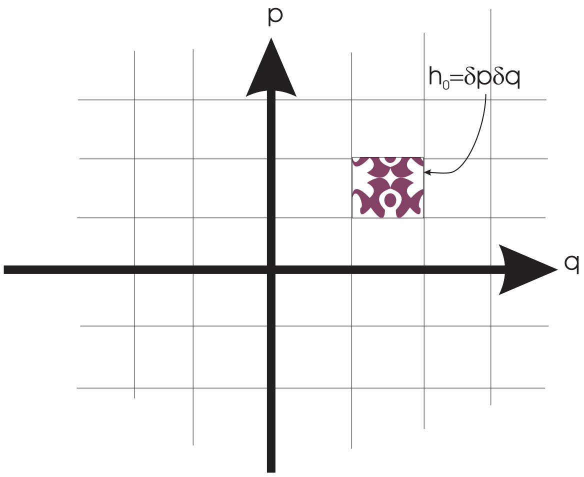

Figure 7.3: Coarse graining classical phase space

describing the microstates. Sums over quantum microstates are discrete,

$$\sum_r ... \tag{7.3.10}$$

where r represents the distinct quantum states available to the system. To sum over classical states we must sum over the phase space cells of volume h_o^f, in principle taking the limit as $h_o \to 0$ in the end if possible. Thus

$$\sum_{\text{cells}} ... \to \lim_{h_o \to 0} \frac{1}{h_o^f} \int_{\mathcal{R}} d^f\vec{q} d^f\vec{p} ... \tag{7.3.11}$$

where $\mathcal{R}$ is some relevant region of phase-space.

7.4 Statistical Ensembles

Although it is true that for a given macrostate there generally exist a large number of possible microstates, all obeying the constraints that define the macrostate, the system itself of course can be in only one of these microstates at any given time. We have, however, no way of knowing precisely which one of the possible microstates it "occupies" because we only know the value of the macroscopic variables. We could speak about this in terms of probabilities: with what probability does the system find itself in a given microstate at any given time? How would we answer such questions of probability? The concept of probability is basically an experimental one and we must therefore imagine that we have a very large number of *identical* systems at our disposal to perform the same experiment simultaneously on each one of the systems. By identical we mean systems with the same number of degrees of freedom, governed by the same Hamiltonian and subject to the same boundary conditions. Such an imaginary collection of identical systems is called an **ensemble**. How large should our collection of identical systems be? At least as large as the number of states available to the system subject to the initial constraints. We then perform the same experiment or set of experiments on each member of the ensemble to determine the microscopic state of that member. If there are N such identical systems and state r is found N_r times, then the probability that state r occurs in any experiment is $P_r = N_r/N$. For example, imagine that we know the total energy of the system only. An ensemble of identical systems would then consist of a large number of systems having the same energy. Now suppose that we want to know something more about the system, for example about some property $\mathcal{Y}$. The property will not generally be the same in every microstate because the allowed microstates must only have the same *energy.* So it will obviously depend on the particular microstate the system is in. Because we cannot know the precise microstate the system is in, we ask for the *average value* of the property $\mathcal{Y}$. In other words, if we know that the variable $\mathcal{Y}$ has the value $\mathcal{Y}_r$ in state r and the probability of finding a system in the state r is

$$P_r = \frac{N_r}{N}, \quad \sum_r P_r = 1 \tag{7.4.1}$$

then the average value of $\mathcal{Y}$ is

$$\langle \mathcal{Y} \rangle = \sum_r P_r \mathcal{Y}_r. \tag{7.4.2}$$

Of course, $\mathcal{Y}$ may never actually take the value $\langle \mathcal{Y} \rangle$ and will in general fluctuate about this average value. The **statistical dispersion** of the observable, defined by

$$\Delta \mathcal{Y} = \sqrt{\langle (\mathcal{Y} - \langle \mathcal{Y} \rangle)^2} = \sqrt{\langle \mathcal{Y}^2 \rangle - \langle Y \rangle^2}, \tag{7.4.3}$$

measures how much the observable fluctuates in the ensemble. For the average value of any macroscopic variable to have experimental significance its statistical fluctuations must be small compared with its average value,

$$\frac{\Delta \mathcal{Y}}{\langle \mathcal{Y} \rangle} \ll 1. \tag{7.4.4}$$

As we will see, this is generically true when the system is “sufficiently” large.

Now, P_r is a probability distribution over the states of the system. When the states are continuous, $P_r \to P(q,p)$ is a density in phase space and is called the probability density function. In quantum mechanics, the density function turns into the density matrix, which will be defined and treated in some detail later, when we begin a formal study of quantum systems. In a classical system, the formal sum over states that we have used goes over to an integral over phase space and the normalization condition for the probability density reads

$$\frac{1}{h_o^f}\int d^f q d^f p\ P(q,p) = 1, \tag{7.4.5}$$

where we have used the abbreviation, $(q,p) = \{\vec{r}_1, ..., \vec{r}_N, \vec{p}_1, ..., \vec{p}_N\}$ and the integral is over all the degrees of freedom of the system. With this normalization we say that $d^f q d^f p\ P(q,p)$ represents the probability of finding a member of the ensemble whose phase-space lies between $(\vec{q},\vec{p})$ and $(\vec{q}+d\vec{q},\vec{p}+d\vec{p})$. The average value of the variable $\mathcal{Y}$ is then

$$\langle\mathcal{Y}\rangle = \frac{1}{h_o^f}\int d^f q d^f p\ P(q,p)\mathcal{Y}(q,p) \tag{7.4.6}$$

etc. The probability density function, $P(q,p)$, may be replaced with a density function, $\rho(q,p)$, obtained from $P(q,p)$ by a different normalization. We could, for example, normalize to the total number of members in the ensemble, then $d^f q d^f p\ \rho(q,p)$ would represent the number of members in the ensemble whose phase space lies between $(\vec{q},\vec{p})$ and $(\vec{q}+d\vec{q},\vec{p}+d\vec{p})$. Equivalently, we could normalize to the total number of states available to the system, then $d^f q d^f p\ \rho(q,p)$ represents the number of states lying between $(\vec{q},\vec{p})$ and $(\vec{q}+d\vec{q},\vec{p}+d\vec{p})$, or the number of **representative points** in this phase space volume. (In a classical system $d^f q d^f p$ is taken to be macroscopically small by microscopically large, in particular much larger than say h_o^f.) Whatever the preferred normalization of the density function, the average value of any observable would be

$$\langle\mathcal{Y}\rangle = \frac{\int d^f q d^f p\ \rho(q,p)\mathcal{Y}(q,p)}{\int d^f q d^f p\ \rho(q,p)} \tag{7.4.7}$$

where we have explicitly included the normalization factor.

7.5 Liouville's Theorem

Liouville's theorem states simply that the density function (however one chooses to normalize it) is conserved along the phase space trajectory of freely evolving *Hamiltonian* systems, so long as the systems in the ensemble do not interact significantly with the environment, *i.e.*,

$$\frac{d\rho}{dt} = 0 \tag{7.5.1}$$

along phase space trajectories. The physical content of the theorem is illustrated in figure (7.4). On the left is a region in phase space, occupied by the systems in the ensemble at an initial time t_i, on the right is the region after a certain time interval has elapsed and

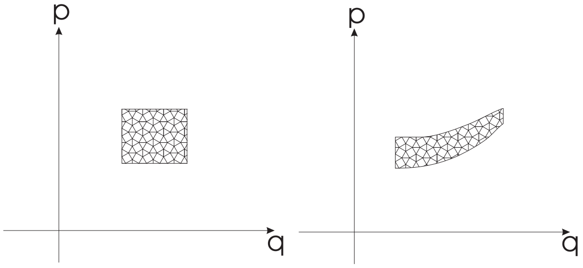

Figure 7.4: Liouville's Theorem

each of the systems have evolved according to Hamilton's equations. Liouville's theorem says that the volume of the region, or the number of representative points in the region, defined by $V = \int_{\mathcal{R}} d^f q d^f p\ \rho(q,p)$, remains constant. The proof of this theorem is based on the conservation of the probability current. Since the systems in our ensemble do not have significant interactions with the rest of the universe and no systems in the ensemble are created or destroyed, the probability current must be conserved. Let the index i represent the coordinates, ξ^i, of phase space such that $\xi^i = q^i,\ i \in \{1, ..., 3N\}$ and $\xi^i = p_i\ i \in \{3N+1, ..., 6N\}$. Conservation of the probability current implies that,

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial \xi^i}(\dot{\xi}^i \rho) = 0 \tag{7.5.2}$$

Expanding, we find

$$\frac{\partial \rho}{\partial t} + \left[\dot{\xi}^i \frac{\partial \rho}{\partial \xi^i} + \rho \frac{\partial \dot{\xi}^i}{\partial \xi^i}\right] = 0 \tag{7.5.3}$$

Now we recall that Hamilton's equations require that

$$\dot{\xi}^i = \{\xi^i, \mathcal{H}\}_{P.B.} = \omega^{ij} \frac{\partial \mathcal{H}}{\partial \xi^j} \tag{7.5.4}$$

where $\hat{\omega}$ is the symplectic form in the $6N$ dimensional phase-space. Because $\hat{\omega}$ is antisymmetric it follows immediately that

$$\frac{\partial \dot{\xi}^i}{\partial \xi^i} = \omega^{ij} \frac{\partial^2 \mathcal{H}}{\partial \xi^i \partial \xi^j} \equiv 0 \tag{7.5.5}$$

Therefore the conservation of the probability current gives simply

$$\frac{\partial \rho}{\partial t} + \dot{\xi}^i \frac{\partial \rho}{\partial \xi^i} = \frac{\partial \rho}{\partial t} + \omega^{ij} \frac{\partial \rho}{\partial \xi^i} \frac{\partial \mathcal{H}}{\partial \xi^j} = \frac{\partial \rho}{\partial t} + \{\rho, \mathcal{H}\}_{P.B.} = 0 = \frac{d\rho}{dt} \tag{7.5.6}$$

where we have used (7.5.4) in the second step.

In equilibrium, we must restrict ourselves to density functions that do not depend explicitly on time. This implies that the Poisson brackets of the probability density with the Hamiltonian should vanish identically, which is possible if and only if it is either a numerical constant or some function of only the conserved quantities, such as the energy. Other commonly occurring conserved quantities are obviously the angular momentum, the charge, the number of particles, etc.

A quantum mechanical version of Liouville's theorem exists and we will pursue this further when we examine quantum statistics in greater detail. Here we simply state the result: the density function, $\rho(q,p)$ turns into the density matrix (operator), $\hat{\rho}$, which obeys the analogue of (7.5.6):

$$i\hbar\frac{\partial\hat{\rho}}{\partial t}+[\hat{\rho},\hat{\mathcal{H}}]=0 \tag{7.5.7}$$

Again, in equilibrium there should be no explicit dependence on time in $\hat{\rho}$, implying that $\hat{\rho}$ commutes with the Hamiltonian and therefore is a function only of those observables that are diagonal in the Hamiltonian basis.

7.6 Isolated Systems

In discussing statistical ensembles, we had to perform experiments on each member of the ensemble in order to determine the probabilities P_r. We cannot do this in practice, of course, and in order to make theoretical progress, we must make further assumptions about these probabilities. Such assumptions would have to be quite complex indeed if they were to attempt to describe general thermodynamic states and/or processes. However, we expect that they would greatly simplify for equilibrium states of isolated systems. This hope has proved to be justified for, as we shall see, a relatively simple assumption for such systems provides incredible insights and makes superb predictions for a wide variety of thermodynamic systems and processes. This is the fundamental postulate of statistical mechanics which states that

- an isolated system in equilibrium is equally likely to be found in any one of its accessible states, that is $P_r = P_s$ for any two accessible states r and s.

A collection of identical isolated systems in equilibrium constitutes the first of three "canonical" ensembles, and is called the *microcanonical* ensemble. It is easy to calculate probabilities in the microcanonical ensemble. Suppose that the macrostate is fixed by some set (of macroscopic variables) including, say, the energy, E, and that we are interested in finding the average value of some quantity $\mathcal{Y}$ which is not constrained by the macrostate. Corresponding to this macrostate, there is a huge number of possible microstates of course, and each one of these microstates is occupied with the same probability. Let $\Omega(E,\alpha)$ be the total number of microstates for a given energy, where α denotes

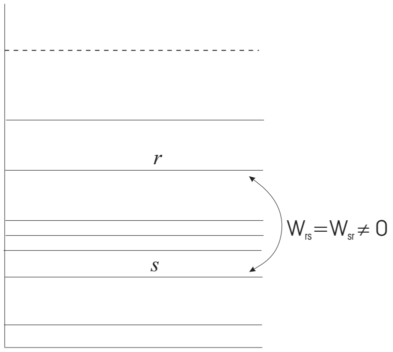

Figure 7.5: States and transitions

all the other macrovariables defining the macrostate. The probability of finding the system in *any* accessible state, r, is then

$$P_r = \frac{1}{\Omega(E,\alpha)}. \tag{7.6.1}$$

Now let the number of states in which $\mathcal{Y}$ has value $\mathcal{Y}_k$ be $\Omega(E,\alpha;\mathcal{Y}_k)$. Clearly, $\Omega(E,\alpha;\mathcal{Y}_k) < \Omega(E,\alpha)$ and $\sum_k \Omega(E,\alpha;\mathcal{Y}_k) = \Omega(E,\alpha)$ where the sum is over all possible values $\mathcal{Y}_k$ of $\mathcal{Y}$. The probability of finding value $\mathcal{Y}_k$ is then

$$P_k = \frac{\Omega(E,\alpha;\mathcal{Y}_k)}{\Omega(E,\alpha)} \tag{7.6.2}$$

and the average value of $\mathcal{Y}$ is

$$\langle\mathcal{Y}\rangle = \sum_k P_k\mathcal{Y}_k = \sum_k \frac{\Omega(E,\alpha;\mathcal{Y}_k)}{\Omega(E,\alpha)}\mathcal{Y}_k \tag{7.6.3}$$

Thus the fundamental principle has allowed us to write the above expression for P_k in the microcanonical ensemble. $\Omega(E,\alpha)$ is called the density of states.

7.7 Approach to equilibrium: the "H" Theorem

We now consider the approach to equilibrium, but only briefly as this topic falls outside of the scope of these notes. Equilibrium states are macrostates that do not change appreciably in time. If a system is not in equilibrium, the probability of finding it in any one of its accessible states cannot be equal for all states because, after all, the system is evolving. In fact, the probability distribution will depend explicitly on time.

Consider an ensemble of identical isolated systems that are not in equilibrium and let $\{r, s...\}$ label all the possible states of the systems.[2] To the state r, associate a probability P_r *i.e.,* P_r is the probability of finding a member of the ensemble in the state r. P_r will have some explicit dependence on time. As the ensemble evolves, some of the systems will make transitions to the state r and others will make transitions out of this state. The probability of finding a given system in state r therefore increases due to transitions into state r and decreases due to transitions out of state r. Let W_{rs} be the probability of transition from state r to state s per unit time and W_{sr} the probability of transition from s to r per unit time. They are called the **transition** or **jump rates** from r to s and s to r respectively. We will make the following three assumptions:

- **Fermi's Master equation:** The time rate of change of the probability for the system to occupy state r is given by[3]

$$\frac{\partial P_r}{\partial t} = \sum_{s \neq r} [W_{sr} P_s - W_{rs} P_r] \tag{7.7.1}$$

- **Symmetry of the jump rates:** The transition or jump rates W_{sr} and W_{rs} are symmetric,[4] $W_{rs} = W_{sr}$, and

- **The system is ergodic:** For any two states, $W_{rs} \neq 0$.[5] This is called the **ergodic** hypothesis because it implies that the system will always jump from one state to another, so that over a very long time (an *infinite* time) the system will have occupied *all* of its accessible states.

Then

$$\frac{\partial P_r}{\partial t} = \sum_{s \neq r} W_{rs}(P_s - P_r). \tag{7.7.2}$$

Let us define the following quantity,

$$H = \sum_r P_r \ln P_r \tag{7.7.3}$$

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[2] It is most transparent to prove the "H" theorem in the abstract labelling of states by $r, s, ...$ To describe continuous systems, replace the suffix $r, ..$ with the phase space variables (q, p) and the sum over states by the corresponding integral over phase space.

[3] There is no proof of this equation.

[4] While there is no rigorous proof of this assumption in general, it is reasonable to expect this behavior from the quantum theory.

[5] This assumption is very strong and probably not strictly correct. However, most isolated systems are expected to be ergodic to an excellent approximation. In this course we will build *from* the microcanonical ensemble despite the questions surrounding the ergodic hypothesis (and Fermi's Master equation) because its assumptions are clear. Therefore, it should also be clear how modifications arise when the hypotheses are no longer valid.

and study its behavior in time. Taking the derivative of (7.7.3) gives,

$$\begin{aligned}\frac{\partial H}{\partial t} &= \sum_r \left(\frac{\partial P_r}{\partial t}\ln P_r + \frac{\partial P_r}{\partial t}\right)\\ &= \sum_{r,s\neq r} W_{rs}\left[(P_s - P_r)\ln P_r + (P_s - P_r)\right]\end{aligned} \tag{7.7.4}$$

Interchanging r and s (which we can, because these are summed over)

$$\frac{\partial H}{\partial t} = \sum_{r,s\neq r} W_{rs}\left[(P_r - P_s)\ln P_s + (P_r - P_s)\right] \tag{7.7.5}$$

and adding (7.7.4) and (7.7.5) gives

$$\frac{\partial H}{\partial t} = \frac{1}{2}\sum_{r,s\neq r} W_{rs}(P_r - P_s)(\ln P_s - \ln P_r). \tag{7.7.6}$$

Now, W_{rs} is non-negative (it is a probability) and $(P_r - P_s)(\ln P_s - \ln P_r)$ is never positive, so that

$$\frac{\partial H}{\partial t} \leq 0. \tag{7.7.7}$$

Thus H is a monotonically decreasing function of time. Now the ergodic assumption implies that if H achieves a minimum, then at this time $\partial H/\partial t = 0 \to P_r = P_s$. The state in which H achieves a local minimum is an equilibrium state. Therefore, if the system is isolated and in equilibrium, the probabilities, P_r,are all equal and we must have $P_r = \Omega^{-1}$, which is precisely the distribution postulated in the previous section. For such systems it follows that

$$H = -\ln\Omega \tag{7.7.8}$$

As H is minimized in equilibrium, Ω must be maximized in the microcanonical ensemble.

The fundamental postulate is precisely equivalent to the statement that $W_{rs} = W_{sr}$ (which agrees with the rules of quantum mechanics.) Furthermore, we have seen that in equilibrium $P_r = P_s$, which was the fundamental postulate of statistical mechanics. One can either begin from the fundamental postulate or replace it with the three assumptions made in this sub-section.

Combined with the fact that the jump rate for any transition is equal to the jump rate for the reverse transition, this means that: *the average rate at which an isolated system in equilibrium actually jumps from r to s is the same as the average rate of the reverse jump.* This is known as the principle of detailed balance. The conclusion in (7.7.7) is commonly referred to as the $H-$theorem. Notice the similarity between the quantity H and the entropy S in thermodynamics: during any thermodynamic process both are monotonic functions of time. Equilibrium states *minimize* H and *maximize* S.

Chapter 8

The Microcanonical Ensemble

A microcanonical ensemble is a collection of identical isolated systems that have achieved equilibrium in the same macrostate. A system is isolated from its environment if it exchanges neither particles nor energy with it by heat and therefore microcanoncial ensembles are defined by the number of particles they contain, their total energy and the external constraints. According to the fundamental postulate of statistical mechanics, the probability of finding a member of the ensemble in a given microstate r is

$$P_r = \begin{cases} 1/\Omega(E, N, X_\alpha) & E_r = E, \quad N_r = N \\ \\ 0 & \text{otherwise} \end{cases} \tag{8.0.1}$$

where $\Omega(E, N, X_\alpha)$ is the number of states[1] accessible to the systems and X_α are other extensive parameters possibly defining the system, such as the volume. We see that all configurations that are consistent with the energy and number of particles occur with equal probability.

For isolated systems, it is thus a knowledge of $\Omega(E, N, X_\alpha)$ that allows us to proceed in statistical physics and so it is worth spending a little time analyzing its behavior. In the previous examples we have explicitly calculated $\Omega(E, N, X_\alpha)$, for a few isolated systems. Here we will attempt to get some feeling for the way it behaves during thermodynamic processes in which the systems remain isolated. Again, by the $H-$theorem we know that $\Omega(E, N, X_\alpha)$ is related to the entropy. This will allow us to make the connection between the number of states and the temperature, pressure and other "generalized forces" of isolated systems.

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[1] In practice one is not really able to measure the energy of a macroscopic system with infinite precision. It is therefore sometimes more useful to speak in terms of the number of states that have energy lying between E and $E + \Delta E$. In that case, evidently, $\Omega(E, N, X_\alpha) = \sum_{r, E_r \in [E, E+\Delta E]} \Omega(E_r, N_r, X_\alpha)$; in most cases we can write $\Omega(E, N, X_\alpha) = \omega(E, N, X_\alpha)\Delta E$, where $\omega(E, N, X_\alpha)$ is the **density of states.**

8.1 Behavior of the Number of Microstates

The examples worked out so far have shown that if we had a system in a well defined macrostate, defined by extensive parameters $X_1, ...X_N$, the number of these microstates will be a function of all the external parameters, $X_1, ...X_N$, the number, N, of constituents and the internal energy, E,

$$\Omega = \Omega(E, N, X_1, ...X_N). \tag{8.1.1}$$

The system is kept in a definite macrostate by the imposition of external constraints. For example, consider a gas in an isolated cylinder with a piston at one end. The macrostate is defined by giving the number of particles, the internal energy and the volume of the gas in the cylinder. The volume of the cylinder is maintained by keeping the position of the piston fixed.

If some of the constraints are removed, the external parameters change accordingly. The system is not in equilibrium immediately after the constraint is removed because the release of one constraint has allowed the system to access a much larger number of states, yet at the instant the constraint is removed it occupies only a fraction of them. Let's see how this works for the number of states occupied by the ideal gas. Imagine that the gas is allowed to *freely* expand to some final volume V_f. We know from experience that the final volume will be larger than the initial volume (experimentally, an isolated gas never spontaneously contracts) but, because the expansion is free and the system is isolated, the internal energy stays the same. Again, because the gas *expands* the number of states accessible to it according to (6.2.9) clearly increases. On the other hand, what happens during a quasi-static process? Imagine a quasi-static, adiabatic process in which the volume is changed by an infinitesimal quantity dV. If the number of particles is held fixed, the change in the number of states, $d\Omega(E, V)$ is just proportional to $d(E^{\frac{f}{2}} V^{\frac{f}{3}})$. For an adiabatic process, the equation of state, $pV^\gamma = \alpha$ (const.), implies by the first law of thermodynamics that $dE = -\alpha V^{-\gamma} dV$. Using the fact that $E = \frac{3}{2}NkT$ and that the equation of state for the adiabatic process can also be put in the form $TV^{\gamma-1} = \frac{\alpha}{Nk}$, it is easy to see that $d\Omega(E, V) \equiv 0$. Therefore, the number of states remains constant in a quasi-static process.

What happens to the number of microstates available to an isolated system when a new equilibrium is reached after *any* thermodynamic process? The $H-$theorem guarantess that the number of states will either increase or stay the same but never decrease. If the process resulted from the release of a constraint, let the constraint which keeps the macroscopic variable X_α constant be released so that the value of X_α changes. Corresponding to this new equilibrium there will be either the same or a larger number of states than the initial macrostate allowed, and each state, say r, will correspond to a certain value of the

Figure 8.1: A box with a partition and a cylinder with a piston

parameter X_α, say X_{α_r}. In other words, X_α will have a certain average value

$$\langle X_\alpha \rangle = \frac{\sum_r \Omega(X_1, ..., \widehat{X}_\alpha, ..., X_N; X_{\alpha_r}) X_{\alpha_r}}{\Omega(X_1, ...\widehat{X}_\alpha, ..., X_N)} \tag{8.1.2}$$

where $\Omega(X_1, ...\widehat{X}_\alpha, ..., X_N; X_{\alpha_r})$ is the number of accessible states when the macrostate is defined by $X_1, ...X_N$ *excluding* X_α and in which X_α admits the value X_{α_r}. Evidently, $\Omega(X_1, ...\widehat{X}_\alpha, ..., X_N; X_{\alpha_r})$ must be peaked at the average value, $\langle X_\alpha \rangle$ of X_α. If it is not, then the statistical dispersion of X_α would be large, and every time we performed a measurement we would be likely to find a significantly different value of X_α, but experimentally we find that the dispersion about the mean value is in fact very small compared to the mean value itself. In other words, when one or more constraints on an isolated system are removed, the system evolves to a new equilibrium in which

- the number of accessible microstates has either increased or stayed the same,

  $$\Omega_f(X_1, ...\widehat{X}_\alpha, ..., X_N) \geq \Omega_i(X_1, ..., X_N), \tag{8.1.3}$$

  and

- if X_α represents the constraint that has been removed, the new number of microstates is sharply peaked about the new average value of X_α.

If $\Omega_f > \Omega_i$, simply reimposing the constraints on the isolated system will not in general reduce the number of states to the original value Ω_i. Two examples will illustrate this:

1. Imagine a gas in an isolated box with a partition in it as shown in figure 8.1, so that the gas occupies only one half of the box. The partition is a constraint that keeps the volume occupied by the gas fixed. Removing this constraint allows the gas to occupy the entire box which increases the number of accessible states by essentially allowing it to double its volume. Replacing the partition does not cause the gas to return to its original state.

2. Consider a gas in an insulated cylinder with a piston at one end, again as shown in figure 8.1. At some initial time, let the macrostate be given by the total energy and

> the volume of the gas. The volume of the gas is maintained fixed by holding the position of the piston secure. Releasing the piston will obviously change its volume, its macrostate and the number of accessible states. Again, simply compressing the gas will not return it to its original state.

Of course, in each case, the gas *can* be returned to its original state, but the steps involved include interactions with the environment and the systems are no longer isolated. In the second example, for instance, we would have to place the cylinder in contact with a heat reservoir at a fixed temperature (equal to the initial temperature of the gas in the cylinder) and compress the piston till the gas achieves its original volume. Compression will tend to increase the internal energy of the gas, but it will give up this energy to the heat reservoir in order to maintain its temperature. The system consisting only of the gas in the cylinder has been returned to its initial state, but the larger system which includes the heat reservoir has received heat from the gas, and external work has been done on the gas, so the entire system has indeed changed. In fact the final number of states of the gas and its environment taken together (this is the isolated system during the process) has either increased or stayed the same.

A similar process can be carried out to return the first system to its initial state (place a thin piston against the wall of the box on the right hand side and slowly compress the gas keeping it in contact with a heat reservoir). Again, the remarks made earlier in connection with the second system are applicable.

8.2 The Absolute Temperature

Consider now two systems, A and B, and the system obtained by placing A and B in thermal contact with each other so that energy can be exchanged between them but only by heat. We will refer to this system as $A+B$. Since A and B interact thermally they are individually not isolated, but we will assume that $A+B$ is isolated. At the moment they are brought into thermal contact with each other, if they are not already in equilibrium then they will exchange energy until they eventually achieve equilibrium. Furthermore, the process of heat exchange is a transformation that will, in general, increase the number of states available to the system as a whole. Equilibrium will be reached when the number of states is maximized.

Consider the final equilibrium situation. The total energy of $A+B$ will be $E^{(0)} = E_A + E_B$ where E_A and E_B are the energies respectively of A and B (not necessarily known). $E^{(0)}$ is a fixed by the fact that $A+B$ is isolated, so if A has energy E_A then B will have energy $E^{(0)} - E_A$ and the number of states of $A+B$ in which system A has energy E_A is

$$\Omega(E^{(0)}, E_A) = \Omega_A(E_A)\Omega_B(E^{(0)} - E_A). \tag{8.2.1}$$

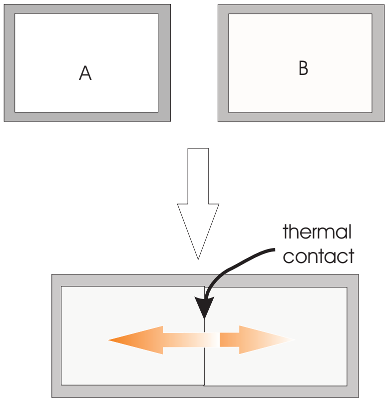

Figure 8.2: Two isolated systems making thermal contact

However, because only the total energy is fixed and not the energy of A by itself, the total number of states accessible to the system will be a sum over all the possible values of E_A

$$\Omega(E^{(0)}) = \sum_{E_A} \Omega_A(E_A)\Omega_B(E^{(0)} - E_A) \tag{8.2.2}$$

What, then, is the probability of finding a given value, say E, for the energy of A? This is simply the ratio of the number of states of $A + B$ in which A has energy E divided by the total number of states available to $A + B$,

$$P(E) = \frac{\Omega_A(E)\Omega_B(E^{(0)} - E)}{\sum_{E_A} \Omega_A(E_A)\Omega_B(E^{(0)} - E_A)} \tag{8.2.3}$$

The denominator is some constant representing the total number of states available to $A + B$, which we call $\mathcal{C}^{-1}$, so that we may write the expression (8.2.3) above as

$$P(E) = \mathcal{C}\Omega_A(E)\Omega_B(E^{(0)} - E) \tag{8.2.4}$$

Taking logarithms on both sides, we have

$$\ln P(E) = \ln \mathcal{C} + \ln \Omega_A(E) + \ln \Omega_B(E^{(0)} - E). \tag{8.2.5}$$

Now, in equilibrium, the number of states of $A + B$ must be a maximum. At this stage the energy of one of the systems, say A, will be $\widetilde{E}$ and the other (B) will have energy $\widetilde{E}' = E^{(0)} - \widetilde{E}$. We therefore want $P(\widetilde{E})$ to be maximum, which implies that $\partial P(E)/\partial E|_{\widetilde{E}} = 0$. Therefore,

$$\frac{\partial \ln \Omega_A(E)}{\partial E}|_{\widetilde{E}} + \frac{\partial \ln \Omega_B(E^{(0)} - E)}{\partial E}|_{\widetilde{E}} = 0 \tag{8.2.6}$$

Call E' the energy of B, so that $E' = E^{(0)} - E$, then

$$\frac{\partial \ln \Omega_A(E)}{\partial E}|_{\widetilde{E}} = \frac{\partial \ln \Omega_B(E')}{\partial E'}|_{\widetilde{E'}} \tag{8.2.7}$$

If we define

$$\beta(E) = \frac{\partial \ln \Omega(E)}{\partial E} \tag{8.2.8}$$

then, in equilibrium,

$$\beta_A(\widetilde{E}) = \beta_B(\widetilde{E'}) \tag{8.2.9}$$

The quantity β has dimension [J^{-1}]. Introducing a constant k, we write

$$\beta(E) = \frac{1}{kT(E)} \tag{8.2.10}$$

then $T(E)$ is called the **absolute temperature** of the system and is measured in Kelvin. The constant we introduced, k, is Boltzmann's constant. It has dimension [J/°K]. We have therefore seen that for two systems to be in equilibrium their absolute temperatures must be the same and so justified the thermodynamic concept of temperature, which asserts that temperature is that variable which determines whether or not two systems will be in thermal equilibrium (the *zeroeth law* of thermodynamics).

The absolute temperature also determines the direction of heat flow when two or more systems are brought into thermal contact. Consider two systems, A and B, which are initially isolated and in equilibrium. Let them now be brought into thermal contact in such a way that $A + B$ is isolated. Heat will therefore flow from A to B (or vice versa) but no heat will leave the combined system $A + B$. During the exchange process, the number of states of $A + B$ will increase. At the initial instant, let E_i be the energy of the system A and $E'_i = E^{(0)} - E_i$ be the energy of B, where $E^{(0)}$ is the total energy of $A + B$. Therefore, when the systems are brought together, the number of states of $A + B$ is

$$\Omega(E_i) = \mathcal{C}\Omega_A(E_i)\Omega_B(E^{(0)} - E_i) \tag{8.2.11}$$

Since the number of states is increasing,

$$\delta \ln \Omega(E) = \frac{\partial \ln \Omega_A}{\partial E}|_{E_i}(E - E_i) + \frac{\partial \ln \Omega_B}{\partial E'}|_{E'_i}(E' - E'_i) \geq 0 \tag{8.2.12}$$

Or, in terms of the temperatures of A and B

$$\beta_A(E_i)(E - E_i) + \beta_B(E'_i)(E' - E'_i) \geq 0 \tag{8.2.13}$$

Now, since the system $A + B$ is isolated, the total energy must stay fixed through any exchange of heat between A and B. In other words whatever energy is gained (lost) by A is lost (gained) by B, or, $E - E_i = -(E' - E'_i)$,

$$\left[\beta_A(E_i) - \beta_B(E'_i)\right](E - E_i) \geq 0 \tag{8.2.14}$$

It follows that, if $\beta_A > \beta_B$ then $E > E_i$ and vice-versa. Energy flows from B to A. On the other hand, if $\beta_A < \beta_B$ then $E < E_i$ and heat flows from A to B. Since β is inversely proportional to the absolute temperature, it follows that energy flows from the body at a higher temperature to the one with the lower temperature.

The condition of being a maximum at $\widetilde{E}$ is also a statement of the behavior of the absolute temperature with energy, because

$$\begin{aligned} \lambda = -\frac{\partial^2 \ln \Omega(E)}{\partial E^2}|_{\widetilde{E}} &\geq 0 \\ \Rightarrow \frac{\partial \beta}{\partial E}|_{\widetilde{E}} &\leq 0 \\ \Rightarrow \frac{\partial T}{\partial E}|_{\widetilde{E}} &\geq 0 \end{aligned} \tag{8.2.15}$$

where we have used $\beta = (kT)^{-1}$. The absolute temperature of a system therefore increases with its energy.

We had shown earlier that, for a classical gas, the number of states $\Omega(E, V)$ behaves roughly as $E^{f/2}$ where f is the number of degrees of freedom of the gas. Thus, if f is very large,

$$\begin{aligned} \Omega(E) &\approx E^{f/2} \Rightarrow \ln \Omega(E) \approx \frac{f}{2} \ln E \\ \Rightarrow \frac{\partial \ln \Omega}{\partial E} &= \beta(E) \approx \frac{f}{2E} \\ \Rightarrow E &= \frac{f}{2} kT \end{aligned} \tag{8.2.16}$$

Thus, in equilibrium, the temperature is a measure of the internal energy of the classical gas. The above relation is familiar from the kinetic theory of gasses: every degree of freedom contributes an amount $kT/2$ to the total energy of the gas.

As another example, consider the system consisting of N oscillators with Q quanta distributed among them. We had calculated the number of states to be

$$\ln \Omega(Q, N) \approx Q \ln \left[1 + \frac{N}{Q}\right] + N \ln \left[1 + \frac{Q}{N}\right] \tag{8.2.17}$$

in the limit of large N and Q. When a single quantum of energy, $\hbar\omega$ is added to the system the number of states changes approximately by

$$\delta \ln \Omega = \ln \Omega(Q + 1, N) - \ln \Omega(Q, N) \approx \ln \left[1 + \frac{N}{Q}\right] \tag{8.2.18}$$

so that the temperature of the system as defined in (8.2.10) will be

$$\beta = \frac{1}{kT} = \frac{\delta\Omega}{\hbar\omega} = \frac{1}{\hbar\omega}\ln\left[1+\frac{N}{Q}\right] \tag{8.2.19}$$

neglecting terms of order $1/Q$ and $1/N$. We can then write

$$E = \frac{1}{2}N\hbar\omega + \frac{N\hbar\omega}{e^{\frac{\hbar\omega}{kT}}-1} = \frac{N\hbar\omega}{2}\coth\left(\frac{\hbar\omega}{2kT}\right) \tag{8.2.20}$$

Finally take the system of N spin 1/2 particles that we had also studied earlier. If n of the particles have spin down, the number of states was

$$\ln\Omega(n,N) \approx N\ln\left[\frac{N}{N-n}\right] - n\ln\left[\frac{n}{N-n}\right] \tag{8.2.21}$$

Now imagine that the energy of the system were increased by increasing the number of particles with spins anti-parallel to the magnetic field (while keeping the total number of particles, N, fixed). Evidently the energy will increase by $\mu_z B$ and the number of states by approximately $\ln[(N-n)/n]$. The temperature of the system is therefore

$$\beta = \frac{1}{kT} = \frac{1}{\mu B}\ln\left[\frac{N-n}{n}\right] \tag{8.2.22}$$

Interestingly this temperature can be *negative* if $n > N/2$.

8.3 Generalized forces, Work and Energy

In our discussion of temperature we examined the behavior of the number of states in systems with thermal interactions so that we could concentrate only on changes in the internal energy of the systems due to energy transfer by heat. More general interactions involve changes in the external parameters as well.

Consider a macroscopic system undergoing an *arbitrary* process and label *all the possible* macrostates available to the system by r. Call the probability with which microstate r is occupied P_r. If some states are not accessible in the initial state, the occupation probabilities corresponding to those microstates will be identically zero. During the process, the states have characteristic energies, E_r, which will depend on the external parameters $X_1, ...X_N$. In other words, there will be a functional relation of the form $E_r = E_r(X_1, ...X_N)$. If some or all of these macroscopic parameters, X_α, change during the process, the energy corresponding to the state r will change accordingly. Likewise, the probability that the system will be in state r will in general change. Because of these changes, the average energy

$$E = \langle E\rangle = \sum_r E_r P_r \tag{8.3.1}$$

of the system will also change according to

$$dE = d\langle E\rangle = \sum_r dE_r P_r + \sum_r E_r dP_r \tag{8.3.2}$$

If the system is isolated during the quasi-static process, it will always obey the fundamental postulate because it never goes out of equilibrium. Therefore $P_r = \Omega^{-1}$ will remain constant throughout the process and the second term on the right hand side will vanish. The first term on the right hand side is thus associated with the external work done by the system

$$đW = -\sum_r dE_r P_r \tag{8.3.3}$$

Of course, if the system is not isolated during the process, the second term is non-vanishing and can be associated with energy transfer by "heat"

$$đQ = \sum_r E_r dP_r \tag{8.3.4}$$

From (8.3.2), (8.3.3) and (8.3.4) we have the formal result

$$dE = -đW + đQ \tag{8.3.5}$$

which is simply the First Law of thermodynamics. But now, statistical mechanics has given a microscopic meaning to the quantities that appear: macroscopic work is a related to changes in the state energies and heat is related to changes in the occupation probability distribution.

What (8.3.3) says is that if the system does an amount of work $đW_r$, always staying in the state r, then the external work done by the system must be equal to the loss in energy of the state r. The change in the energy of the state r is

$$dE_r = \sum_\alpha \frac{\partial E_r(X_1, ...X_N)}{\partial X_\alpha} dX_\alpha \tag{8.3.6}$$

and so

$$dW_r = -dE_r = -\sum_\alpha \frac{\partial E_r}{\partial X_\alpha} dX_\alpha = \sum_\alpha F_{\alpha,r} dX_\alpha \tag{8.3.7}$$

where $F_{\alpha,r} = \partial E_r/\partial X_\alpha$. The macroscopic external work done is the average of the above,

$$đW = \sum_\alpha \left(\sum_r F_{\alpha,r} P_r\right) dX_\alpha = \sum_\alpha \langle F_\alpha\rangle dX_\alpha \tag{8.3.8}$$

The quantity $\langle F_\alpha\rangle$ is called the **generalized force conjugate to** X_α.

We can obtain a relationship between the generalized forces and the number of states if we consider an infinitesimal quasi-static process during which $d\Omega(E, X_1, ..., X_N) = 0$. Because the number of states does not change,

$$\begin{aligned} & \frac{\partial \ln \Omega}{\partial E} dE + \sum_\alpha \frac{\partial \ln \Omega}{\partial X_\alpha} dX_\alpha = 0 \\ \Rightarrow \quad & \frac{\partial \ln \Omega}{\partial E} dE = -\sum_\alpha \frac{\partial \ln \Omega}{\partial X_\alpha} dX_\alpha \\ \Rightarrow \quad & \beta dE = -\sum_\alpha \frac{\partial \ln \Omega}{\partial X_\alpha} dX_\alpha \end{aligned} \tag{8.3.9}$$

Furthermore because no energy is exchanged by heat, $dE = -đW = -\langle F_\alpha \rangle dX_\alpha$ according to (8.3.7). Comparison yields the relation

$$\langle F_\alpha \rangle = \frac{1}{\beta} \frac{\partial \ln \Omega}{\partial X_\alpha} \tag{8.3.10}$$

As an application of the above, lets us calculate the equation of state for an ideal gas. We had earlier determined the number of states to be

$$\Omega(E, V) \approx B(N) V^N E^{3N/2}. \tag{8.3.11}$$

The external parameter of interest is the volume and the generalized force corresponding to this parameter is just the pressure

$$p = \frac{1}{\beta} \frac{\partial \ln \Omega(E, V)}{\partial E} = \frac{N}{\beta V} = \frac{NkT}{V}, \tag{8.3.12}$$

from which we derive

$$pV = NkT \tag{8.3.13}$$

(the equation of state) and the commonly used expression

$$đW = pdV \tag{8.3.14}$$

for the work done by the gas.

8.4 Entropy

The thermodynamic entropy has the remarkable property that S of an isolated system can only increase or stay the same in any thermodynamic process. We have already discovered a quantity, H, which satisfies an analogous property according to the general proof of the H theorem. It makes sense therefore to simply adopt the following definition of entropy:

$$S = -kH = -k \sum_r P_r \ln P_r \tag{8.4.1}$$

where the sum is over all accessible states. Boltzmann's constant appears above only for convenience. The quantity H was introduced into gas kinetics by Boltzmann and later applied to general systems by Gibbs. Since $S = -kH$, it is called the Boltzmann-Gibbs entropy. For systems belonging to the microcanonical ensemble, we know that $H = -\ln \Omega$ therefore

$$S = k \ln \Omega \tag{8.4.2}$$

where Ω is the number of states. Equation (8.4.2) is the original statistical definition of entropy due to Boltzmann. It satisfies the requirement that $\Delta S \geq 0$ during any process. Now consider a system initially belonging to the microcanonical ensemble and undergoing an arbitrary quasi-static process. For a small transformation immediately after the process begins, we can write,

$$dS = kd \ln \Omega \approx k \frac{\partial \ln \Omega}{\partial E} dE + k \sum_\alpha \frac{\partial \ln \Omega}{\partial X_\alpha} dX_\alpha \tag{8.4.3}$$

Using the relations we derived earlier in the microcanonical ensemble, we write therefore

$$\begin{aligned} dS &= k\beta \left(dE + đW \right) \\ TdS &= dE + đW \end{aligned} \tag{8.4.4}$$

which, comparing with expression (8.3.5), gives the thermodynamic definition of the entropy

$$dS = \frac{đQ}{T} \tag{8.4.5}$$

The left hand side of (8.4.5) is an exact differential, therefore

$$\Delta_{if} S = S(f) - S(i) = \int_{i,(\text{q.s.})}^{f} \frac{đQ}{T} \tag{8.4.6}$$

It follows that, for a thermally isolated system, quasi-static processes are reversible.

In summary, we have succeeded not only in obtaining the thermodynamic laws but also in acquiring a sense of the microscopic significance of some important everyday thermodynamic variables. Before proceeding to describe other interesting ensembles let us first collect the important relations we have derived for the microcanonical ensemble:

Temperature, T:	$\beta = \frac{1}{kT} = \frac{\partial \ln \Omega(E)}{\partial E}$
Generalized force, $\langle F_\alpha \rangle$:	$\langle F_\alpha \rangle = \frac{1}{\beta}\frac{\partial \ln \Omega}{\partial X_\alpha}$
Work, $\text{đ}W$:	$\text{đ}W = \sum_\alpha \langle F_\alpha \rangle dX_\alpha$
(Boltzmann) Entropy, S:	$S = -k\ \ln \Omega$
Gibbs Entropy, S_G:	$S_G = -k \sum_r P_r \ln P_r$

8.5 Fluctuations

Let us return to our considerations concerning two isolated systems A and B that are brought into thermal contact with one another to form a new (isolated) system $A+B$. By placing the two systems in thermal contact we have relaxed the constraints that keep the energy of each system fixed. As the new equilibrium situation is reached, however, we expect that the probability distribution will be sharply peaked about the (new) *average* energy of A. We will now check that both these expectations: (a) that the peak is about the average value of the energy of A, and (b) that the peak is sharp, are justified. Let the maximum of $P(E)$ lie at $\widetilde{E}$, then expanding about $\widetilde{E}$ we get

$$\ln P(E) = \ln P(\widetilde{E}) + \left[\frac{\partial \ln P(E)}{\partial E}\right]_{\widetilde{E}} (E - \widetilde{E}) + \frac{1}{2}\left[\frac{\partial^2 \ln P(E)}{\partial E^2}\right]_{\widetilde{E}} (E - \widetilde{E})^2 \ ... \qquad (8.5.1)$$

Now $P(E)$ is a maximum at $\widetilde{E} \Rightarrow \partial \ln P(E)/\partial E|_{\widetilde{E}} = 0$. Call $\partial^2 \ln P(E)/\partial E^2|_{\widetilde{E}} = -\lambda$, then, again because $P(E)$ is maximum at $\widetilde{E}$, it should be clear that λ is positive. Neglecting all the higher order terms, we get

$$P(E) \approx P(\widetilde{E}) e^{-\frac{\lambda}{2}(E-\widetilde{E})^2} \qquad (8.5.2)$$

This is a "gaussian" distribution which immediately proves (a) because, for a gaussian distribution, the average is indeed the peak. The sharpness of the peak will be determined by the dispersion in the energy

$$\Delta E = \sqrt{\langle (E - \widetilde{E})^2 \rangle} \qquad (8.5.3)$$

This is easy to calculate, of course, given the probability distribution in (8.5.2), the answer being[2]:

$$\Delta E \approx \lambda^{-1/2} \qquad (8.5.4)$$

Now, using the rough behavior of the number of states, $\Omega(E) \approx E^f$, where f is the number of degrees of freedom, one finds that

$$\lambda \approx \frac{f}{\widetilde{E}^2}, \quad \text{or} \quad \Delta E = \frac{\widetilde{E}}{\sqrt{f}} \qquad (8.5.5)$$

---

[2] Problem: Prove this.

Thus,

$$\frac{\Delta E}{\widetilde{E}} = \frac{1}{\sqrt{f}} \tag{8.5.6}$$

which decreases with increasing number of degrees of freedom. Recall that $f \sim 10^{24}$, so that $\Delta E/\widetilde{E} \approx 10^{-12}$ which is small indeed. We conclude that the peak is very sharp and we have justified, by example, the claim made earlier that in large systems the number of states attains a maximum about the average value of the external macroscopic parameter relaxed.

Chapter 9

The Canonical and Grand Canonical Ensembles

A statistical ensemble is a collection of identical systems in the same equilibrium state. What *kinds* of systems and what equilibrium states we consider will, of course, depend upon the physical system and the processes that are of interest. We have already described the microcanonical ensemble, which is a collection of isolated systems. Often we are interested in describing systems that interact with other systems. Here we want to describe systems that are in contact with reservoirs of energy and/or particles, able freely to exchange energy by heat and/or particles with it.

9.1 The Canonical Ensemble

Let us begin by describing an ensemble of systems that are able to freely exchange energy but not particles with a heat reservoir. The energy of any member of the ensemble is therefore not fixed but, in thermal equilibrium, its temperature will be the temperature of the reservoir. Therefore, just as the members of a microcanonical ensemble are characterized by their internal energy and the number of particles they contain, such an ensemble will be characterized by the temperature of the reservoir and the particle number. It is called a **canonical ensemble**.

Recall that a heat reservoir is any system that is very large (in terms of its number of degrees of freedom) compared with the system of interest that is in thermal contact with it. Because the energy of the system is not fixed, we might ask the following question: what is the probability of finding a member of the ensemble in a given state r with energy E_r? To answer this question, consider a system A in equilibrium with a heat reservoir, R, so that the combined system $A+R$ is isolated (therefore a member of the micro canonical ensemble. For any energy E of A the total number of states available to $A+R$ is

$$\Omega(E) \quad = \quad \Omega_A(E)\Omega_R(E^{(0)}-E) \tag{9.1.1}$$

where $E^{(0)}$ is the energy of the combined system. The *total* number of states available to the system is (as before) the sum over all possible values of the energy of A, *i.e.,*

$$\Omega(E^{(0)}) \quad = \quad \sum_E \Omega_A(E)\Omega_R(E^{(0)}-E) \tag{9.1.2}$$

Since the combined system belongs to a microcanonical ensemble, the probability of finding our system with energy E is

$$P(E) = \frac{\Omega_A(E)\Omega_R(E^{(0)}-E)}{\sum_E \Omega_A(E)\Omega_R(E^{(0)}-E)} = C\Omega_A(E)\Omega_R(E^{(0)}-E). \tag{9.1.3}$$

Now since the reservoir is very large compared with our system, $E \ll E^{(0)}$. So let's expand $\Omega_R(E^{(0)}-E)$ in a Taylor series about $E^{(0)}$. We get

$$\ln P(E) = \ln C + \ln \Omega_R(E^{(0)}) + \ln \Omega_A(E) - E\frac{\partial \ln \Omega_R(E')}{\partial E'}|_{E'=E^{(0)}} + \ldots, \tag{9.1.4}$$

where we have set $E' = E^{(0)} - E$. Since the temperature of heat reservoir is

$$\beta = \frac{\partial \ln \Omega_R(E')}{\partial E'}|_{E'=E^{(0)}}, \tag{9.1.5}$$

we could rewrite the probability of finding A with energy E as

$$\ln P(E) \approx \ln C + \ln \Omega_R(E^{(0)}) + \ln \Omega_A(E) - \beta E \tag{9.1.6}$$

which, upon exponentiating both sides, gives

$$\begin{aligned} P(E) \quad &= \quad C\Omega_R(E^{(0)})\Omega_A(E)e^{-\beta E} \\ &= \quad \bar{C}\Omega_A(E)e^{-\beta E} \end{aligned} \tag{9.1.7}$$

where $\bar{C} = C\Omega_R(E^{(0)})$ is some constant and $\Omega_A(E)$ is the number of states available to the system A if all we know is that it has energy E. The factor $\Omega_A(E)$ counts the number of states of energy E available to A and is called the **degeneracy** of the energy level E. But now, because the combined system is in the microcanonical ensemble, we can interpret (9.1.7) as asserting that the probability of finding A in *any one state*, r, of energy $E = E_r$ is

$$P_r(E_r) = \text{const.} \times e^{-\beta E_r} \tag{9.1.8}$$

(thus the probability of being in *any* of the states is just the above times the number of states of the same energy, which is equation (9.1.7)). The constant is to be determined by normalization, *i.e.,*

$$\sum_r P_r = \text{const.} \times \sum_r e^{-\beta E_r} = 1. \tag{9.1.9}$$

This is the Boltzamann distribution and it characterizes the **canonical ensemble**. Notice that nothing has been said about A except that it must be small relative to R and that it must be in thermal equilibrium with it. This is required only to ensure that A is at a fixed temperature. Thus, we could, for example, take A to be a single microscopic component of R itself. For example, we could take A to be a single molecule of a gas at a fixed temperature, T, so that the rest of the gas then acts as the heat reservoir. Then the probability of finding the molecule with energy E is given precisely by (9.1.7).

Given any distribution, we can calculate the average values of interesting quantities as explained earlier. Let the quantity Xtake the value X_r in state r, then the average value (or the expectation value) of X is just

$$\langle X\rangle = \frac{\sum_r X_r P_r}{\sum_r P_r} \tag{9.1.10}$$

where the denominator is unity if the distribution is normalized. For a classical system, the sum in (9.1.10) should be replaced by the phase-space integral:

$$\langle X\rangle = \frac{\int \prod_i d^3\vec{r}_i \prod_i d^3\vec{p}_i \; \rho(\vec{r}_i,\vec{p}_i) X(\vec{r}_i,\vec{p}_i)}{\int \prod_i d^3\vec{r}_i \prod_i d^3\vec{p}_i \; \rho(\vec{r}_i,\vec{p}_i)} \tag{9.1.11}$$

over all accessible values of $\vec{r}$ and $\vec{p}$ for each particle of the system A. $\rho(\vec{r}_i,\vec{p}_i)$ is the density function,

$$\rho(\vec{r}_i,\vec{p}_i) = \Omega(E(\vec{r}_i,\vec{p}_i))e^{-\beta E(\vec{r}_i,\vec{p}_i)} \tag{9.1.12}$$

which is a function of the internal energy of A and agrees with Liouville's theorem. The statistical dispersion of X,

$$\Delta X = \sqrt{\langle (X - \langle X\rangle)^2\rangle} = \sqrt{\langle X^2\rangle - \langle X\rangle^2} \tag{9.1.13}$$

gives the sharpness of the distribution about the average value of X.

9.2 Examples

9.2.1 The Ideal gas

Let us now derive some of the results of the elementary kinetic theory of gases with the machinery we have so far developed. As we have noted before, for a single molecule the rest of the gas acts as a heat reservoir and, applying the Boltzmann distribution, the probability of finding a molecule with energy E is

$$P(E) = \text{const.} \times e^{-\beta E} \tag{9.2.1}$$

We first want the normalized probability, that is we want to evaluate the constant, which we'll henceforth call $\mathcal{N}$, appearing on the right hand side above. Obviously, the probability of the molecule having *any* energy is one, so

$$\frac{\mathcal{N}}{h_o^3} \int d^3\vec{r} d^3\vec{p} e^{-\beta E} = 1 \tag{9.2.2}$$

where the integration is carried out over the volume of the container and all possible momenta. The energy of a molecule belonging to an ideal gas is purely kinetic because, by definition, we ignore any interactions between the molecules of the gas. In other words, $E = p^2/2m$ where m is the mass of the molecule. Since the energy does not depend on the position of the molecule we can immediately perform the integration over $\vec{r}$ to get simply the volume of the container. Therefore,

$$\begin{aligned} \frac{\mathcal{N}V}{h_o^3} \int d^3\vec{p} e^{-\beta E} &= 1 \\ \Rightarrow \frac{\mathcal{N}V}{h_o^3} \int p^2 \sin\theta dp d\theta d\phi e^{-\frac{\beta p^2}{2m}} &= 1 \end{aligned} \tag{9.2.3}$$

where we have used spherical coordinates in momentum space. Performing the integration over the solid angle, we get 4π and

$$\frac{4\pi\mathcal{N}V}{h_o^3} \int dp p^2 e^{-\frac{p^2}{2mkT}} = 1 \tag{9.2.4}$$

The integral can be evaluated to give

$$\mathcal{N} = \frac{h_o^3}{(2\pi mkT)^{3/2} V} \tag{9.2.5}$$

and therefore

$$P(E) = \frac{h_o^3}{(2\pi mkT)^{3/2} V} \, e^{-\frac{p^2}{2mkT}} \tag{9.2.6}$$

for the normalized probability distribution.

You may easily convince yourself that the average velocity of the molecule is zero, *i.e.,*

$$\langle v_x \rangle = \langle v_y \rangle = \langle v_z \rangle = 0, \tag{9.2.7}$$

which says that the molecule random walks through the gas. On the other hand, the average energy of a molecule is

$$\langle E\rangle = \frac{\langle p^2\rangle}{2m} = \frac{1}{2m}\frac{\int d^3x d^3p^2 p e^{-\frac{p^2}{2\pi mkT}}}{\int d^3x d^3 p e^{-\frac{p^2}{2\pi mkT}}} = \frac{3}{2}kT, \tag{9.2.8}$$

which is the classic result we had derived earlier in a completely different way. Therefore we also find

$$\begin{aligned} \langle v^2\rangle &= \frac{2\langle E\rangle}{m} = \frac{3kT}{m} \\ \Rightarrow v_{\text{r.m.s}} &= \sqrt{\langle v^2\rangle} = \sqrt{\frac{3kT}{m}} \end{aligned} \tag{9.2.9}$$

$v_{\text{r.m.s.}}$ is the root-mean-square velocity of the molecule.

9.2.2 Ideal gas in an external gravitational field

Complicate the problem a little by taking into account the influence of the gravitational field on the molecules of the gas. Consider a gas in a cylindrical container of height H. Because of its potential energy, the total energy of a molecule in the container at height $z \le H$ is

$$E = \frac{p^2}{2m} + mgz \tag{9.2.10}$$

where the last term on the right hand side is its potential energy if $z << R$ the radius of the earth. Boltzmann's distribution then gives the probability of finding a molecule with this energy:

$$P(E) = \text{const.} \times e^{-\beta(\frac{p^2}{2m}+mgz)} \tag{9.2.11}$$

As a simple exercise, shows that the normalized distribution is

$$P(E) = \frac{mgh_o^3}{(2\pi mkT)^{3/2}A} e^{-\beta(\frac{p^2}{2m}+mgz)} \tag{9.2.12}$$

where A is the cross-sectional area of the cylinder and, by integrating over all possible momentum values as well as over x and y, that the probability of finding a molecule at height z is

$$P(z) = \frac{mg}{kT} e^{-\frac{mgz}{kT}} \tag{9.2.13}$$

9.2.3 Spin $\frac{1}{2}$ Paramagnetism

Consider our previous example of a system of charged, weakly interacting spin $\frac{1}{2}$ particles, but suppose that the system, instead of being isolated, is kept in contact with a heat reservoir at a fixed temperature, T. Imagine that the system is placed in an external, constant, magnetic field, B, which defines, say, the z direction.

The "particles" could be charged atoms, for example, whose total angular momentum is due to an extra electron or due to lack of one electron in its outermost shell. Physically we expect the following: Due to the presence of the field, the atoms will tend to align themselves with the field in order to reduce the total energy of the system (recall that each atom contributes

$$E = -\vec{\mu} \cdot \vec{B} \tag{9.2.14}$$

to the total energy, where $\vec{\mu}$ is its magnetic moment, $\vec{\mu} = g\hbar e\vec{s}/2m$). This tendency to alignment corresponds to an attempt by the system to develop "order" within itself in the presence of an external field. However, due to thermal energy, this alignment will not be complete in the sense that not *all* the atoms will align themselves. Thermal energy introduces disorder within the system. The degree to which alignment occurs will depend on the magnitude of the energy due to the magnetic field compared with its thermal energy.

Let μ be the magnitude of the magnetic moment, $\mu = |g\hbar e/2m|$, and let the atoms be positively charged. As we are working within the canonical ensemble, the probability of finding an atom with energy E is just given by the Boltzmann factor. Moreover, since they have spin $\frac{1}{2}$, for any atom there are two possibilities depending on the orientation of its magnetic moment: either the latter aligns itself with the field, in which case its energy is $E_- = -\mu B$, or it anti-aligns itself in which case its energy is $E_+ = +\mu B$. According to the Boltzmann distribution, the probabilities of finding a single aligned or anti-aligned atom are therefore, respectively

$$\begin{aligned} P(E_+) &= \mathcal{N} e^{-\beta\mu B} \\ P(E_-) &= \mathcal{N} e^{\beta\mu B} \end{aligned} \tag{9.2.15}$$

where $\mathcal{N}$ is the normalization,

$$\begin{aligned} \mathcal{N} &= \left(\sum_r e^{-\beta E_r}\right)^{-1} = \left(e^{-\beta\mu B} + e^{\beta\mu B}\right)^{-1} \\ &= \frac{1}{2}\operatorname{sech}(\beta\mu B) \end{aligned} \tag{9.2.16}$$

In other words, the normalized probabilities are

$$P(E_\pm) = \frac{e^{\mp\beta\mu B}}{2\cosh(\beta\mu B)} \tag{9.2.17}$$

so the average energy of each atom is

$$\begin{aligned}\langle E\rangle &= \frac{\sum_r E_r e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} \\ &= -\mu\beta B\tanh(\mu\beta B) \end{aligned}\tag{9.2.18}$$

and the average magnetic moment is

$$\begin{aligned}\langle \mu\rangle &= \frac{\mu e^{-\beta E_+} - \mu e^{-\beta E_-}}{\sum_r e^{-\beta E_r}} \\ &= \mu\tanh(\mu\beta B). \end{aligned}\tag{9.2.19}$$

Because the atoms do not interact among themselves, the average total magnetization is $\langle M\rangle = N\langle\mu\rangle = N\mu\tanh(\mu\beta B)$.

Now let us consider the behavior of the total magnetization in two limits: (a) when the thermal energy (kT) of the atoms is much larger than their energy due to the presence of the external magnetic field (μB), and (b) when kT is much less than μB.

When $kT \gg \mu B$, or $\beta\mu B \ll 1$, we expect that, due to their thermal energy there will be a high degree of randomness or lack of order in the system. In other words, not *all* the atoms will align, or anti-align themselves with the field. A measure of this lack of order is the total magnetic moment, $\langle M\rangle$. In the limit $\beta\mu B \ll 1$, $\tanh(\beta\mu B) \approx \beta\mu B$ and

$$\langle M\rangle \approx \frac{\mu^2 NB}{kT} \tag{9.2.20}$$

or the magnetic susceptibility per atom

$$\chi = \frac{1}{N}\frac{\partial\langle M\rangle}{\partial B} \approx \frac{\mu^2}{kT} \tag{9.2.21}$$

which is *Curie's* law: it is inversely proportional to the temperature. On the other hand, if $\beta\mu B \gg 1$, the randomness in the orientation of spins induced by the thermal energy of the atoms is small compared with the order induced by the magnetic field and we expect that all the atoms will be aligned in such a way as to minimize the total magnetic energy of the system. Indeed, in this limit $\tanh(\mu\beta B) \approx 1$ giving

$$\langle M\rangle \approx N\mu \tag{9.2.22}$$

What we have just described is the phenomenon of "paramagnetism". Paramagnetism is defined as the bulk magnetization of a material, upon application of an external magnetic field, which appears as a consequence of its atoms possessing a net angular momentum (in this special case, spin $\frac{1}{2}$) from unpaired electrons.

9.2.4 Harmonic oscillators

Consider a system of N harmonic oscillators, all of the same natural frequency, in contact with a heat reservoir at a fixed temperature T. The probability of finding a single oscillator with energy $E = (n + \frac{1}{2})\hbar\omega$ is evidently

$$P(E) = \mathcal{N} e^{-\beta(n+\frac{1}{2})\hbar\omega} \tag{9.2.23}$$

where $\mathcal{N}$ is, as usual, the normalization. Of course, the probability of finding *any* number of quanta in the oscillator is simply unity, and this determines the normalization according to

$$\mathcal{N} e^{-\beta\hbar\omega/2} \sum_{n=0}^{\infty} e^{-\beta n\hbar\omega} = 1 \tag{9.2.24}$$

The sum is just an infinite geometric series in $e^{-\beta\hbar\omega}$, so it can be directly evaluated to find,

$$\mathcal{N} = 2\sinh\left[\frac{\beta\hbar\omega}{2}\right] \tag{9.2.25}$$

Show, then, that the average energy per oscillator is

$$\begin{aligned} \langle E \rangle &= \mathcal{N} \sum_{n=0}^{\infty} \left(n + \frac{1}{2}\right) \hbar\omega e^{-\beta(n+\frac{1}{2})\hbar\omega} \\ &= \frac{1}{2}\hbar\omega \coth\left(\frac{\beta\hbar\omega}{2}\right) \end{aligned} \tag{9.2.26}$$

If the energy of the ground state, $\hbar\omega/2$, is ignored in the calculation of the mean energy, one obtains the formula used by Planck in his treatment of black-body radiation. The entire system, consisting of N weakly interacting oscillators will obviously have energy $= N\langle E \rangle$. It is instructive to compare the results for all the systems above with their analogues in the microcanonical ensemble.

9.3 The Partition Function

A more direct way to perform calculations in the canonical ensemble uses the partition function. If the energy levels are all discrete, let r label the microstates then the partition function is defined by the sum over all configurations

$$Z(\beta, \vec{X}) = \sum_r e^{-\beta E_r} \tag{9.3.1}$$

or by the sum over all microstates with *distinct energies*

$$Z(\beta,\vec{X}) = \sum_k g_k e^{-\beta E_k} \tag{9.3.2}$$

where we have used "k" to indicate all states of distinct energies and g_k labels the degeneracy of the state k. The partition function for a classical system with continuous energy levels would be

$$Z(\beta,\vec{X}) = \int \prod_i d\vec{r}_i d\vec{p}_i \rho(\vec{r}_i,\vec{p}_i)$$

The partition function does not depend explicitly on the energy but on the temperature. It plays a role analogous to that of the number of microstates in the microcanonical ensemble and, as we will now show, all the thermodynamic functions can be expressed directly it terms of it and its derivatives, so that a knowledge of the partition function is sufficient for a complete treatment of systems in the canonical ensemble. Simple algebra should easily convince you of the following expressions:

- The average energy is

$$\langle E\rangle = -\frac{\partial}{\partial\beta}\ln Z = \frac{\sum_r g_r E_r e^{-\beta E_r}}{\sum_r g_r e^{-\beta E_r}} \tag{9.3.3}$$

- The mean square energy is

$$\langle E^2\rangle = \frac{1}{Z}\frac{\partial^2 Z}{\partial\beta^2} = \frac{\sum_r g_r E_r^2 e^{-\beta E_r}}{\sum_r g_r e^{-\beta E_r}} \tag{9.3.4}$$

- the energy dispersion is

$$\Delta E^2 = \frac{\partial^2 \ln Z}{\partial\beta^2} = \langle E^2\rangle - \langle E\rangle^2, \tag{9.3.5}$$

  and,

- The generalized forces are

$$\langle F_\alpha\rangle = \frac{1}{\beta}\frac{\partial \ln Z}{\partial X_\alpha} = -\frac{\sum_r g_r \frac{\partial E_r}{\partial X_\alpha} e^{-\beta E_r}}{\sum_r g_r e^{-\beta E_r}} \tag{9.3.6}$$

- From these we also derive an expression for the entropy as follows: consider an isothermal quasi-static process in which the partition function undergoes a change dZ. Notice that $Z = Z(\beta, X_\alpha)$ and one has

$$d\ln Z \quad = \quad \frac{\partial \ln Z}{\partial\beta}d\beta + \sum_\alpha \frac{\partial \ln Z}{\partial X_\alpha}dX_\alpha$$

$$\begin{aligned} &= -\langle E\rangle d\beta + \beta\sum_\alpha \langle F_\alpha\rangle dX_\alpha \\ &= -d(\langle E\rangle\beta) + \beta d\langle E\rangle + \beta\sum_\alpha đW_\alpha \\ \Rightarrow\ \beta^{-1}d(\ln Z + \beta\langle E\rangle) &= d\langle E\rangle + \sum_\alpha đW_\alpha \qquad (9.3.7)\end{aligned}$$

which, comparing the last expression with the first law of thermodynamics, means that the left hand side must be associated with the entropy according to

$$\begin{aligned} TdS &= \beta^{-1}d(\ln Z + \beta\langle E\rangle) \\ \Rightarrow\ S &= k(\ln Z + \beta\langle E\rangle) \qquad (9.3.8)\end{aligned}$$

We have seen that the Gibbs definition of the entropy

$$S_G = -k\sum_r P_r \ln P_r \qquad (9.3.9)$$

reduces in the microcanonical ensemble to the original Boltzmann definition. To see that it reduces to the definition we had in (3.38), which followed from the first law of thermodynamics, simply notice that in the canonical ensemble the normalized probability has the form

$$\begin{aligned} P_r &= \frac{e^{-\beta E_r}}{\sum_s e^{-\beta E_s}} = \frac{e^{-\beta E_r}}{Z} \\ \Rightarrow\ \ln P_r &= -\beta E_r - \ln Z \qquad (9.3.10)\end{aligned}$$

which, when substituted into Gibbs' expression, gives

$$\begin{aligned} S_G &= -k\sum_r \frac{e^{-\beta E_r}}{Z}\left[-\beta E_r - \ln Z\right] \\ &= k\left[\ln Z + \beta\langle E\rangle\right] = S \qquad (9.3.11)\end{aligned}$$

as we expected. We see that indeed the Gibbs definition is the more general, under appropriate conditions giving the expressions in the microcanonical ensemble and in the canonical ensemble.

The other thermodynamic functions also have expressions in terms of Z and its derivatives:

- The enthalpy is

$$H = \langle E\rangle + pV = -\frac{1}{\beta}\left(\beta\frac{\partial \ln Z}{\partial\beta} - V\frac{\partial \ln Z}{\partial V}\right), \qquad (9.3.12)$$

- The Helmholtz free energy is

$$F = \langle E \rangle - TS = -\frac{1}{\beta} \ln Z, \tag{9.3.13}$$

  and

- The Gibbs free energy (or thermodynamic potential) is

$$G = \langle E \rangle - TS + pV = -\frac{1}{\beta} \left(\ln Z + V \frac{\partial \ln Z}{\partial V} \right) \tag{9.3.14}$$

The partition functions for the systems we treated earlier can be written down directly. They are just the inverses of the probability normalizations we have already calculated:

- for a single molecule in a classical ideal gas:

$$Z = V \left(\frac{2\pi m}{\beta h_o^2} \right)^{3/2} \tag{9.3.15}$$

- for a single spin $\frac{1}{2}$ particle in an external magnetic field:

$$Z = 2 \cosh(\beta \mu B) \tag{9.3.16}$$

  and

- for a single harmonic oscillator:

$$Z = \frac{1}{2 \sinh(\beta \hbar \omega / 2)} \tag{9.3.17}$$

9.4 Properties of the Partition Function

9.4.1 Weakly interacting sub-systems.

Consider a system C consisting of two parts, A and B, ($C = A + B$), which do not interact, or interact weakly but are in contact with the same heat reservoir at inverse temperature β. The microstates of the combined system, C, will be labelled by the pair (r, s) where r is a state of A and s a state of B. Let A be in state r and B in state s, so that the energy of C is just $E_{rs} = E_r + E_s$ as there is no interaction between A and B. The partition function for C is therefore

$$Z_C = \sum_{r,s} e^{-\beta(E_r + E_s)} = \sum_{r,s} e^{-\beta E_r} e^{-\beta E_s} \tag{9.4.1}$$

Now, since r and s are independent summations, we can write the above as

$$Z_C = \sum_r e^{-\beta E_r} \sum_s e^{-\beta E_s} = Z_A Z_B \tag{9.4.2}$$

By induction we may generalize the above result to a system, C, consisting of N sub-systems none of which interact. We will have

$$Z_C = \prod_{j=1}^{N} Z_j \tag{9.4.3}$$

which is the powerful result that the partition function of a system consisting of n non-interacting sub-systems is just the product over all partition functions of the individual sub-systems. It is easy to see now that the average energy is extensive, *i.e.,* the average energy of C will just be the sum over the average energies of each sub-system,

$$\langle E\rangle = -\frac{\partial \ln Z}{\partial \beta} = -\frac{\partial}{\partial \beta} \sum_{j=1}^{N} \ln Z_j = \sum_{j=1}^{N} \langle E_j\rangle \tag{9.4.4}$$

where we have made use of the properties of the logarithm. Indeed, because the logarithm of a product is the sum of logarithms, we see immediately that the following variables are extensive: the mean energy, the energy dispersion, the entropy and all the thermodynamic potentials.

The systems we have studied so far consisted of atoms or molecules which did not interact with each other. Each atom or molecule can then be thought of as a non-interacting sub-system and the partition functions for the entire system written as the product over the partition functions for each atom or molecule. Thus, for example, the partition function

- for a classical ideal gas of N particles is

$$Z_N = V^N \left(\frac{2\pi m}{\beta h_o^2}\right)^{3N/2} \tag{9.4.5}$$

- for the system of N spin $\frac{1}{2}$ particles in an external magnetic field is

$$Z_N = 2^N \cosh^N(\beta\mu B) \tag{9.4.6}$$

  and

- for the system of N oscillators is

$$Z_N = \frac{1}{2^N \sinh^N(\beta\hbar\omega/2)} \tag{9.4.7}$$

With these expressions it is possible to compute all the thermodynamic quantities of interest[1]

9.4.2 Change of zero-point energy.

What happens to the partition function if the zero of energy is changed? This will only change the energy of each state by a constant and, as you know, the only differences in energy have physical consequences. Suppose that, by changing the zero of energy, the energy of each state is changed by the addition of a constant ϵ_o i.e.,

$$E_r \to E_r' = E_r + \epsilon_o \tag{9.4.8}$$

The partition function changes accordingly:

$$Z' = \sum_r e^{-\beta E_r'} = e^{-\beta\epsilon_o} \sum_r e^{-\beta E_r} = e^{-\beta\epsilon_o} Z \tag{9.4.9}$$

Thus,

$$\ln Z' = \ln Z - \beta\epsilon_o \tag{9.4.10}$$

and

$$\langle E' \rangle = -\frac{\partial \ln Z'}{\partial \beta} = \langle E \rangle + \epsilon_o \tag{9.4.11}$$

that is, the average energy is just modified by the addition of the same constant, as one would expect. In the same way, it is easy to see that

$$\begin{aligned}
&\Delta E' = \frac{\partial^2 \ln Z'}{\partial \beta^2} = \Delta E \\
&\langle F_\alpha' \rangle = \frac{1}{\beta}\frac{\partial \ln Z'}{\partial X_\alpha} = \langle F_\alpha \rangle \\
&S' = k(\ln Z' + \beta\langle E' \rangle) = k(\ln Z - \beta\epsilon_o + \beta\langle E \rangle + \beta\epsilon_o) = S \\
&H' = H + \epsilon_o, \quad F' = F + \epsilon_o, \quad G' = G + \epsilon_o
\end{aligned} \tag{9.4.12}$$

9.4.3 The Equipartition Theorem

The Equipartition Theorem can be a useful way to quickly write down the total average kinetic and potential energies for a system at a given temperature. In its simplest form, it states that the mean value of each *independent, quadratic term* in the classical mechanical

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[1] Problem: In each case, compute the entropy and the thermodynamic potentials. Compute also the energy dispersion and examine its behavior for large N.

energy is $\frac{1}{2}kT$. The proof of this form of the theorem is straightforward. The classical mechanical energy of any system is given as a function of phase space $E = E(\vec{r}_i, \vec{p}_i)$ and, generally, the dependence on momenta and coordinates separates into a "kinetic" piece, K and a "potential" piece, V,

$$E = K(p_i) + V(q_i). \tag{9.4.13}$$

The kinetic energy is generally quadratic in momenta whereas the potential energy depends only on the relative positions of the constituents. Since K is almost always quadratic in the momenta,

$$K(p_i) = \sum_i b_i p_i^2 \overset{\text{def}}{=} \sum_i K_i \tag{9.4.14}$$

where the sum is over all the degrees of freedom, let us find the its mean value. Using the properties of the exponential function this can be written as by

$$\langle K_j \rangle = \frac{\int \prod_i dp_i K_j e^{-\beta b_i p_i^2} \times \int \prod_i dq_i e^{-\beta V(q_i)}}{\int \prod_i dp_i e^{-\beta b_i p_i^2} \times \int \prod_i dq_i e^{-\beta V(q_i)}} \tag{9.4.15}$$

and therefore, after canceling common factors we find

$$\langle K_j \rangle = \frac{\int dp_j (b_j p_j^2) e^{-\beta b_j p_j^2}}{\int dp_j e^{-\beta b_j p_j^2}} \equiv \frac{1}{2}kT, \tag{9.4.16}$$

which is the equipartition theorem for the kinetic energy. Likewise, a potential energy function that is a sum of quadratic terms in the configuration space variables would yield $\frac{1}{2}kT$ for each independent quadratic term.

We now prove a more general form of the equipartition theorem, which can be stated as follows: for any physical system with Hamiltonian energy function, $E = E(\vec{r}_i, \vec{p}_i)$, the following holds under conditions that will become apparent later in the proof:

$$\begin{aligned} \langle q_i \frac{\partial E}{\partial q_j} \rangle &= \delta_{ij} kT \\ \langle p_i \frac{\partial E}{\partial p_j} \rangle &= \delta_{ij} kT \end{aligned} \tag{9.4.17}$$

Let's prove the first form. Consider the fact that

$$\int \prod_l dp_l dq_l \left[q_i \frac{\partial E}{\partial q_j} \right] e^{-\beta E} = \frac{1}{\beta} \int \prod_l dp_l \prod_{m \neq j} dq_m \int dq_j \left\{ -\frac{\partial}{\partial q_j} \left[q_i e^{-\beta E} \right] + \delta_{ij} e^{-\beta E} \right\} \tag{9.4.18}$$

and concentrate on the integral over q_j:

$$\int_a^b dq_j \left\{ -\frac{\partial}{\partial q_j} \left[q_i e^{-\beta E} \right] + \delta_{ij} e^{-\beta E} \right\} = -\left[e^{-\beta E} q_i \right]_a^b + \delta_{ij} \int_a^b dq_j e^{-\beta E} \tag{9.4.19}$$

where we have explicitly introduced the integration limits. Now suppose that the energy function, $E(\vec{r}_i, \vec{p}_i)$, becomes unboundedly large at the limits a and b of the integration (this would be the case, for example, if a and b are $\mp\infty$ respectively and $E \sim q_j^2$ as we considered for the simplified form above). Then the first term on the right hand side vanishes and we find

$$\int \prod_l dp_l dq_l \left[q_i \frac{\partial E}{\partial q_j} \right] e^{-\beta E} = \frac{\delta_{ij}}{\beta} \int_a^b dq_j e^{-\beta E} \tag{9.4.20}$$

from which it follows that

$$\langle q_i \frac{\partial E}{\partial q_j} \rangle = \frac{\int \prod_l dp_l dq_l \left[q_i \frac{\partial E}{\partial q_j} \right] e^{-\beta E}}{\int \prod_l dp_l dq_l e^{-\beta E}} = \frac{\delta_{ij}}{\beta} = \delta_{ij} kT \tag{9.4.21}$$

It should be obvious that the second form would hold under the same conditions on p_i. Similarly, one can prove

$$\langle p_i \frac{\partial E}{\partial q_j} \rangle = 0 = \langle q_i \frac{\partial E}{\partial p_j} \rangle \tag{9.4.22}$$

and, moreover, it follows from the Hamilton equations of motion that

$$\langle q_i \dot{p}_j \rangle = -\langle p_i \dot{q}_j \rangle = -\delta_{ij} kT \tag{9.4.23}$$

Below are some examples of the use of this generalized form.

According to (9.4.23),

$$\langle q_i F_j \rangle = -\delta_{ij} kT \tag{9.4.24}$$

so let us consider the ideal gas, for which the energy function is just $E = \sum_l p_l^2/2m$. Let i and j represent the coordinate directions for a single particle, then according to (9.4.23) we will have

$$\langle \vec{q} \cdot \vec{F} \rangle = -3kT \tag{9.4.25}$$

where $\vec{F}$ is the force on this particle. The force on the particle is exerted by the wall, so by Newton's third law, the force on the wall due to the single particle will be $-\vec{F}$. With N particles, we could write

$$\sum_{n=1}^{N} \langle \vec{q}_n \cdot \vec{F}_{n,\text{wall}} \rangle = 3NkT. \tag{9.4.26}$$

In the continuum limit,

$$p \oint_S \vec{q} \cdot d\vec{S} = 3NkT, \tag{9.4.27}$$

where we have expressed the force on the wall in terms of the pressure. In this limit, using Gauss' theorem,

$$p \oint_S \vec{q} \cdot d\vec{S} = p \int_V (\vec{\nabla} \cdot \vec{q}) dV = 3pV \tag{9.4.28}$$

we derive the ideal gas law, $pV = NkT$.

Consider another example in which the Hamiltonian separates into a kinetic piece depending only on the momenta and a potential piece of the form $V(q) = \sum_l a_l q_l^s$, where s is any positive real number. According to (9.4.17),

$$\sum_i \langle q_i \frac{\partial V}{\partial q_i} \rangle = s\langle V \rangle = fkT \tag{9.4.29}$$

where f is the number of degrees of freedom. Thus $\langle V \rangle = (f/s)kT$, which generalizes the formula for harmonic oscillators ($s = 2$).

When applying the equipartition theorem it should be remembered that the theorem is valid only in classical statistical mechanics. Classical statistical mechanics is an excellent approximation so long as the separation between successive energy levels is small compared with the thermal energy or, more precisely, when $\Delta E \ll kT$. In this case the relevant "quantum effect", namely the separation between the energy levels, can be ignored. In most quantum systems the spacing between successive energy levels decreases with increasing energy and the equipartition theorem becomes a good approximation at high temperatures. On the other hand, the spacing between the energy levels lying close to the ground state can be large and equipartition will fail at low temperatures as a consequence.

9.4.4 Galilean Boosts

Until now we have considered only systems that are at rest relative to the observer. One should also be able to consider systems that are in motion with the observer. Of course we already have a description of such systems in the rest frame, so it remains to transform this description to arbitrary frames related to the rest frame by Galilean boosts.

9.5 The Grand Canonical Ensemble

In the canonical ensemble, if we relax the condition that no matter is exchanged between the system and its reservoir,we obtain the grand canonical ensemble. In this ensemble, therefore, the systems are all in thermal equilibrium with a heat reservoir at some fixed temperature, T, but they are also able to exchange particles with this reservoir. Such systems are said to be **open**.

Assume that the system, A, is in thermal equilibrium with a reservoir, R, and that together they form an isolated system with total energy $E^{(0)}$ and total number of particles $N^{(0)}$. Both $E^{(0)}$ and $N^{(0)}$ are fixed. Assume also that A is tiny compared to R. Then we might ask: what is the probability of finding A in a given state, r, with energy E_r and containing N_r particles? If A has energy E,

$$\Omega(E, N) = \Omega_A(E, N)\Omega_R(E^{(0)} - E, N^{(0)} - N) \tag{9.5.1}$$

In the ensemble we are considering, each system is in contact with a heat reservoir at a fixed temperature, T, and each is able to exchange particles with the reservoir. This implies that the probability of finding a system obeying these conditions is

$$\begin{aligned} P(E) &= C\Omega_A(E,N)\Omega_R(E^{(0)}-E,N^{(0)}-N) \\ \ln P(E) &= \ln C + \ln\Omega_A(E,N) + \ln\Omega_R(E^{(0)}-E,N^{(0)}-N) \\ &\approx \ln C + \ln\Omega_A(E,N) + \ln\Omega_R(E^{(0)},N^{(0)}) \\ &+ E\frac{\partial \ln\Omega_R(E',N')}{\partial E'}|_{E^{(0)},N^{(0)}} - N\frac{\partial \ln\Omega_R(E',N')}{\partial N'}|_{E^{(0)},N^{(0)}} + \ldots, \end{aligned} \tag{9.5.2}$$

where we have put $N' = N^{(0)} - N$ and $E' = E^{(0)} - E$. Again,

$$\beta = \frac{\partial \ln\Omega_R(E',N')}{\partial E'}|_{E^{(0)},N^{(0)}} \tag{9.5.3}$$

is the temperature of the reservoir and we shall call

$$\mu = -\frac{1}{\beta}\frac{\partial \ln\Omega_R(E',N')}{\partial N'}|_{E^{(0)},N^{(0)}} \tag{9.5.4}$$

the "chemical potential" of the reservoir. Then

$$P(E,N) = \overline{C}\Omega_A(E,N)e^{-\beta(E-\mu N)} \tag{9.5.5}$$

is the required probability. $\Omega(E,N)$ is the number of states available to A at a fixed E and N, the degeneracy. Therefore, the probability of finding A in *one* of the allowed states is just

$$P(E,N) = \overline{C}e^{-\beta(E-\mu N)} \tag{9.5.6}$$

It is called the grand canonical distribution.

Systems belonging to the grand canonical ensemble have variable contents. This occurs often in many physically interesting situations. For instance, consider the diffusion of molecules across a semi-permeable membrane that separates two containers, A and B. We can adjust the intermolecular separation of the partition is such that only molecules of one type may pass through. If we wish to speak of A and B individually as thermodynamic systems, we must take into account the fact that their contents vary as one of the gases diffuses across the membrane. Another situation in which we may wish to treat systems with varying contents as thermodynamic systems is when we consider changes of phase. Consider the melting of ice or the boiling of water. In either of these processes, the substance (ice or water) is changing phase from solid to liquid or liquid to gas. If we want to treat the ice and water (or water and water vapor) as separate thermodynamic systems we must account for the fact that the amount of matter contained in each system is continuously changing. Other examples of systems with varying contents include a mixture of chemical reagents, for example H_2 and O_2 which will react according to

$$2\mathrm{H}_2 + \mathrm{O}_2 \Leftrightarrow 2\mathrm{H}_2\mathrm{O} \tag{9.5.7}$$

so that the numbers of hydrogen, oxygen and water molecules are constantly changing, or a plasma in which the proportion of ionized and unionized atoms is continuously changing, One of the more interesting applications that we shall encounter in these notes is in phenomena associated with quantum statistics.

The partition function is therefore

$$\Xi = \sum_r e^{-\beta E_r - \alpha N_r} = \sum_r e^{-\beta(E_r - \mu N_r)} \tag{9.5.8}$$

where β and α are *independent*, α being defined by[2],

$$\alpha = \frac{\partial \ln \Omega_R(E', N')}{\partial N'}\Big|_{E^{(0)},N^{(0)}} \tag{9.5.9}$$

This is the grand partition function and the corresponding distribution

$$P_r = \frac{1}{\Xi} e^{-\beta E_r - \alpha N_r} \tag{9.5.10}$$

is the grand canonical or Gibbs distribution. Let us now study the resulting thermodynamics.

9.6 Thermodynamics in the Grand Canonical Ensemble

Differentiating the partition function in (9.5.8), we have

$$\begin{aligned} \langle E \rangle &= -\frac{\partial \ln \Xi}{\partial \beta} \\ \langle N \rangle &= \frac{1}{\beta}\frac{\partial \ln \Xi}{\partial \mu} \end{aligned} \tag{9.6.1}$$

and we define the generalized forces, as usual,

$$\langle F_\alpha \rangle = \frac{1}{\beta}\frac{\partial \ln \Xi}{\partial X_\alpha} \tag{9.6.2}$$

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[2] As long as derivatives are being taken, it is convenient to write it in terms of the *independent* quantities α and β to ensure that derivatives are taken consistently.

Then, as $\Xi = \Xi(\beta, \mu, X_\alpha)$,

$$\begin{aligned} d\ln\Xi &= \frac{\partial \ln \Xi}{\partial \beta} d\beta + \sum_\alpha \frac{\partial \ln \Xi}{\partial X_\alpha} dX_\alpha + \frac{\partial \ln \Xi}{\partial \mu} d\mu \\ &= -\langle E\rangle d\beta + \beta \sum_\alpha \langle F_\alpha \rangle dX_\alpha - \beta \langle N \rangle d\mu \end{aligned} \tag{9.6.3}$$

or, noting β is held constant that in the last term,

$$d\left[\ln\Xi + \beta\langle E\rangle - \beta\mu\langle N\rangle\right] = \beta d\langle E\rangle - \mu\beta d\langle N\rangle + \beta \sum_\alpha \langle F\rangle dX_\alpha$$

$$TdS = d\langle E\rangle + \sum_\alpha \langle F_\alpha\rangle dX_\alpha - \mu d\langle N\rangle \tag{9.6.4}$$

where the entropy is now

$$S = k\left[\ln\Xi + \beta\langle E\rangle - \beta\mu\langle N\rangle\right] \tag{9.6.5}$$

Thus we have the following thermodynamic relations,

$$\begin{aligned} \left(\frac{\partial S}{\partial \langle E\rangle}\right)_{X_\alpha, \langle N\rangle} &= \frac{1}{T} \\ \left(\frac{\partial S}{\partial X_\alpha}\right)_{\langle E\rangle, \langle N\rangle} &= \frac{\langle F_\alpha\rangle}{T} \\ \left(\frac{\partial S}{\partial \langle N\rangle}\right)_{\langle E\rangle, X_\alpha} &= -\frac{\mu}{T}. \end{aligned} \tag{9.6.6}$$

9.7 Fluctuations

In the canonical ensemble, the fluctuations in the average energy are given by

$$\Delta E^2 = \frac{\partial^2 \ln Z}{\partial \beta^2} = \frac{\partial \langle E\rangle}{\partial \beta} = kT^2 C_V \tag{9.7.1}$$

where C_V is the heat capacity at constant volume. If we let c_V and ε be respectively the heat capacity per particle and the average energy per particle, we can put this expression in the form

$$\frac{\Delta E}{\langle E\rangle} = \sqrt{\frac{kc_V}{N}} \frac{T}{\varepsilon} \tag{9.7.2}$$

which displays the same dependence on $1/\sqrt{N}$ that we discovered in (8.5.6) and shows that the distribution in the canonical ensemble is very sharply peaked about the average energy for large N. Therefore in the thermodynamic limit the canonical ensemble *is equivalent to the microcanonical ensemble.*

The particle number fluctuations in the Gibbs ensemble are obtained similarly. One easily sees that

$$\langle N^2 \rangle = \frac{1}{\beta^2} \frac{1}{\Xi} \frac{\partial^2 \Xi}{\partial \mu^2} \tag{9.7.3}$$

and therefore

$$\Delta N^2 = \frac{1}{\beta^2} \frac{\partial^2 \ln \Xi}{\partial \mu^2} = \frac{1}{\beta} \frac{\partial \langle N \rangle}{\partial \mu} \tag{9.7.4}$$

Now note that the Grand Potential, $\Phi_F = \langle E \rangle - TS + \mu \langle N \rangle$ admits a simple expression in terms of the grand partition function:[3]

$$\Phi_F = -\frac{1}{\beta} \ln \Xi. \tag{9.7.5}$$

Specializing to fluids and using (5.5.2), one finds that $-pV = -\frac{1}{\beta} \ln \Xi$. Then, taking a derivative with respect to μ holding β and V fixed we get

$$\langle N \rangle = V \frac{\partial p}{\partial \mu} \Rightarrow \left(\frac{\partial \langle N \rangle}{\partial \mu} \right)_{V,T} = V \frac{\partial^2 p}{\partial \mu^2} \tag{9.7.6}$$

and therefore,

$$\Delta N^2 = \frac{V}{\beta} \frac{\partial^2 p}{\partial \mu^2}. \tag{9.7.7}$$

We want to re-express the second derivative above in terms of some recognizable fluid properties. Now again using (5.5.2)

$$d\Phi_F = -pdV - SdT - Nd\mu = -pdV - Vdp \tag{9.7.8}$$

and dividing by N, we find

$$d\mu = -sdT - vdp \tag{9.7.9}$$

where s and v are respectively the entropy and volume per particle. The chemical potential is therefore rightly viewed as a function of (T, p). Furthermore,

$$v = -\left(\frac{\partial \mu}{\partial p} \right)_T \tag{9.7.10}$$

shows that v is also a function of (T, p). The number fluctuations can be written in terms of the specific volume, v,

$$\Delta N^2 = -\frac{V}{\beta v^2} \left(\frac{\partial v}{\partial \mu} \right)_T = -\frac{V}{\beta v^2} \left(\frac{\partial v}{\partial p} \right)_T \left(\frac{\partial p}{\partial \mu} \right)_T = -\frac{V}{\beta v^3} \left(\frac{\partial v}{\partial p} \right)_T \tag{9.7.11}$$

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[3] Problem: Show this.

and rewritten in terms of the isothermal compressibility of the fluid

$$\kappa = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T, \tag{9.7.12}$$

finally giving

$$\frac{\Delta N}{\langle N\rangle} = \sqrt{\frac{kT\kappa}{Nv}}. \tag{9.7.13}$$

The result shows that, like the energy fluctuations in the canonical ensemble, the fluctuations in the particle number also drop off as $1/\sqrt{N}$. We conclude that in the thermodynamic limit the grand canonical ensemble is equivalent to the microcanonical ensemble. This leads to the question of which ensemble is appropriate for a given problem. The answer is that so long as we work in the limit of large N the choice is to be based entirely on convenience and computability.

Chapter 10

Further Developments

We are now ready to study some simple applications of the canonical ensemble, but first let us gather together all the formulæ that we will find useful in a table:

Canonical Ensemble

Partition function, Z:	$Z = \sum_r e^{-\beta E_r}$
Mean Energy, $\langle E\rangle$:	$\langle E\rangle = -\frac{\partial \ln Z}{\partial \beta}$
Mean square energy, $\langle E^2\rangle$:	$\langle E^2\rangle = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2}$
Energy dispersion, ΔE:	$(\Delta E)^2 = \frac{\partial^2 \ln Z}{\partial \beta^2}$
Generalized Force, $\langle F_\alpha\rangle$:	$\langle F_\alpha\rangle = \frac{1}{\beta}\frac{\partial \ln Z}{\partial X_\alpha}$
Entropy, S:	$S = k\left[\ln Z + \beta\langle E\rangle\right]$
Enthalpy, H:	$H = -\frac{\partial \ln Z}{\partial \beta} + \frac{1}{\beta}\sum_\alpha \frac{\partial \ln Z}{\partial X_\alpha} X_\alpha$
Free Energy (Helmholtz), F:	$F = -\frac{1}{\beta}\ln Z$
Gibbs potential, G:	$G = -\frac{1}{\beta}\ln Z + \frac{1}{\beta}\sum_\alpha \frac{\partial \ln Z}{\partial X_\alpha} X_\alpha$

Gibbs Ensemble

Partition function, Ξ:	$\Xi = \sum_r e^{-\beta(E_r - \mu N_r}$
Mean Energy, $\langle E\rangle$:	$\langle E\rangle = -\frac{\partial \ln \Xi}{\partial \beta}$
Mean square energy, $\langle E^2\rangle$:	$\langle E^2\rangle = \frac{1}{\Xi}\frac{\partial^2 \Xi}{\partial \beta^2}$
Energy dispersion, ΔE:	$(\Delta E)^2 = \frac{\partial^2 \ln \Xi}{\partial \beta^2}$
Generalized Force, $\langle F_\alpha\rangle$:	$\langle F_\alpha\rangle = \frac{1}{\beta}\frac{\partial \ln \Xi}{\partial X_\alpha}$
Entropy, S:	$S = k\left[\ln \Xi + \beta\langle E\rangle - \beta\mu\langle N\rangle\right]$
Enthalpy, Φ_H:	$\Phi_H = -\frac{\partial \ln \Xi}{\partial \beta} + \frac{1}{\beta}\sum_\alpha \frac{\partial \ln \Xi}{\partial X_\alpha} X_\alpha - \frac{\mu}{\beta}\frac{\partial \ln \Xi}{\partial \mu}$
Free Energy (Helmholtz), Φ_F:	$\Phi_F = -\frac{1}{\beta}\ln \Xi$
Gibbs potential, Φ_G:	$\Phi_G = -\frac{1}{\beta}\ln \Xi + \frac{1}{\beta}\sum_\alpha \frac{\partial \ln \Xi}{\partial X_\alpha} X_\alpha$

10.1 The Gibbs Paradox

In the previous chapter, we had determined the partition function for the classical ideal gas of N particles,

$$Z_N = V^N \left(\frac{2\pi m}{h_o^2 \beta}\right)^{3N/2} \tag{10.1.1}$$

from which one computes the entropy of the ideal gas as follows:

$$\begin{aligned}
\ln Z_N &= N\left[\ln V + \frac{3}{2}\ln\left(\frac{2\pi m}{h_o^2\beta}\right)\right] \\
\langle E\rangle &= -\frac{\partial \ln Z_N}{\partial\beta} = \frac{3N}{2\beta} = \frac{3}{2}NkT \\
S &= k\left[\ln Z_N + \beta\langle E\rangle\right] = kN\left[\ln V + \frac{3}{2}\ln\left(\frac{2\pi m}{h_o^2\beta}\right) + \frac{3}{2}\right] \\
&= kN\left[\ln V + \frac{3}{2}\ln T + \sigma\right], \sigma = \frac{3}{2}\ln\left(\frac{2\pi m k}{h_o^2}\right) + \frac{3}{2}
\end{aligned} \tag{10.1.2}$$

Unfortunately, the above expression for the entropy suffers from the obvious problem that it does not possess the limit required by the third law of Thermodynamics. On the contrary we find $\lim_{T\to 0} S(T)$ diverges, which is a good indicator that we need to go beyond the classical approximation of an ideal gas and look to the quantum theory to correct this problem. At low temperatures this becomes important because the molecules are moving "slowly" so their momentum is low and therefore their de-Broglie wave-lengths can get larger than the average spacing between them, implying that at low temperatures quantum interference of the wave-functions will play an important role. Still, at high temperatures, we expect the classical theory to yield a very good approximation because the molecules have large average momenta and small wavelengths and interference of the particle wave-functions can be ignored.

For an ideal gas of N molecules in a volume V the condition for the validity of the classical approximation is given in (6.4.3)

$$\left(\frac{kT}{p}\right)^{1/3} \gg \frac{h}{\sqrt{3mkT}}. \tag{10.1.3}$$

Notice what an important role the molecular mass plays: lighter particles are less likely to satisfy the condition at a given temperature and pressure. Consider, for example, Hydrogen at room STP. We have $T = 300°\text{K}$, $\langle p\rangle = 1.013\times 10^5\ \text{N/m}^2$ and $m_{H_2} = 2m_p \approx 3.34\times 10^{-27}$ kg, which gives

$$\left(\frac{kT}{p}\right)^{1/3} \approx 3.4\times 10^{-9}\text{m}$$

$$\frac{h}{\sqrt{3mkT}} \approx 0.1 \times 10^{-9}\text{m} \tag{10.1.4}$$

so the condition for the validity of the classical approximation is met by molecular Hydrogen at STP. The situation changes for a gas of free electrons, again at STP. The relevant difference is that the mass of an electron, $m_e = 9 \times 10^{-31}$ kg, is about four thousand times less than that of a Hydrogen molecule, which makes the right hand side of (10.1.3) about 61 times larger than it is for the Hydrogen molecule or about 1.8 times the left hand side. The classical approximation breaks down for the free electron gas at STP.

To treat a gas of identical (but distinguishable) particles quantum mechanically, we consider for convenience a cubical box of length L. The Schroedinger wavefunction of a spinless point-like particle in this box is determined by three quantum numbers (the energy quantum numbers), one for each degree of freedom

$$\psi_{n,m,r}(x,y,z) = \left(\frac{2}{L}\right)^{3/2} \sin\left(\frac{n\pi x}{L}\right) \sin\left(\frac{m\pi y}{L}\right) \sin\left(\frac{r\pi z}{L}\right) \tag{10.1.5}$$

where n, m, and $r \in \mathbb{Z}$, and the energy and momentum of the particle are respectively

$$\begin{aligned} E_{n,m,r} &= \frac{(n^2+m^2+r^2)\pi^2\hbar^2}{2mL^2} \\ p_x &= \frac{n\pi\hbar}{L}, p_y = \frac{m\pi\hbar}{L}, p_z = \frac{r\pi\hbar}{L} \end{aligned} \tag{10.1.6}$$

The partition function is therefore the sum

$$\begin{aligned} Z_N &= \left(\sum_{n,m,r} e^{-\beta(n^2+m^2+r^2)\pi^2\hbar^2/2mL^2}\right)^N \\ &= \left(\sum_n e^{-\beta n^2\pi^2\hbar^2/2mL^2}\right)^{3N} \end{aligned} \tag{10.1.7}$$

where the last step follows because all summations are the same and independent. The sums above are difficult to actually carry out, but we can see how the classical limit emerges as follows: consider, for instance,

$$\sum_n e^{-\beta n^2\pi^2\hbar^2/2mL^2} \tag{10.1.8}$$

For large values of n, the energy, $E_n = n^2\pi^2\hbar^2/2mL^2$, and momentum, $p_x = n\pi\hbar/L$, of the particle increase slowly with n. Because

$$\frac{\Delta E_n}{E_n} = \frac{E_{n+1} - E_n}{E_n} = \frac{2n+1}{n^2} \ll 1$$

$$\frac{\Delta p_n}{p_n} = \frac{1}{n} \ll 1 \tag{10.1.9}$$

at large n, successive terms in the sum in (10.1.8) differ by a very small amount. Therefore we can *approximate* the sum in (10.1.8) by grouping together all terms in the momentum range p_x and $p_x+\Delta p_x$, corresponding to the integer values n and $n+\Delta n$ where $n = Lp_x/\pi\hbar$ ($\Delta n = L\Delta p_x/\pi\hbar$). In this group,

$$\sum_{n}^{n+\Delta n} e^{-\beta n^2\pi^2\hbar^2/2mL^2} \approx e^{-\beta n^2\pi^2\hbar^2/2mL^2} \times \Delta n = e^{-\beta p_x^2/2m} \times \left(\frac{L}{\pi\hbar}\right) \Delta p_x \tag{10.1.10}$$

This sort of approximation is called a "ladder" approximation. We find

$$\begin{aligned} \sum_{n=-\infty}^{\infty} e^{-\beta E_n} &\approx \left(\frac{L}{\pi\hbar}\right) \sum_{p_x} e^{-\beta p_x^2/2m} \times \Delta p_x \\ &\to \left(\frac{L}{\pi\hbar}\right) \int_{-\infty}^{\infty} e^{-\beta p_x^2/2m} dp_x = \frac{1}{h_o} \int dx dp_x e^{-\beta p_x^2/2m}, \end{aligned} \tag{10.1.11}$$

which is simply the one dimensional partition function for a single point-like molecule in an ideal gas. Putting all the molecules together and taking three dimensions into account gives us the usual classical partition functions. This approximation is good only in the limit of large quantum numbers or very high average energies. At low energies, the "ladder" approximation fails and quantum effects will dominate. We will treat quantum gases separately.

There is yet another problem with the expressions in (10.1.2). We had shown earlier that the entropy of a gas of non-interacting particles is extensive. This means that the entropy should, for example, double if the volume of the gas doubles. But this is not true of the entropy in (10.1.2). To see this consider an ideal gas confined in a partitioned box and let the gas molecules not be able to pass through the partition. If there are $N_{L,R}$ molecules of the gas in the left and right sections respectively, and if the sections have volumes $V_{L,R}$ respectively, then the entropies of the portions of the gas in the left and right sections are

$$\begin{aligned} S_L &= kN_L \left(\ln V_L + \frac{3}{2}\ln T + \sigma_L\right) \\ S_R &= kN_R \left(\ln V_R + \frac{3}{2}\ln T + \sigma_R\right) \end{aligned} \tag{10.1.12}$$

Because the gas on each side of the partition is the same, the constants $\sigma_L = \sigma_R = \sigma$ (say). Let us arrange things so that $V_L = V_R = V/2$ and $N_L = N_R = N/2$, then

$$S_L + S_R = kN \left(\ln \frac{V}{2} + \frac{3}{2}\ln T + \sigma\right) \tag{10.1.13}$$

However, if the partition were removed isentropically the entropy would be

$$S = kN\left(\ln V + \frac{3}{2}\ln T + \sigma\right) \tag{10.1.14}$$

which differs from $S_L + S_R$, the entropy is extensive therefore S *must* be $S_L + S_R$ and our expression for S must be wrong. This is the **Gibbs paradox**. The Gibbs paradox exists at any temperature, even in the "classical" regime, unlike the problem with its zero temperature limit that we discussed in the beginning of this chapter. It arises because we have completely ignored the fact that the molecules, which can freely occupy any position within the box, are **indistinguishable**. To take indistinguishability into account, Gibbs proposed dividing the partition function by $N!$, the number of possible rearrangements of N objects between themselves, so

$$Z_{\text{correct}} = \frac{Z}{N!} \tag{10.1.15}$$

Thus, the entropy of the gas on either side of the partition is

$$\begin{aligned} S_{L,R} &= \frac{1}{2}Nk\left(\ln\frac{V}{2} + \frac{3}{2}\ln T + \sigma\right) - \frac{1}{2}Nk\ln\frac{N}{2} + \frac{1}{2}Nk \\ &= \frac{1}{2}Nk\left(\ln\frac{V}{N} + \frac{3}{2}\ln T + \sigma'\right) \\ \Rightarrow \quad S_L + S_R &= kN\left(\ln\frac{V}{N} + \frac{3}{2}\ln T + \sigma'\right) \qquad (10.1.16) \end{aligned}$$

where

$$\sigma' = \sigma + 1 = \frac{3}{2}\ln\left(\frac{2\pi mk}{h_o^2}\right) + \frac{5}{2} \tag{10.1.17}$$

Furthermore, the entropy of the gas upon removal of the partition is

$$\begin{aligned} S &= kN\left(\ln V + \frac{3}{2}\ln T + \sigma\right) - kN\ln N + kN \\ &= kN\left(\ln\frac{V}{N} + \frac{3}{2}\ln T + \sigma'\right) = S_L + S_R \qquad (10.1.18) \end{aligned}$$

which is the sum of the individual entropies as required. Indistinguishability of the elementary constituents of a thermodynamic system must be thought of as an additional property they may or may not satisfy.[1]

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[1] Problem: Argue that the paradox is resolved in the same way even when the partition is placed so that $V_{L,R}$ and $N_{L,R}$ are arbitrary.

10.2 Maxwell's Distribution of Speeds

In a classical system, the probability distribution can be replaced by distribution functions obtained from the probability distribution by a different normalization, for instance to the number of particles in the system. For a classical fluid

$$P(\vec{r},\vec{p})d^3\vec{r}d^3\vec{p} = \mathcal{C}e^{-\beta(\frac{p^2}{2m}+E_{int})}d^3\vec{r}d^3\vec{p} \tag{10.2.1}$$

represents the probability of finding a molecule in the gas within the interval $(\vec{r},\vec{p};\vec{r}+d\vec{r},\vec{p}+d\vec{p})$ of phase space. Equivalently, if $f(\vec{r},\vec{v})d^3\vec{r}d^3\vec{v}$ represents the number of particles in this interval, it is clear that f is related to P because the probability of finding a molecule in any interval must be proportional to the number of molecules in that interval. Indeed, the two can differ at most by a normalization. While $P(\vec{r},\vec{p})d^3\vec{r}d^3\vec{p}$ is normalized to unity, the number distribution must be normalized to the total number of molecules present, i.e.,

$$\begin{aligned} f(\vec{r},\vec{v})d^3\vec{r}d^3\vec{v} &= \mathcal{C}'e^{-\beta(mv^2/2+E_{int})}d^3\vec{r}d^3\vec{v} \\ \int f(\vec{r},\vec{v})d^3\vec{r}d^3\vec{v} &= N \end{aligned} \tag{10.2.2}$$

The normalization constant $\mathcal{C}'$ is easily evaluated for an ideal gas (of non-interacting point-like particles, $E_{int}=0$),

$$\mathcal{C}' = n\left(\frac{\beta m}{2\pi}\right)^{\frac{3}{2}}, \tag{10.2.3}$$

where $n = N/V$ is the number density of particles, so that

$$f(\vec{r},\vec{v})d^3\vec{r}d^3\vec{v} = n\left(\frac{\beta m}{2\pi}\right)^{\frac{3}{2}} e^{-\beta mv^2/2}d^3\vec{r}d^3\vec{v}. \tag{10.2.4}$$

The exponent above does not depend on the positions of the molecules and we can define the number of molecules per unit volume with velocities between $\vec{v}$ and $\vec{v}+d\vec{v}$,

$$f(\vec{v})d^3\vec{v} = n\left(\frac{\beta m}{2\pi}\right)^{\frac{3}{2}} e^{-\beta mv^2/2}d^3\vec{v} \tag{10.2.5}$$

Moreover the exponent in (10.2.4) depends only on the the speed because there are no preferred directions within an ideal gas in equilibrium. Information about directions is contained in the measure $d^3\vec{v}$. If we agree to ask questions related only to the speed of molecules, we can write $d^3\vec{v}$ in spherical coordinates, $d^3\vec{v} = v^2\sin\theta d\theta d\phi$, and perform the integration over the solid angle to get

$$f(\vec{v})d^3\vec{v} = 4\pi n\left(\frac{\beta m}{2\pi}\right)^{\frac{3}{2}} e^{-\beta mv^2/2}v^2dv = F(v)dv \tag{10.2.6}$$

The distribution $F(v)dv$ is the Maxwell distribution of speeds. It represents the number of molecules of the gas per unit volume with speeds between v and $v + dv$

Maxwell's distribution also allows us to calculate some significant average values. The mean speed of a molecule in the gas is given by

$$\begin{aligned}\langle v\rangle &= \frac{1}{n}\int_0^\infty F(v)dv \\ &= 4\pi\left(\frac{\beta m}{2\pi}\right)^{\frac{3}{2}}\int_0^\infty v^3 e^{-\beta m v^2/2}dv \qquad (10.2.7)\end{aligned}$$

The integral is easily evaluated[2] to give

$$\langle v\rangle = \sqrt{\frac{8kT}{\pi m}} \qquad (10.2.8)$$

Likewise, the mean square velocity is

$$\begin{aligned}\langle v^2\rangle &= \frac{1}{n}\int v^2 F(v)dv \\ &= 4\pi\left(\frac{\beta m}{2\pi}\right)^{\frac{3}{2}}\int_0^\infty v^4 e^{-\beta m v^2/2}dv \\ &= \frac{3kT}{m} \\ \Rightarrow\quad v_{\text{r.m.s}} &= \sqrt{\frac{3kT}{m}} \qquad (10.2.9)\end{aligned}$$

and the most probable velocity, $\widetilde{v}$, is obtained by maximizing $F(v)$,

$$\frac{dF(v)}{dv} = 0, \quad \Rightarrow \quad \tilde{v} = \sqrt{\frac{2kT}{m}} \qquad (10.2.10)$$

which can be checked to be a maximum of $F(v)$.

The **flux**, Φ, across any surface is the number of particles crossing the surface per unit time. Fluxes are extremely important in flow problems but a knowledge of the flux can be important even in equilibrium situations. For example, the flux per unit area, called the **current**, of photons out of a tiny hole in a black body cavity in equilibrium at temperature T is the spectral radiancy of the black body and is related to the number density of photons within the cavity. Here we will derive an expression for the flux of an ideal gas in equilibrium at temperature T, showing explicitly its relationship with the

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[2] $\int_0^\infty dx x^{2n+1}e^{-px^2} = \frac{n!}{2p^{n+1}}$ and $\int_0^\infty dx x^{2n}e^{-px^2} = \left(-\frac{\partial}{\partial p}\right)^n \int_0^\infty dx e^{-px^2}$

number density of molecules. Consider, first, the simple case of a stream of molecules, all having the same velocity striking a surface such that the velocity of the molecules is parallel to the surface. The number of molecules striking an element, dS, of the surface in time dt will obviously be all the molecules which exist in a cylindrical volume of length vdt and base area, dS, *i.e.,*

$$dN = nvdtdS \tag{10.2.11}$$

where n is the number density of the molecules in the gas. On the other hand, if the angle of incidence is $\theta \neq 0$, then

$$dN = ndtvdS\cos\theta = ndt\vec{v}\cdot d\vec{S} \tag{10.2.12}$$

and the number of molecules striking the surface per unit time (the flux) is

$$d\Phi = \frac{dN}{dt} = n\vec{v}\cdot d\vec{S} \tag{10.2.13}$$

The quantity $\vec{j} = n\vec{v}$ is the number of particles crossing a unit area of the surface per unit time and is called the "current". Now, in general, one cannot expect that all the molecules have the same velocity. What is relevant is therefore the *average* flux

$$\langle d\Phi\rangle = \langle j_z\rangle dS \tag{10.2.14}$$

where, for convenience we let the normal to $d\vec{S}$ define the z axis. We want to calculate $\langle j_z\rangle = n\langle v_z\rangle$, or

$$\langle v_z\rangle = \int_{v_z>0} d^3\vec{v}v\cos\theta f(\vec{v}) \tag{10.2.15}$$

where we have used $v_z = v\cos\theta$ and restricted the integration to velocities with positive $z-$components to ensure that we count only those molecules that will cross the surface from left to right. Thus we have

$$\langle v_z\rangle = n\left(\frac{\beta m}{2\pi}\right)^{\frac{3}{2}}\int_0^\infty v^2dv\int_0^{2\pi}d\phi\int_0^{\pi/2}\sin\theta d\theta v\cos\theta e^{-\beta mv^2/2} \tag{10.2.16}$$

using spherical coordinates in velocity space. The ϕ (azimuthal) integration is straightforward and gives 2π. The θ integration is taken from 0 to $\pi/2$ so as to account only for the right hemisphere (remember that we're interested only in the molecules that cross the surface from left to right) instead of the whole sphere. Let us separate the integrations

$$\langle v_z\rangle = 4\pi n\left(\frac{\beta m}{2\pi}\right)\left[\int_0^\infty v^3e^{-\beta mv^2/2}\right]\times\frac{1}{2}\times\left[\int_0^{\pi/2}\sin\theta\cos\theta d\theta\right] \tag{10.2.17}$$

The first part of the above is just $\langle v\rangle$. The second integral (over θ) gives simply $\frac{1}{2}$. Putting it all together and inserting the value of $\langle v\rangle$ calculated in (10.2.8), we finally get

$$\langle j_z\rangle = \frac{n}{4}\langle v\rangle = \frac{n}{4}\sqrt{\frac{8kT}{m\pi}} \tag{10.2.18}$$

which gives the average current in any one direction and thence the average flux according to (10.2.14).

10.3 Osmosis

Osmosis is the motion of molecules across a semi-permeable membrane from a region of higher potential to a region of lower potential. Here we will consider a toy model of osmosis in which a box of N non-interacting particles is divided into two parts by a semi-permeable membrane through which the molecules may flow and which divides the box into two parts, "1" and "2" of volumes V_1 and V_2. All particles may exist in one of two states: in state A the molecules have only kinetic energy, but molecules in state B have in addition a certain potential energy, ε_0. Particles in region V_1 *always* exist in state A but particles in V_2 may be either in state A or in state B. This means that a molecule in state B may not pass through the semi-permeable membrane from V_2 into V_1 but a molecule in A can pass from V_1 to V_2 and vice-versa.

Let N_A be the number of molecules in state A, then $N_B = N - N_A$ is the number of molecules in state B . The partition function of the system will be

$$Z = \frac{(V_1+V_2)^{N_A} V_2^{N_B}}{N_A! N_B!}\left(\frac{2m\pi}{\beta h_o^2}\right)^{\frac{3}{2}(N_A+N_B)} e^{-\beta N_B\varepsilon_0} \tag{10.3.1}$$

and its Free Energy, $F = -\frac{1}{\beta}\ln Z$, is

$$F = -\frac{1}{\beta}\left[N_A \ln\left(\frac{V}{N_A}\right) + N_B \ln\left(\frac{V}{N_B}\right) + \frac{3}{2}(N_A+N_B)\ln\left(\frac{2m\pi}{\beta h_o^2}\right) - \beta N_B\varepsilon_0 + (N_A+N_B)\right]. \tag{10.3.2}$$

From this we compute the chemical potential of the molecules in state A:

$$\mu_A = \left(\frac{\partial F}{\partial N_A}\right)_{V,T} = -\frac{1}{\beta}\left[\ln\left(\frac{V}{N_A}\right) + \frac{3}{2}\ln\left(\frac{2m\pi}{\beta h_o^2}\right)\right] \tag{10.3.3}$$

and that of the molecules in state B,

$$\mu_B = \left(\frac{\partial F}{\partial N_B}\right)_{V_2,T} = -\frac{1}{\beta}\left[\ln\left(\frac{V_2}{N_B}\right) + \frac{3}{2}\ln\left(\frac{2m\pi}{\beta h_o^2}\right) - \beta\varepsilon_0\right] \tag{10.3.4}$$

Since the two must be equal in equilibrium

$$\ln\left(\frac{V}{N_A}\right) = \ln\left(\frac{V_2}{N_B}\right) - \beta\varepsilon_0 \tag{10.3.5}$$

which means that, using $N_B = N - N_A$

$$\begin{aligned} N_A &= \frac{N(V_1+V_2)e^{\beta\varepsilon_0}}{V_2+(V_1+V_2)e^{\beta\varepsilon_0}} \\ N_B &= \frac{NV_2}{V_2+(V_1+V_2)e^{\beta\varepsilon_0}} \end{aligned} \tag{10.3.6}$$

The pressure in volume V_1 is also calculated directly,

$$p_1 = -\left(\frac{\partial F}{\partial V_1}\right)_{T,V_2,N_A,N_B} = \frac{N_A}{\beta V} = \frac{NkTe^{\beta\varepsilon_0}}{V_2+Ve^{\beta\varepsilon_0}} \tag{10.3.7}$$

as well as the pressure in V_2,

$$p_2 = -\left(\frac{\partial F}{\partial V_2}\right)_{T,V_2,N_A,N_B} = \frac{1}{\beta}\left[\frac{N_A}{V} + \frac{N_B}{V_2}\right] = \frac{NkT(1+e^{\beta\varepsilon_0})}{V_2+Ve^{\beta\varepsilon_0}}. \tag{10.3.8}$$

We find the **osmotic pressure**, *i.e.,* the excess pressure

$$\Delta p = p_2 - p_1 = \frac{NkT}{V_2+Ve^{\beta\varepsilon_0}} \tag{10.3.9}$$

in region "2" over region "1". This excess pressure exists because only molecules in state A may freely flow across the semi-permeable membrane. Osmosis is vital to biological life forms as most cell membranes are semi-permeable. Generally these membranes are not permeable to large molecules but to small molecules like water and small solutes. Osmosis provides the primary means by which water is transported into and out of cells. Solute concentration in water lowers the potential energy of water molecules. Thus water molecules pass through a cell membrane from a region of low solute concentration outside the cell to a region of high solute concentration inside the cell.

10.4 Real Gases

If we relax the assumptions that make a gas "ideal", *i.e.,* if we take into account the non-zero molecular size as well as the electromagnetic interaction between molecules we get the 'real" gas. The energy of the system of molecules can always be written as

$$E = T + U = \sum_i \frac{\vec{p}_i^2}{2m_i} + U(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) \tag{10.4.1}$$

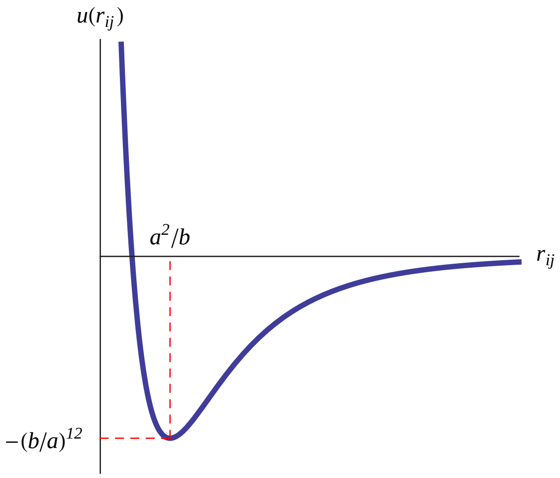

Figure 10.1: The Lennard-Jones Potential

where i labels the molecules and $\vec{r}_i$ is the position vector of the molecule labeled by i. The form of U is of interest. We can think of it as a sum over the potential energies of the interactions between pairs of molecules,

$$U(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) = \sum_{i<j} u_{ij}(r_{ij}) \tag{10.4.2}$$

where $r_{ij} = |\vec{r}_i - \vec{r}_j|$ and we have made sure not to overcount the pairs by requiring $i < j$ in the sum. The intermolecular interaction is roughly speaking such as to prevent the molecules from actually coming into contact with one another – it is repulsive at very short distances, on the order of the molecular size – and it is attractive when the molecular separation is greater than the molecular size. Phenomenologically, the **Lennard-Jones** potential represents this situation well in terms of two adjustable parameters. It is shown in figure 10.4.3 and given by

$$u_{ij}(\vec{r}_{ij}) = u_0 \left[\left(\frac{a}{r_{ij}} \right)^{12} - 2 \left(\frac{b}{r_{ij}} \right)^6 \right] \tag{10.4.3}$$

where $\vec{r}_{ij} = \vec{r}_j - \vec{r}_i$ is the position of molecule j with respect to molecule i. The potential will admit a minimum of $u_{\min} = -u_0(b/a)^{12}$ at $r_{ij} = a^2/b$. The total energy of the molecules will be

$$E = \sum_i \frac{p_i^2}{2m_i} + \sum_{i<j} u_{ij}(r_{ij}) \tag{10.4.4}$$

where we have taken care not to sum over potential energies more than once per pair. This can also be written as

$$E = \sum_i \frac{p_i^2}{2m_i} + \frac{1}{2}\sum_{i\neq j} u_{ij}(r_{ij}) \tag{10.4.5}$$

and therefore the partition function will be

$$Z_N = \frac{1}{h_0^{3N}N!}\int d^3\vec{r}_1 \ldots d^3\vec{r}_N d^3\vec{p}_1 \ldots d^3\vec{p}_N e^{-\beta\left(\sum_i \frac{p_i^2}{2m_i} + \frac{1}{2}\sum_{i\neq j} u_{ij}(r_{ij})\right)} \tag{10.4.6}$$

Performing the momentum integrals we are left with

$$Z_N = \frac{1}{N!}\left(\frac{2\pi m}{h_o^2\beta}\right)^{3N/2}\int d^3\vec{r}_1 \ldots d^3\vec{r}_N e^{-\frac{\beta}{2}\sum_{i\neq j} u_{ij}(r_{ij})} \tag{10.4.7}$$

As one can easily see the difficulty is in evaluating the spatial integrals. Let us therefore concentrate on

$$Z_U \overset{\text{def}}{=} \int d^3\vec{r}_1 \ldots d^3\vec{r}_N e^{-\frac{\beta}{2}\sum_{i\neq j} u_{ij}(r_{ij})} \tag{10.4.8}$$

If both a and b are zero, so that the pairwise interaction potentials vanish, then the integral will just give $Z_U = V^N$. The same result is obtained at very high temperatures, as $\beta \to 0$. On the other hand,

$$\langle U\rangle = -\frac{\partial \ln Z_U}{\partial\beta} \tag{10.4.9}$$

where $U = \sum_{i<j} u_{ij}(r_{ij})$ is the total potential energy of the molecules, so we can write

$$\ln Z_U = N\ln V - \int_0^\beta \langle U(\beta')\rangle\, d\beta' \tag{10.4.10}$$

Now there are $N(N-1)/2$ terms in the sum defining U and it is reasonable to assume that each term contributes equally, say $\langle u\rangle$ to the sum in the mean, so

$$\langle U\rangle \approx \frac{1}{2}N(N-1)\langle u\rangle \approx \frac{N^2}{2}\langle u\rangle \tag{10.4.11}$$

This is the **mean field** approximation. We can now write

$$\ln Z_U \approx N\ln V - \frac{N^2}{2}\int_0^\beta \langle u\rangle\, d\beta' \tag{10.4.12}$$

and calculate the mean pair interaction potential from

$$\langle u\rangle = \frac{\int_V d^3\vec{r} u(r) e^{-\beta u(r)}}{\int_V d^3\vec{r} e^{-\beta u(r)}} = -\frac{\partial}{\partial\beta}\ln\int_V d^3\vec{r} e^{-\beta u(r)} \tag{10.4.13}$$

The integral is over all possible mean separation of the molecular pairs, *i.e.,* over the entire volume of the gas. It is most convenient to rewrite the integral above as follows:

$$\int_V d^3\vec{r}e^{-\beta u(r)} = \int_V d^3\vec{r}[1 + (e^{-\beta u(r)} - 1)] \overset{\text{def}}{=} V + I(\beta) \tag{10.4.14}$$

and

$$\langle u \rangle = -\frac{\partial}{\partial\beta} \ln\left(1 + \frac{I(\beta)}{V}\right) = -\frac{\partial}{\partial\beta}\left[\frac{I(\beta)}{V} + \mathcal{O}\left(\frac{I(\beta)}{V}\right)^2\right] \tag{10.4.15}$$

If we now integrate w.r.t. β to get Z_U, we find

$$\ln Z_U = N \ln V + \frac{N^2}{2}\left[\frac{I(\beta)}{V} + \mathcal{O}\left(\frac{I(\beta)}{V}\right)^2\right] \tag{10.4.16}$$

and

$$\ln Z = \frac{3N}{2}\ln\left(\frac{2\pi m}{h_o^2\beta}\right) + N + N\ln\left(\frac{V}{N}\right) + \frac{N^2}{2}\left[\frac{I(\beta)}{V} + \mathcal{O}\left(\frac{I(\beta)}{V}\right)^2\right], \tag{10.4.17}$$

which gives the average internal energy

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial\beta} = \frac{3N}{2\beta} - \frac{N^2}{2}\frac{\partial}{\partial\beta}\left[\frac{I(\beta)}{V} + \mathcal{O}\left(\frac{I(\beta)}{V}\right)^2\right], \tag{10.4.18}$$

and pressure

$$p = \frac{1}{\beta}\frac{\partial \ln Z}{\partial\beta} = \frac{N}{\beta V} - \frac{N^2}{2}\frac{I(\beta)}{V^2} + \mathcal{O}(V^3) \tag{10.4.19}$$

in terms of the integral $I(\beta)$, which we must now attempt to evaluate.

Notice that the corrections to the ideal gas equation of state are in the form of a Taylor expansion in the number density, n,

$$p = \frac{n}{\beta} + B_2(T)n^2 + B_3(T)n^3 + \ldots \tag{10.4.20}$$

That is why this approximation is valid at low densities; the temperature dependent coefficients $B_2(T)$, $(B_3(T)$, etc., are called the second, third, etc., **virial coefficients** and it is our task to evaluate them in this mean field approximation. The expansion in (10.4.20) is called the **virial expansion**.

It is very difficult to evaluate the integral in (10.4.13) in closed form with the interaction potential given by the Lennard-Jones potential. Instead we shall use the following approximation of it:

$$u(r) = \begin{cases} \infty & r < r_0 \\ u_0\left(\frac{r_0}{r}\right)^s & r > r_0 \end{cases} \tag{10.4.21}$$

We will compute the integral

$$\int_V d^3\vec{r}[e^{-\beta u(r)} - 1] = 4\pi \int r^2 dr[e^{-\beta u(r)} - 1] \tag{10.4.22}$$

Now when $r < r_0$ the potential is infinite and $e^{-\beta u} = 0$ so we have

$$4\pi \int_0^{r_0} r^2 dr[e^{-\beta u(r)} - 1] \approx -\frac{4\pi}{3} r_0^3. \tag{10.4.23}$$

On the other hand, when $r > r_0$ the temperature is high (β is small) and so is the pair interaction potential, so

$$e^{-\beta u} \approx 1 - \beta u \Rightarrow 4\pi \int_{r_0}^{\infty} r^2 dr[e^{-\beta u(r)} - 1] \approx 4\pi\beta u_0 r_0^s \int_{r_0}^{\infty} dr r^{2-s} = \frac{4\pi\beta u_0 r_0^3}{s-3} \tag{10.4.24}$$

where we have assumed that $s > 3$ so that the integral is convergent.

Now we have an approximation for the second virial coefficient:

$$B_2(T) = -\frac{1}{2} I(\beta) = \frac{2}{3}\pi r_0^3 \left[1 - \frac{3\beta u_0}{(s-3)}\right] \tag{10.4.25}$$

which we will write as

$$B_2(T) = b' \left[1 - \frac{a'}{kT}\right], \tag{10.4.26}$$

where $b' = 2\pi r_0^3/3$ characterizes the molecular volume and $a = 3\beta u_0/(s-3)$ characterizes the interaction strength. To this approximation,

$$p = nkT + b' \left[kT + a'\right] n^2 \tag{10.4.27}$$

Rearranging terms,

$$p + a'b'n^2 = nkT(1 + nb') \approx \frac{nkT}{1 - nb'} = \frac{kT}{\frac{1}{n} - b'} \tag{10.4.28}$$

assuming $nb' \ll 1$. Therefore

$$(p + a'b'n^2)\left(\frac{1}{n} - b'\right) = kT \tag{10.4.29}$$

and rewriting the number density as the inverse volume per particle,

$$\left(p + \frac{a'b'}{v^2}\right)(v - b') = kT \tag{10.4.30}$$

This is of course the Van de Waal's equation of state.

The constant b' is very obviously the "size" of the molecules. The constant $a'b'$ depends on a' which is connected both to the strength, u_0, and the concavity (via s) of the potential when $r > r_0$. It therefore characterizes the strength and range of the intermolecular forces.

10.5 Paramagnetism

In a previous section we had studied paramagnetism in a very special system by considering atoms of spin $\frac{1}{2}$ in an external magnetic field. Because of the spin$-B$ coupling, the material exhibits an overall magnetization which depends on the field strength and on the temperature of the material. The magnetization disappears of course when the driving magnetic field is removed.

We begin this section by treating a system of N classical non-interacting atoms, each having a magnetic moment $\vec{\mu}$, in an external magnetic field, $\vec{B}$ (the Langevin theory of paramagnetism). The energy of each atom will have the form

$$E = -\vec{\mu}\cdot\vec{B} = -\mu B\cos\theta \tag{10.5.1}$$

where θ is the angle between the magnetic moment of the atom and the magnetic field. Let $\vec{B}$ define the $z-$axis. Since this treatment will be classical, all orientations of the magnetic moment are allowed, that is, the angle θ can take on any value between 0 and π and the azimuthal angle, ϕ, can take all values between 0 and 2π. The partition function for a single atom will be the following sum over all the orientations of μ

$$\begin{aligned} Z_1 &= \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta e^{\beta\mu B\cos\theta} \\ &= \frac{4\pi}{\beta\mu B}\sinh(\beta\mu B) \end{aligned} \tag{10.5.2}$$

which gives, for the partition function of the entire system,

$$Z_N = \left(\frac{4\pi}{\beta\mu B}\right)^N \sinh^N(\beta\mu B) \tag{10.5.3}$$

The average energy of the system is therefore

$$\langle E\rangle = -\frac{\partial \ln Z_N}{\partial\beta} = N\mu B\left[\frac{1}{\beta\mu B}\coth(\beta\mu B)\right] \tag{10.5.4}$$

and the average magnetization is

$$\begin{aligned} \langle M\rangle &= N\frac{\int_0^{2\pi} d\phi \int_0^{\pi}\sin\theta d\theta\mu\cos\theta e^{\beta\mu B\cos\theta}}{\int_0^{2\pi} d\phi\int_0^{\pi}\sin\theta d\theta e^{\beta\mu B\cos\theta}} \\ &= \frac{1}{\beta}\frac{\partial\ln Z_N}{\partial B} = \frac{1}{B}\frac{\partial\ln Z_N}{\partial\beta} = -\frac{\langle E\rangle}{B} \end{aligned}$$

$$= N\mu\left[\coth(\beta\mu B) - \frac{1}{\beta\mu B}\right] \tag{10.5.5}$$

From the average magnetization, one can calculate the magnetic susceptibility

$$\chi = \frac{\partial\langle M\rangle}{\partial B} = N\beta\mu^2\left[\left(\frac{1}{\beta\mu B}\right)^2 - \operatorname{csch}^2(\beta\mu B)\right] \tag{10.5.6}$$

At very high temperatures, such that $\beta\mu B << 1$, the susceptibility obeys Curie's law,

$$\lim_{\beta\mu B\to 0}\chi = \frac{N\mu^2}{3kT} \tag{10.5.7}$$

while at very low temperatures, $\beta\mu B >> 1$, the magnetization approaches a constant

$$\lim_{\beta\mu B\to\infty}\langle M\rangle = N\mu \tag{10.5.8}$$

as expected. Let us now calculate the entropy. As we are treating the system classically, we expect that the third law of thermodynamics will be violated. From the partition function in (10.5.3) we see that

$$\begin{aligned} S &= [\ln Z_N + \beta\langle E\rangle] \\ &= Nk\left[\ln(4\pi) + \ln\sinh\alpha - \ln\alpha - \alpha\coth\alpha + 1\right], \quad \alpha = \beta\mu B \end{aligned} \tag{10.5.9}$$

It is clearly extensive. However, in the low temperature limit, $\beta\mu B\to\infty$ (or $\alpha\to\infty$), its behavior is not in keeping with the 3rd law of thermodynamics. Indeed, using

$$\begin{aligned} \lim_{\alpha\to\infty}\ln\sinh\alpha &= \alpha - \ln 2 \\ \lim_{\alpha\to\infty}\coth\alpha &= 1, \end{aligned} \tag{10.5.10}$$

we find

$$\lim_{\beta\mu B\to\infty} S = Nk\left[\ln T + \sigma\right], \quad \sigma = 1 + \ln\left(\frac{2\pi k}{\mu B}\right), \tag{10.5.11}$$

which, characteristically, diverges as $T\to 0$.

If we treat the atoms quantum mechanically we must account for the fact that their net angular momentum is quantized. Consider atoms of *arbitrary* angular momentum, $\vec{J}$, so that the spin$-B$ coupling is

$$\epsilon = -\vec{\mu}\cdot\vec{B}, \quad \vec{\mu} = g_J\frac{e}{2m}\vec{J} \tag{10.5.12}$$

where g_J is the $g-$factor. Thus, if $\vec{B}$ defines the z direction, $\vec{B}=(0,0,B)$, the energy of each molecule will be

$$\begin{aligned}\epsilon &= -\vec{\mu}\cdot\vec{B} = -g_J\frac{e}{2m}\vec{J}\cdot\vec{B}\\ &= -g_J\frac{e\hbar}{2m}\frac{J_z}{\hbar}B = -\mu_J\frac{J_z}{\hbar}B \qquad (10.5.13)\end{aligned}$$

and it is determined by the z component of the angular momentum, which is quantized according to $J_z = m_J\hbar$ for $m_J = 0, \pm1, \pm2, ..., \pm J$ where $\vec{J}^2 = J(J+1)\hbar^2$ is the magnitude squared of the angular momentum.

As the molecules do not interact among themselves, the partition function is

$$Z_N = \left[\sum_{m_J=-J}^{J} e^{\beta\mu_J m_J B}\right]^N \qquad (10.5.14)$$

where N is the total number of molecules in the system. The z component of the magnetic moment of each atom is $\mu_z = m_J\mu_J$, so the average magnetization is

$$\begin{aligned}\langle M_J\rangle &= N\langle\mu_z\rangle = N\frac{\sum_{m_J=-J}^{J} m_J\mu_J e^{\beta\mu_J m_J B}}{\sum_{m_J=-J}^{J} e^{\beta\mu_J m_J B}}\\ &= \frac{1}{\beta}\frac{\partial \ln Z_N}{\partial B} = \frac{1}{B}\frac{\partial \ln Z_N}{\partial \beta} = -\frac{\langle E\rangle}{B} \qquad (10.5.15)\end{aligned}$$

So, we need to evaluate Z_N. Consider

$$Z_1 = \sum_{m_J=-J}^{J} e^{\beta\mu_J m_J B} \qquad (10.5.16)$$

and let

$$x = e^{\beta\mu_J B} \qquad (10.5.17)$$

so that

$$\begin{aligned}Z_1 &= \sum_{m_J=-J}^{J} x^{m_J} = x^{-J} + x^{-J+1} + ...x^{J-1} + x^J\\ &= x^{-J}\left[1 + x + x^2 + ...x^{2J}\right] = \frac{x^{-J}\left(1-x^{2J+1}\right)}{(1-x)}\\ &= \frac{\left(x^{-J-1/2} - x^{J+1/2}\right)}{\left(x^{-1/2} - x^{1/2}\right)}\end{aligned}$$

$$= \frac{\sinh[(J+1/2)\beta\mu_J B]}{\sinh[\beta\mu_J B/2]} \tag{10.5.18}$$

The full partition function for the system of N particles is therefore

$$Z_N = \frac{\sinh^N[(J+1/2)\beta\mu_J B]}{\sinh^N[\beta\mu_J B/2]} \tag{10.5.19}$$

which reduces, for $J = 1/2$ to the expression we had before. We can now easily calculate the average magnetization:

$$\begin{aligned} \ln Z_N &= N\left\{\ln\sinh[(J+1/2)\beta\mu_J B] - \ln\sinh[\beta\mu_J B/2]\right\} \\ \frac{\partial \ln Z_N}{\partial B} &= N\beta\mu_J\left\{(J+1/2)\coth[(J+1/2)\beta\mu_J B] - \frac{1}{2}\coth[\beta\mu_J B/2]\right\} \\ \langle M_J\rangle &= N\mu_J\left\{(J+1/2)\coth[(J+1/2)\beta\mu_J B] - \frac{1}{2}\coth[\beta\mu_J B/2]\right\} \end{aligned} \tag{10.5.20}$$

The term in parenthesis, divided by J, is called the **Brillouin** function. The magnetic susceptibility is

$$\chi = \frac{\partial\langle M\rangle}{\partial B} \tag{10.5.21}$$

Let us now study the limiting behavior of the magnetization.

At high temperatures, when $\beta\mu_J B << 1$, we apply the limiting behavior

$$\coth\alpha = \frac{\cosh\alpha}{\sinh\alpha} = \frac{1}{\alpha} + \frac{1}{3}\alpha + \mathcal{O}(\alpha^2) \tag{10.5.22}$$

of the hyperbolic cotangent to (4.29) to get (at high temperatures)

$$\begin{aligned} \lim_{\beta\mu_J B\to 0}\langle M_J\rangle &= \frac{N\mu_J^2 B}{3kT}J(J+1) \\ \lim_{\beta\mu_J B\to 0}\chi &= \frac{N\mu_J^2}{3kT}J(J+1) \end{aligned} \tag{10.5.23}$$

which you should recognize as Curie's law and agrees with the result obtained from the classical treatment. This is not surprising as we are in the classical regime. Moreover, in the limit of low temperatures, or more correctly when $\beta\mu_J B >> 1$,

$$\lim_{\beta\mu_J B\to\infty}\langle M_J\rangle = NJ\mu_J \tag{10.5.24}$$

as expected. It is worth comparing the above two expressions with the results in (10.5.7) and (10.5.8). Why do they make sense?

Turning to the entropy, we will now see that quantization leads to a verification of the 3rd law. By straightforward differentiation, we find the average energy of the system

$$\begin{aligned}\langle E\rangle &= -\frac{\partial \ln Z_N}{\partial\beta}\\ &= -N\mu_J B\left[\left(J+\frac{1}{2}\right)\coth\left((J+1/2)\beta\mu_J B\right)-\frac{1}{2}\coth(\beta\mu_J B/2)\right]\end{aligned} \tag{10.5.25}$$

and its entropy

$$\begin{aligned}S &= [\ln Z_N+\beta\langle E\rangle]\\ &= kN\left[\ln\sinh\left((J+\frac{1}{2})\beta\mu_J B\right)-\ln\sinh\left(\frac{\beta\mu_J B}{2}\right)\right.\\ &\quad\left.-\beta\mu_J B\left\{\left(J+\frac{1}{2}\right)\coth\left((J+\frac{1}{2})\beta\mu_J B\right)-\frac{1}{2}\coth\left(\frac{\beta\mu_J B}{2}\right)\right\}\right]\end{aligned} \tag{10.5.26}$$

To check that the 3rd law is indeed obeyed, take the limit $\beta\mu_J B\to\infty$ above, using

$$\begin{aligned}\lim_{\alpha\to\infty}\ln\sinh\alpha &= \alpha-\ln 2\\ \lim_{\alpha\to\infty}\coth\alpha &= 1,\end{aligned} \tag{10.5.27}$$

to get

$$\lim_{T\to 0}S(T)=0 \tag{10.5.28}$$

as required.

10.6 Harmonic Oscillators

Finally, let us consider the system of non-interacting harmonic oscillators. It is instructive to first treat them classically. Thus, the energy of each oscillator is

$$E=\frac{\vec{p}^2}{2m}+\frac{1}{2}m\omega^2\vec{r}^2 \tag{10.6.1}$$

and the partition function for each oscillator is

$$Z_1 = \frac{1}{h_o^3}\int d^3\vec{r}d^3\vec{p}e^{-\beta E(\vec{r},\vec{p})}$$

$$= \left(\frac{4\pi^2}{\omega^2 h_o^2 \beta^2}\right)^{\frac{3}{2}} \tag{10.6.2}$$

where we have performed the two three dimensional gaussian integrations to arrive at the second equation above. The partition function of the system of N non-interacting oscillators is therefore

$$Z_N = \left(\frac{4\pi^2}{\omega^2 h_o^2 \beta^2}\right)^{3N/2} \tag{10.6.3}$$

whence follow the average energy and the entropy as usual

$$\begin{aligned} \langle E \rangle &= -\frac{\partial \ln Z_N}{\partial \beta} = 3NkT \\ S &= [\ln Z + \beta \langle E \rangle] = 3kN\,[\ln T + \sigma] \end{aligned} \tag{10.6.4}$$

where

$$\sigma = 1 + \ln\left(\frac{2\pi k}{\omega h_o}\right) \tag{10.6.5}$$

A few things about the above formulæ are notable: first note that the energy could be deduced directly from the equipartition theorem that says that each gaussian integration in the partition function contributes $kT/2$ to the mean energy of the system. There are in all six gaussian integrations involved, three over the momenta and three over the coordinates because the harmonic oscillator potential is gaussian. Next note that the entropy is extensive – there is no Gibbs paradox here. Finally, the entropy does not satisfy the third law of thermodynamics because we are using the classical theory.

The states of quantum oscillators, on the other hand, are determined by three integers, n, m and r, one for each degree of freedom, having energy

$$E_{n,m,r} = \left(n + m + r + \frac{3}{2}\right)\hbar\omega \tag{10.6.6}$$

The partition function for the system of N oscillators was given before,

$$\begin{aligned} Z_N &= \left[\sum_{n=0}^{\infty} e^{-\beta(n+1/2)\hbar\omega}\right]^{3N} \\ &= 2^{-3N} \operatorname{csch}^{3N}\left(\frac{\hbar\omega}{2kT}\right) \end{aligned} \tag{10.6.7}$$

Thus, the average energy of the system is

$$\langle E \rangle = -\frac{\partial \ln Z_N}{\partial \beta} = \frac{3}{2} N\hbar\omega \coth\left(\frac{\hbar\omega}{2kT}\right) \tag{10.6.8}$$

We see that in the limit $\beta\hbar\omega << 1$, $\langle E\rangle$ takes the value dictated by the classical equipartition theorem

$$\lim_{\beta\hbar\omega\to 0}\langle E\rangle = 3NkT \tag{10.6.9}$$

while, in the limit $\beta\hbar\omega >> 1$, the average energy is the sum of the zero-point energies of the oscillators,

$$\lim_{\beta\hbar\omega\to\infty}\langle E\rangle = \frac{3}{2}N\hbar\omega \tag{10.6.10}$$

The first limit above is the classical limit. Likewise, let us study the behavior of the entropy:

$$\begin{aligned} S &= k\left[\ln Z_N + \beta\langle E\rangle\right] \\ &= 3Nk\left[\frac{\beta\hbar\omega}{2}\left(\coth\left(\frac{\beta\hbar\omega}{2}\right)-1\right) - \ln\left(1-e^{-\beta\hbar\omega}\right)\right] \end{aligned} \tag{10.6.11}$$

It obeys the third law, $S(T\to 0)\to 0$, while at high temperatures, $\beta\hbar\omega\to 0$,

$$\begin{aligned} \lim_{\beta\hbar\omega\to 0} S &\to 3Nk\left[\ln T + \sigma\right] \\ \sigma &= 1+\ln\left(\frac{2\pi k}{h\omega}\right) \end{aligned} \tag{10.6.12}$$

which is precisely the value derived earlier from the classical approximation. Once again, the quantum theory agrees with the classical theory in the limit $\beta\epsilon \ll 1$ and also gives the correct limit, in agreement with the third law, as $T\to 0$.

10.7 Debye's Theory of Specific Heats

If we treat a solid as a collection of molecules held firmly to one another by relatively strong forces of electromagnetic origin derivable from complicated potentials then, provided that the potentials admit minima, the atoms of the solid will oscillate, each about its own equilibrium point. Let us begin with the following general expression for the energy of the system of molecules:

$$E = T + U = \frac{1}{2}\sum_\alpha m_\alpha \dot{\vec{r}}_\alpha^2 + U(\vec{r}_1,\vec{r}_2,\ldots,\ldots) \tag{10.7.1}$$

where α labels the molecules and $\vec{r}_\alpha$ is the position vector of the molecule labeled by α. The precise form of the potential energy will not interest us. Since we assume that the molecules will all oscillate about equilibrium positions in a solid, we simply expand the function in a Taylor polynomial about the equilibrium positions, which we label by $\vec{r}_{\alpha,0}$. Call $\vec{\xi}_\alpha = (\vec{r}_\alpha - \vec{r}_{\alpha,0})$ then

$$U(\vec{r}_1, \vec{r}_2, \ldots, \ldots) = U_0 + \sum_{\alpha,i} (\partial_{x_{\alpha i}} U|_{\vec{r}_{\alpha 0}}) \xi_{\alpha i} + \frac{1}{2!} \sum_{\alpha i, \beta j} (\partial_{x_{\alpha i}} \partial_{x_{\beta j}} U|_{\vec{r}_{\alpha,0}}) \xi_{\alpha i} \xi_{\beta j} + \ldots \quad (10.7.2)$$

Ignoring higher order terms and noting that because $\vec{r}_{\alpha 0}$ is the equilibrium position of each molecule the first term must vanish we have

$$U(\vec{r}_1, \vec{r}_2, \ldots, \ldots) \approx U_0 + \sum_{\alpha,\beta,i,j} \mathcal{A}_{\alpha i, \beta j} \xi_{\alpha i} \xi_{\beta j} \quad (10.7.3)$$

and the energy function becomes

$$E \approx \frac{1}{2} \sum_{\alpha i} m_\alpha \dot{\xi}_{\alpha i}^2 + \sum_{\alpha i, \beta j} \xi_{\alpha i} \mathcal{A}_{\alpha i, \beta j} \xi_{\beta j} + U_0 \quad (10.7.4)$$

Now $\widehat{\mathcal{A}}$ is a $3N \times 3N$ matrix (N coordinates, α, and three coordinates, i), which can be diagonalized by an orthogonal transformation. If we collectively label the pairs (αi) by k then $k \in \{1, 2, \ldots, 3N\}$

$$\begin{aligned} \xi_k \to q_k &= \sum_l S_{kl}\ \xi_l \\ \mathcal{A}_{kl} &\to \kappa_{D,kl}^2 \end{aligned} \quad (10.7.5)$$

where $\widehat{\kappa}_D^2$ is a diaginal matrix of positive elements. The new variables, q_k, obtained from the original displacements by an orthogonal transformation, are generalized coordinates and the elements of $\widehat{\kappa}_D$ are related to the normal mode angular frequencies, ω_k in the usual way. The energy may be put in the form

$$E = \sum_{k=1}^{3N} \frac{1}{2} \left[\dot{q}_k^2 + \omega_k^2 q_k^2 \right] + V_0 \quad (10.7.6)$$

The angular frequencies are clearly the normal frequencies. The overall constant will not affect the heat capacity and will now be dropped. What we have then is a system of oscillators, whose partition function we therefore already know to be

$$Z = \prod_k \left((2 \sinh \frac{\beta \hbar \omega_k}{2} \right)^{-1} \quad (10.7.7)$$

The central problem is now determining the distribution over normal modes in the sum

$$\ln Z = -\sum_k \ln \left(2 \sinh \frac{\beta \hbar \omega_k}{2} \right) \quad (10.7.8)$$

We assume that the normal modes are very closely spaced in a solid and replace the sum over normal modes by the integral

$$\ln Z = -\int d\omega\sigma(\omega)\ln\left(2\sinh\frac{\beta\hbar\omega_k}{2}\right) \tag{10.7.9}$$

so that $\sigma(\omega)d\omega$ represents the number of normal modes available to the solid between ω and $\omega + d\omega$. What can we say about $\sigma(\omega)$? The average energy of the solid becomes

$$\langle E\rangle = -\frac{\partial \ln Z}{\partial\beta} = \frac{\hbar}{2}\int d\omega\sigma(\omega)\omega\coth\left(\frac{\beta\hbar\omega}{2}\right) \tag{10.7.10}$$

and so at high temperatures

$$\langle E\rangle \to \beta^{-1}\int d\omega\sigma(\omega) \tag{10.7.11}$$

gives, for the heat capacity at constant volume

$$C_V = \frac{d\langle E\rangle}{dT} = -k\beta^2\frac{d\langle E\rangle}{d\beta} = k\int d\omega\sigma(\omega), \tag{10.7.12}$$

which we know from the Dulong and Petit law must be $3Nk$. Therefore at high temperatures all $3N$ normal modes are available to the system.

Determining the number of normal modes at low temperature is more difficult. The Debye approximation consists in treating the solid as a continuous medium and neglecting the discreteness of the atomic structure. This is valid under certain conditions: waves in the solid must satisfy the condition that wavelenths are much larger than the intermolecular spacing, $\lambda \gg a$. In this case atoms are all displaced by roughly the same amount, the underlying discreteness is hardly relevant and the number of modes of the effective elastic medium in the interval between λ and $\lambda + d\lambda$ should be a good approximation to the actual number of normal modes in the solid. On the other hand, when $\lambda \leq a$ then atomic displacements are irregular and the microscopic structure of the solid becomes important. So let us write the condition for the Debye approximation as

$$\lambda \gg a = \left(\frac{V}{N}\right)^{\frac{1}{3}} \quad \text{or} \quad \omega \ll 2\pi v_s\left(\frac{N}{V}\right)^{\frac{1}{3}} \tag{10.7.13}$$

where v_s is the speed of sound in the solid. The approximationbreaks down at high frequencies but we expect that the number of normal modes with very high frequencies at low temperatures is small, so the Debye approximation should be a good one in the low temperature limit.

The number of states available to scalar waves

$$\psi = \psi_0 e^{i\vec{k}\cdot\vec{r}-\omega t} \tag{10.7.14}$$

with wavelengths between k and $k+dk$ in a volume V is given by the phase space volume

$$\widetilde{\sigma}(k)dk = \left(\int_V d^3\vec{r}\right)\frac{d^3\vec{k}}{(2\pi)^3} = \frac{4\pi V}{(2\pi)^3}k^2 dk. \tag{10.7.15}$$

It can be used to directly obtain $\sigma(\omega)d\omega$ upon employing the dispersion relation $v_s = \omega/k$ where v_s is the speed of sound in the solid. One finds

$$\sigma(\omega)d\omega = \frac{V}{2\pi^2 v_s^3}\omega^2 d\omega \tag{10.7.16}$$

According to elasticity theory, both longitudinal waves, $\vec{u}_l$, and transverse waves, $\vec{u}_t$, will propagate through the solid, each obeying the wave equation

$$\frac{1}{v^2}\frac{\partial^2\vec{u}}{\partial t^2} = \vec{\nabla}^2\vec{u} \tag{10.7.17}$$

and respectively satisfying the constraints

$$\vec{\nabla}\cdot\vec{u}_l = 0 = \vec{\nabla}\times\vec{u}_t. \tag{10.7.18}$$

The lattice displacements can be written as the sum of them, $\vec{u} = \vec{u}_l + \vec{u}_t$. Longitudinal waves have one degree of freedom and transverse waves have two degrees of freedom, so

$$\begin{aligned}\sigma_l(\omega) &= \frac{V}{2\pi^2 v_l^3}\omega^2 d\omega\\ \sigma_t(\omega) &= \frac{2V}{2\pi^2 v_l^3}\omega^2 d\omega\end{aligned} \tag{10.7.19}$$

and we can write the density of states for the phonons as

$$\sigma(\omega)d\omega = \frac{V}{2\pi^2}\left[\frac{1}{v_l^3}+\frac{2}{v_t^3}\right]\omega^2 d\omega \quad \stackrel{\text{def}}{=} \quad \frac{3V}{2\pi^2 v_s^3}\omega^2 d\omega. \tag{10.7.20}$$

In the Debye approximation, we now set

$$\sigma_D(\omega) = \begin{cases}\sigma(\omega) & \omega < \omega_D\\ \\ 0 & \omega > \omega_D\end{cases} \tag{10.7.21}$$

where $\sigma_D(\omega)$ is chosen so that

$$\int_0^{\omega_D} d\omega\sigma_D(\omega) = 3N \Rightarrow \omega_D = v_s\left(\frac{6\pi^2 N}{V}\right)^{1/3} \tag{10.7.22}$$

Our approximate expression for the internal energy is therefore

$$\langle E\rangle \approx \left(\frac{3V\hbar}{4\pi^2 v_s^3}\right)\int_0^{\omega_D} d\omega\ \omega^3 \coth\left(\frac{\beta\hbar\omega}{2}\right) \tag{10.7.23}$$

and therefore

$$C_V = -k\beta^2\frac{\partial\langle E\rangle}{\partial\beta} = \left(\frac{3V\hbar^2 k\beta^2}{8\pi^2 v_s^3}\right)\int_0^{\omega_D} d\omega\ \omega^4 \text{csch}^2\left(\frac{\beta\hbar\omega}{2}\right). \tag{10.7.24}$$

We may extract all the β dependence from the integrand by defining the dimensionless quantity $x = \beta\hbar\omega/2$ so that, calling $\Theta = \hbar\omega_D/2k$, we have

$$C_V = 9Nk\left(\frac{T}{\Theta}\right)^3\int_0^{\Theta_D/T} dx\ x^4\text{csch}^2 x. \tag{10.7.25}$$

In this way it is easier to extract the temperature dependence of the heat capacity in the limits of interest. At high temperatures, approximate "csch$x$" by $1/x$ and perform the integral to get

$$C_V \overset{T\to\infty}{\longrightarrow} 3Nk, \tag{10.7.26}$$

which is the Dulong and Petit law. At low temperatures, the first order (in T) contribution to the integral is obtained by replacing the upper limit by ∞ and using

$$\int_0^\infty dx\ x^4\text{csch}^2 x = \frac{\pi^2}{30}. \tag{10.7.27}$$

To this order then the heat capacity behaves as T^3 near absolute zero

$$C_V \overset{T\to 0}{\longrightarrow} \frac{3\pi^2}{10}Nk\left(\frac{T}{\Theta}\right)^3. \tag{10.7.28}$$

Beginning with a T^3 dependence very close to absolute zero, it smoothly approaches its asymptotic value of $3Nk$ as shown in figure (6.2) as the temperature rises.

10.8 Linear Expansion in Solids

Let us now address the mean molecular separation in a solid in the simplified model in which two molecules interact with each other by a force that is derivable from some potential $U(x)$ that depends only on their separation. Imagine that the two molecules are in thermal contact with a heat bath whose temperature is high enough that classical statistical mechanics is applicable. The average separation between the molecules will be given by

$$\langle x\rangle = \frac{\int dx \int dp\ x\ e^{-\beta[p^2/2m+U(x)]}}{\int dx \int dp\ e^{-\beta[p^2/2m+U(x)]}} \tag{10.8.1}$$

Evidently, the $p-$ integral cancels and we have

$$\langle x\rangle = \frac{\int dx\ x\ e^{-\beta U(x)}}{\int dx\ e^{-\beta U(x)}} \tag{10.8.2}$$

Expand $U(x)$ in a Taylor series about its minimum, $x = a$,

$$U(x) \approx U_0 + \frac{1}{2!}U''(a)(x-a)^2 + \frac{1}{3!}U'''(a)(x-a)^3 + \dots \tag{10.8.3}$$

then the denominator in (10.8.2) is just

$$\int dx\ e^{-\beta U(x)} \approx e^{-\beta U_0}\int dy\ e^{-\frac{\beta}{2}U''(a)y^2} = e^{-\beta U_0}\sqrt{\frac{2\pi}{\beta U''(a)}}. \tag{10.8.4}$$

whereas the denominator in (10.8.2) can be expanded as

$$\begin{aligned} & e^{-\beta U_0}\int dx\ x\ e^{-\frac{\beta}{2}U''(a)(x-x_0)^2}\left[1-\frac{\beta}{3!}U'''(a)(x-a)^3+\dots\right] \\ = \quad & e^{-\beta U_0}\left[\int dy\ y\ e^{-\frac{\beta}{2}U''(a)y^2} + a\int dy e^{-\frac{\beta}{2}U''(a)y^2} - \frac{\beta}{3!}U'''(a)\int dy\ y^4\ e^{-\frac{\beta}{2}U''(a)y^2} + \dots\right] \end{aligned} \tag{10.8.5}$$

But, since the integrals are over all possible separations, $y = x - a$, the first will vanish. Up to the fourth order in y, we find that the numerator is

$$\approx e^{-\beta U_0}\sqrt{\pi}\left[a\sqrt{\frac{2}{\beta U''(a)}} - \frac{\beta U'''(a)}{8}\left(\sqrt{\frac{2}{\beta U''(a)}}\right)^5\right] \tag{10.8.6}$$

and so, to the same order,

$$\langle x\rangle \approx a - \frac{kU'''(a)}{2U''^2(a)}T. \tag{10.8.7}$$

This is the linear expansion law and it follows that the coefficient of linear expansion is given by the constant

$$\alpha = \frac{\langle x\rangle - a}{a} = -\frac{kU'''(a)}{2aU''^2(a)}, \tag{10.8.8}$$

which depends on the third derivative of the potential at its minimum. Experience tells us that the coefficient of linear expansion for most solids is positive, which means that the third derivative of the potential must be negative at a. Thus $U''(a)$, which is positive at a must decrease with increasing separation, *i.e.,* the potential must tend to "flatten". This behavior is seen in the Lennard-Jones potential of (10.4.3), which changes concavity as the molecular separation increases beyond the minimum.

10.9 Adsorption

Recall from Chapter 5 that certain solid surfaces attract molecules from an adjacent gas or liquid by weak, long range forces that initiate the process and strong short range forces between the molecular electric multipoles that firmly attach fluid molecules to the solid. The phenomenon is called adsorption. Here we will consider a greatly oversimplified treatment of adsorption in which the effect is to form two dimensional layers of the gas or liquid on the solid surface. We will assume that the adsorbent is homogeneous and that the attractive forces on its surface correspond to a potential energy of $-\varepsilon_0$. We are interested in determining the areal density of adsorbed molecules as a function of the fluid pressure. To do so we will think of the fluid as made up of two phases, one of which is three dimensional, surrounding the solid and the other, consisting of the adsorbate, is effectively two dimensional able to move only along the surface of the adsorbent. We then proceed to determine the condition for chemical equilibrium between the phases. The partition function in the canonical ensemble for the two and three dimensional phases are respectively

$$\ln Z_N = N_a \left[\ln\left(\frac{A}{N_a}\right) + \ln\left(\frac{2\pi m}{\beta h_o^2}\right) + \beta\varepsilon_0 + 1\right] \tag{10.9.1}$$

(the compressibility factor here is unity) and

$$\ln Z_N = N \left[\ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln\left(\frac{2\pi m}{\beta h_o^2}\right) + 1\right]. \tag{10.9.2}$$

and from these one may compute the chemical potentials according to

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} = -\frac{1}{\beta}\left(\frac{\partial \ln Z_N}{\partial N}\right)_{V,T} \tag{10.9.3}$$

For the adsorbed gas we find

$$\mu_a = -\frac{1}{\beta}\left[\ln\left(\frac{A}{N}\right) + \ln\left(\frac{2\pi m}{\beta h_o^2}\right) + \beta\varepsilon_0\right] \tag{10.9.4}$$

and for the portion of the fluid that is not adsorbed

$$\mu = -\frac{1}{\beta}\left[\ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln\left(\frac{2\pi m}{\beta h_o^2}\right)\right] \tag{10.9.5}$$

As the two must be the same in equilibrium, $\mu_a = \mu \Rightarrow$

$$\ln\left(\frac{A}{N}\right) = \ln\left(\frac{V}{N}\right) + \frac{1}{2}\ln\left(\frac{2\pi m}{\beta h_o^2}\right) - \beta\varepsilon_0 \tag{10.9.6}$$

Exponentiating both sides and setting $pV = NkT$ for the three dimensional fluid we obtain the condition following condition for equilibrium,

$$\frac{N_a}{A} = p\left(\frac{2\pi m\beta}{h_o^2}\right)^{1/2} e^{\beta\varepsilon_0}, \tag{10.9.7}$$

which should be compared with (5.4.18). Various models in this two-phase approach to adsorption can be constructed with more realistic potentials than we have used above; models that take into account interactions between adsorbate molecules themselves, heterogeneity of the adsorbent, multiple species of adsorbate and the formation of multilayers, in which some molecules are adsorbed not on the solid but on layers of already adsorbed molecules. Another approach to adsorption would be to consider the fluid as if it were in an external field. This approach, though perhaps more realistic, requires a detailed knowledge of the adsorbate-adsorbate and adsorbate-adsorbent interactions and is mathematically very complex. We shall consider alternatives in a later chapter.

Chapter 11

Indistinguishability and Quantum Statistics

So far we have dealt only superficially with the role of indistinguishability in statistical mechanics. It first appeared in the resolution of Gibbs' paradox, where we saw that the entropy as naively computed from the partition function does not end up being extensive. Gibbs resolved this problem by assuming that the molecules of an ideal gas are indistinguishable. He suggested that because one cannot actually say *which* molecule of the N available molecules is in any given interval $(\vec{r}, \vec{r} + d\vec{r})$ and $(\vec{p}, \vec{p} + d\vec{p})$ of phase space, the sum over distinct states in the original definition of the partition function overcounted them by ignoring the fact that interchanges of particles lead to the same state. Gibb's resolution was to divide by the number of possible interchanges of particles, *i.e.,*

$$Z_{correct} = \frac{Z_N}{N!}. \tag{11.0.1}$$

With the advent of quantum mechanics, indistinguishability takes on an even more significant role, leading to altogether new constraints on our counting of states. Our goal to examine this rigorously in the present chapter.[1]

11.1 Quantum Description of an Ideal Gas

The proper quantum description of N non-relativistic particles is given by an N particle wavefunction,

$$\psi_{\mathcal{R}} = \psi_{a_1,a_2,...,a_f}(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) \tag{11.1.1}$$

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[1] We confine ourselves to non-relativistic systems in this book.

where the $a_j \in \mathcal{R}$ represent a set of quantum numbers characteristic of the system and the $\vec{r}_k$ are the classical "position" variables associated with the particles. We will think of the coordinates as labeling them. The wave function satisfies Schroedinger's equation

$$i\hbar\frac{\partial\psi_{\mathcal{R}}}{\partial t} = \widehat{\mathcal{H}}\psi_{\mathcal{R}} \tag{11.1.2}$$

where $\widehat{\mathcal{H}}$ is the "Hamiltonian" or energy operator of the system and takes the form

$$\widehat{\mathcal{H}} = -\hbar^2\sum_{j=1}^{N}\frac{\vec{\nabla}_j^2}{2m_j} + V(\vec{r}_1, ...\vec{r}_N). \tag{11.1.3}$$

The potential energy function, $V(\vec{r}_1, ..., \vec{r}_N)$, is generally quite complicated as we have already seen in the case of the Lennard-Jones potential. However, if we are considering a gas of non-interacting particles, the potential energy breaks up nicely as a sum over the individual particle potential energies, which arise due to the presence of some external field,

$$V(\vec{r}_1, ..., \vec{r}_N) = \sum_{j=1}^{N} V(\vec{r}_j) \Rightarrow \widehat{\mathcal{H}} = \sum_{j=1}^{N}\left(-\hbar^2\frac{\vec{\nabla}_j^2}{2m_j} + V(\vec{r}_j)\right), \tag{11.1.4}$$

and Schroedinger's equation takes the very simple form

$$i\hbar\frac{\partial\psi_{\mathcal{R}}}{\partial t} = -\hbar^2\sum_{j=1}^{N}\frac{\vec{\nabla}_j^2}{2m_j}\psi_{\mathcal{R}} + \sum_{j=1}^{N} V(\vec{r}_j)\psi_{\mathcal{R}} \tag{11.1.5}$$

The equation can be solved by the method of separation of variables and the linearity of Schroedinger's equation ensures that every solution will be a linear combination of solutions of the form

$$\psi_{\mathcal{R}} = \prod_{j=1}^{N}\psi_{\alpha^j}(\vec{r}_j), \tag{11.1.6}$$

where $\alpha^j = \{a_1^j, \ldots, a_f^j\}$ is the set of quantum numbers associated with particle j and each function, $\psi_{\alpha^j}(\vec{r}_j)$, in the product satisfies the single particle Schroedinger equation.[2]

If the particles are identical in all their physical properties and the external potentials have the same form for all the particles, they will share the same set of quantum numbers, $\mathcal{R}$. Let particle "1" be in state α and particle "2" in β, then the wavefunction of the system of two particles will be

$$\psi_{\alpha,\beta}^{1,2} = \psi_\alpha^1\psi_\beta^2. \tag{11.1.7}$$

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[2] Problem: Prove this for two particles. Then extend the proof to an arbitrary number of particles by induction.

Vice-versa if "1" is in state β an 2 in state α, then

$$\psi^{1,2}_{\beta,\alpha} = \psi^1_\beta \psi^2_\alpha \tag{11.1.8}$$

is now the state of the system. The wave function that describes the two particles will in general be a linear combination of the two. To say that the particles are distinguishable is to insist that $\psi^{1,2}_{\alpha,\beta} \neq \psi^{1,2}_{\beta,\alpha}$.

However, if the particles are not simply identical but also *indistinguishble*, then whether "1" is in α and "2" in β or vice-versa should have no physical outcome. This in turn implies that the linear combination that makes up the wave function describing the two particles should satisfy

$$|\psi^{1,2}_{\alpha,\beta}|^2 = |\psi^{1,2}_{\beta,\alpha}|^2, \tag{11.1.9}$$

because $|\psi^{1,2}_{\alpha,\beta}|^2$ represents the probability of finding particle "1" in state α and particle "2" in state β and vice-versa $|\psi^{1,2}_{\beta,\alpha}|^2$ represents the probability of finding particle "1" in state β and particle "2" in state α. Thus the correct solution to Schroedinger's equation satisfying indistinguishability cannot be either of the states in (11.1.7) and (11.1.8). Indeed, (11.1.9) implies that

$$\psi^{1,2}_{\alpha,\beta} = e^{i\phi}\psi^{1,2}_{\beta,\alpha}. \tag{11.1.10}$$

and neither solution obeys this condition. What can we say about the phase? The spin-statistics theorem[3] guarantees that only two values for ϕ are possible, *viz.,* $\phi = 0$ and $\phi = \pi$. Thus wave functions describing indistinguishable particles can only satisfy one of two conditions

$$\psi^{1,2}_{\alpha,\beta} = \pm\psi^{1,2}_{\beta,\alpha} \tag{11.1.11}$$

i.e., they must either be **symmetric** functions or **antisymmetric** functions under exchanges of "1" and "2",

$$\begin{aligned}
\psi_{S;\alpha,\beta}^{1,2} &= \frac{1}{\sqrt{2}}\left[\psi^1_\alpha\psi^2_\beta + \psi^1_\beta\psi^2_\alpha\right] \\
\psi_{A;\alpha,\beta}^{1,2} &= \frac{1}{\sqrt{2}}\left[\psi^1_\alpha\psi^2_\beta - \psi^1_\beta\psi^2_\alpha\right].
\end{aligned} \tag{11.1.12}$$

Note that it is impossible to find particles described by the antisymmetric wave function in the same state, since $\psi_{A;\alpha,\alpha}^{1,2}$ vanishes identically. On the other hand the probability of finding particles described by symmetric wavefunctions in the same state is not only von-vanishing but indeed *enhanced* over the probability of finding distinguishable (Boltzmann) particles in the same state because

$$|\psi_{S;\alpha,\alpha}^{1,2}|^2 = 2|\psi^1_\alpha|^2|\psi^2_\alpha|^2. \tag{11.1.13}$$

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[3] The spin-statistics theorem has its origins in relativistic quantum field theory. It was first systematically derived by W. Pauli and later re-derived by J. Schwinger and R. Feynman.

We call particles described by symmetric wavefunctions **Bosons** after Satyendranath Bose who first proposed statistics in which indistinguishability had to be taken into account. Particles described by antisymmetric wavefunctions are called **Fermions** after Enrico Fermi.

It is evident that the distribution functions of systems of non-interacting particles will differ depending on whether or not they are distinguishable in the first place and secondly, if they are indistinguishable, whether they are Bosons or Fermions. But how do we take indistinguishability into account? This is the question we now address, first heuristically and then rigorously in two ways: (i) combinatorically and (ii) via the partition function.

11.2 Heuristic Considerations

Let us begin with a heuristic approach, determining the number distribution between states by comparing the N particle wave functions. For distinguishable (Boltzmann) particles, the N particle wave function is

$$\psi(1,\ldots,N) = \psi^1_{\alpha_1}\psi^2_{\alpha_2}\psi^3_{\alpha_3}\ldots\psi^N_{\alpha_N}, \tag{11.2.1}$$

where we assume that each single particle wave-function is normalized. Therefore, the amplitude for finding all N particles in the state α is just

$$\psi(1,\ldots,N) = \psi^1_{\alpha}\psi^2_{\alpha}\psi^3_{\alpha}\ldots\psi^N_{\alpha}. \tag{11.2.2}$$

On the other hand for Bosons the N particle wave-function should be

$$\psi_S(1,\ldots,N) = \frac{1}{\sqrt{N!}}\sum_{\{\sigma\}}\psi^{\sigma_1}_{\alpha_1}\psi^{\sigma_2}_{\alpha_2}\ldots\psi^{\sigma_N}_{\alpha_N} \tag{11.2.3}$$

where $\{\sigma\}$ is the set of all permutations of $\{1,2,\ldots,N\}$ and $\vec{\sigma}$ is a particular permutation, $\vec{\sigma} = (\sigma_1,\sigma_2,\ldots,\sigma_N)$. Since there are $N!$ permutations of N particles, the amplitude for finding all the particles in the same state,

$$\psi(1,\ldots,N) = \sqrt{N!}\ \psi^1_{\alpha}\psi^2_{\alpha}\ldots\psi^N_{\alpha}, \tag{11.2.4}$$

is enhanced over the Boltzmann case by a factor of $\sqrt{N!}$. Comparing the two amplitudes, we conclude that the probability of finding a state α of energy E_α containing n_α Bosons will be

$$P^B_\alpha(n_\alpha) = n_\alpha!(P^M_\alpha)^{n_\alpha}, \tag{11.2.5}$$

where $(P^M_\alpha)^{n_\alpha}$ is the probability of finding n_α distinguishable particles in the state α. Likewise

$$P^B_\alpha(n_\alpha+1) = (n_\alpha+1)!(P^M_\alpha)^{n_\alpha+1} = [(n_\alpha+1)P^M_\alpha](P^B_\alpha(n_\alpha)) \tag{11.2.6}$$

is the probability of finding the same state containing $n_\alpha + 1$ Bosons. We can say that the probability of *adding* a boson to a state α which already contains n_α bosons is

$$\mathcal{P}^B_\alpha = (n_\alpha + 1)P^M_\alpha \tag{11.2.7}$$

and depends on n_α. But, since $P^M_\alpha = Ce^{-\beta E_\alpha}$,

$$\mathcal{P}^B_\alpha = (n + 1)Ce^{-\beta E_\alpha} \tag{11.2.8}$$

Now consider particles distributed in two states, α and β. In equilibrium we require detailed balance, *i.e.,* the number of Bosons leaving state α should be equal to the number of Bosons entering it, or $n_\alpha \mathcal{P}^B_{\alpha\to\beta} = n_\beta \mathcal{P}^B_{\beta\to\alpha}$. This means that

$$\frac{n_\alpha}{n_\beta} = \frac{\mathcal{P}^B_{\beta\to\alpha}}{\mathcal{P}^B_{\alpha\to\beta}} \tag{11.2.9}$$

and therefore, using (11.2.8),

$$\frac{n_\alpha}{n_\beta} = \frac{(n_\alpha + 1)e^{-E_\alpha/kT}}{(n_\beta + 1)e^{-E_\beta/kT}}. \tag{11.2.10}$$

Gathering factors, this can be re-expressed as

$$\frac{n_\alpha e^{E_\alpha/kT}}{(n_\alpha + 1)} = \frac{n_\beta e^{E_\beta/kT}}{(n_\beta + 1)} \tag{11.2.11}$$

but, because the states α and β were arbitrary to begin with, the above statement can be true only if each side of the equation is equal to the same constant so we can say that

$$\frac{n_\alpha e^{E_\alpha/kT}}{(n_\alpha + 1)} = e^{-a}, \tag{11.2.12}$$

for some a that does not depend on the states. Solving for n_α, we obtain a distribution of particles appropriate for Bosonic particles,

$$n_\alpha = \frac{1}{e^{a+E_\alpha/kT} - 1}. \tag{11.2.13}$$

Notice that when $\beta E_\alpha \gg -a$, the exponential term in the denominator dominates and

$$n_\alpha \approx e^{-a-E_\alpha/kT} \tag{11.2.14}$$

which is the Maxwell-Boltzmann distribution. Therefore the Bosonic number distribution approaches the Maxwell-Boltzmann distribution and Bosons will behave more or less like distinguishable particles at high enough temperatures.

Wave functions describing Fermions must be totally antisymmetric, of the form

$$\psi_A(1,\ldots,N) = \frac{1}{\sqrt{N!}}\sum_{\{\sigma\}}(-)^\sigma \psi^{\sigma_1}_{\alpha_1}\psi^{\sigma_2}_{\alpha_2}\ldots\psi^{\sigma_N}_{\alpha_N}, \tag{11.2.15}$$

where $(-)^\sigma = +1$ if the permutation is even and $(-)^\sigma = -1$ if it is odd. Since no two particles can be in the same state, the probability to *add* a Fermion to a state α which already contains n_α Fermions must be zero unless $n_\alpha = 0$. We can express this as

$$\mathcal{P}^F_\alpha = (1-n_\alpha)P^M_\alpha \tag{11.2.16}$$

and detailed balance will now require that

$$\frac{n_\alpha}{n_\beta} = \frac{\mathcal{P}^B_{\beta\to\alpha}}{\mathcal{P}^B_{\alpha\to\beta}} = \frac{(1-n_\alpha)e^{-E_\alpha/kT}}{(1-n_\beta)e^{-E_\beta/kT}}. \tag{11.2.17}$$

or that

$$\frac{n_\alpha e^{-E_\alpha/kT}}{1-n_\alpha} = e^{-a} \tag{11.2.18}$$

for some constant, a. This can be simplified to give the Fermi-Dirac distribution,

$$n_\alpha = \frac{1}{e^{a+E_\alpha/kT}+1}, \tag{11.2.19}$$

and again, when $\beta E_\alpha \gg -a$, the exponential term in the denominator dominates giving

$$n_\alpha \approx e^{-a-E_\alpha/kT}. \tag{11.2.20}$$

This shows that Fermions also behave as distinguishable (Maxwell-Boltzmann) particles when the temperature is sufficiently high.

11.3 Combinatoric Derivation of the Distribution Functions

The number distributions derived above can be obtained more rigorously via a combinatoric analysis. To introduce the approach we begin by examining the following experiment. Balls are thrown into a box at random so that no part of the box is favored. Suppose that the box is divided into K cells, of volume v_1, v_2,…, v_K. If, after throwing N balls we find that there are n_1 balls in v_1, n_2 balls in v_2 and so on, we will say that the system is in the state $\{n_1, n_2, n_3, \ldots, n_K\}$, *i.e.,* a state of the system is a particular distribution of the N balls among the K cells. We want to answer the following question: what is the most likely distribution of the balls within the cells, subject to the constraints

$$\sum_{j=1}^K n_j = N, \quad \sum_{j=1}^K v_j = V \tag{11.3.1}$$

Assuming that the balls are thrown randomly, the *à priori* probability that a ball will fall into cell v_j is just

$$p_j = \frac{v_j}{V} \tag{11.3.2}$$

Since every ball is thrown independently of the other the probability of finding n_j balls in volume v_j at the end of the experiment is $p_j^{n_j}$ and the *à priori* probability of having precisely n_1 balls in v_1, n_2 balls in v_2, etc., *i.e.,* the *state* $\{n_1, n_2, \ldots, n_K\}$, will be

$$p = \prod_{j=1}^{K} p_j^{n_j} \tag{11.3.3}$$

Now because the N balls are distinguishable, there are actually

$$W = \frac{N!}{n_1!n_2!\ldots n_K!} \tag{11.3.4}$$

ways in which the state $\{n_1, n_2, \ldots, n_K\}$ may be formed. Therefore the probability of finding the state $\{n_1, n_2, \ldots, n_K\}$ will be

$$P_{\{n_1,n_2,\ldots,n_K\}} = \frac{N!}{n_1!n_2!\ldots n_K!} p_1^{n_1} p_2^{n_2} \ldots p_K^{n_K} \tag{11.3.5}$$

We should check this result by verifying that the probability for *any* state is unity. Summing over all possible distributions,

$$\begin{aligned} \sum_{n_1,n_2,\ldots,n_K} P_{\{n_1,n_2,\ldots,n_K\}} &= \sum_{n_1,n_2,\ldots,n_K} \frac{N!}{n_1!n_2!\ldots n_K!} p_1^{n_1} p_2^{n_2} \ldots p_K^{n_K} \\ &= (p_1 + p_2 + \ldots + p_K)^N = 1 \end{aligned} \tag{11.3.6}$$

where we have used the multinomial theorem in writing the second equality. Now we might ask: what is the most probable distribution of balls? This is given by the variation of $P_{\{n_1,n_2,\ldots,n_K\}}$ with respect to the occupation numbers n_1, n_2, etc., holding the total number of balls, N, fixed. It's more convenient to vary the natural logarithm of the probability $P_{\{n_1,n_2,\ldots,n_K\}}$. Since

$$\begin{aligned} \ln P_{\{n_1,n_2,\ldots,n_K\}} &= N \ln N - N + \sum_{j=1}^{K} (n_j \ln p_j - n_j \ln n_j + n_j) \\ &= N \ln N + \sum_{j=1}^{K} (n_j \ln p_j - n_j \ln n_j) \end{aligned} \tag{11.3.7}$$

the variation gives

$$\delta \ln P_{\{n_1,n_2,\ldots,n_K\}} = \sum_{j=1}^{K}[\ln p_j - \ln n_j - 1]\delta n_j = \sum_{j=1}^{K}[\ln p_j - \ln n_j]\delta n_j \quad (11.3.8)$$

when N is held fixed (therefore the variations are not all independent and must satisfy $\sum_j \delta n_j = 0$). This implies that for every cell

$$\ln p_j - \ln n_j + \alpha = 0, \quad (11.3.9)$$

where α is a constant, the same for all cells. Exponentiation gives

$$n_j = p_j e^{\alpha} \quad (11.3.10)$$

and α is determined by summing over all cells. Since $\sum_j n_j = N$ and $\sum_j p_j = 1$ we find $N = e^{\alpha}$ and thus

$$n_j = N p_j \quad (11.3.11)$$

is the most probable distribution.

Let us now use this reasoning for a situation of greater physical interest. Consider a gas of N distinguishable particles with fixed total energy E and think of the cells in the previous example as cells in phase space, each corresponding to an energy u_j. Let the N particles be distributed among the cells so that n_1 particles are in cell "1", n_2 in cell "2" etc., forming the state $\{n_1, n_2, \ldots, n_K\}$ as before and require that

$$\begin{aligned} \sum_j n_j = N &\Rightarrow \sum_j \delta n_j = 0 \\ \sum_j n_j u_j = E &\Rightarrow \sum_j \delta n_j u_j = 0. \end{aligned} \quad (11.3.12)$$

Since the particles are distinguishable there are

$$W = \frac{N!}{n_1! n_2! \ldots n_K!} \quad (11.3.13)$$

possible ways to form the state $\{n_1, n_2, \ldots, n_K\}$. Allow each cell to have an additional degeneracy. This is reasonable because, for example, two particles can have different momenta and yet possess the same total energy. But if we allow for an extra degeneracy *within* each cell then we are led to think of each cell as made up of sub-cells such that any different distribution of the particles in the cell among the sub-cells leads to a different state. Let cell j have degeneracy g_j. Then in cell j the first particle could be in any of g_j states, the second in any of g_j states and so on for every one of the n_j particles. In other words the number of distinguishable states within cell j will be $(g_j)^{n_j}$.[4] Therefore the total number of states becomes

$$\Omega = \frac{N!}{n_1!n_2!\dots n_K!} g_1^{n_1} g_2^{n_2} \dots g_K^{n_K} \tag{11.3.14}$$

Our aim is to find the distribution that maximizes Ω subject to the constraints in (11.3.12), so we use the method of Lagrange multipliers. Thus we define the function

$$\begin{aligned} f(n_1, \dots, n_K; \alpha, \beta) &= \ln \Omega - \alpha(N - \sum_j n_j) + \beta(E - \sum_j n_j u_j) \\ &= N \ln N - N - \sum_j (n_j \ln n_j - n_j - n_j \ln g_j) \\ &\qquad + \alpha(N - \sum_j n_j) + \beta(E - \sum_j n_j u_j), \end{aligned} \tag{11.3.15}$$

where α and β are Lagrange multipliers, and set its variation to zero. This procedure gives

$$[\ln n_j - \ln g_j + \alpha + \beta u_j] = 0 \Rightarrow n_j^{\mathrm{M}} = g_j e^{-\alpha - \beta u_j} \tag{11.3.16}$$

for each j. What physical meaning do the Lagrange multipliers have? To find out, consider a classical, ideal gas, for which each cell is simply a volume $d^3\vec{r}\, d^3\vec{p}$ of phase space. The degeneracy of each cell represents the number of distinguishable phase space sub-cells (of volume h_o^3) that each cell contains,

$$g_j \to \frac{1}{h_o^3}\, d^3\vec{r}\, d^3\vec{p} \tag{11.3.17}$$

The energy of each cell is just

$$u_j \to u = \frac{\vec{p}_j^{\,2}}{2m} \tag{11.3.18}$$

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[4] Another way to think of this is as follows: there are

$$\frac{n_j!}{n_j^1! n_j^2! \dots n_j^{g_j}}$$

ways for the n_j particles in cell j to be distributed among the g_j sub-cells such that n_j^1 particles are in sub-cell "1" of j, n_j^2 particles in sub-cell "2" of j, etc. The total number of ways to distribute the cells is then the sum over all possible distributions among the sub-cells, *i.e.,*

$$\sum_{n_j^1, \dots, n_j^{g_j}} \frac{n_j!}{n_j^1! n_j^2! \dots n_j^{g_j}} \equiv (g_j)^{n_j}$$

by the multinomial theorem.

and the number of particles must be

$$n_j \to dn = \frac{1}{h_o^3}\, d^3\vec{r}\, d^3\vec{p}\, e^{-\alpha-\beta\vec{p}^2/2m} \tag{11.3.19}$$

It follows that the total number of particles is

$$N = \int dn = \frac{e^{-\alpha}}{h_o^3} \int d^3\vec{r}\, d^3\vec{p}\, e^{-\beta\vec{p}^2/2m} = Ve^{-\alpha}\left(\frac{2\pi m}{\beta h_o^2}\right)^{3/2} \tag{11.3.20}$$

Solving the above for α and inserting the solution into (11.3.19) we find

$$dn = 4\pi N\left(\frac{\beta}{2\pi m}\right)^{3/2} p^2 e^{-\beta p^2/2m} dp \tag{11.3.21}$$

assuming isotropy. Another equation may be obtained by computing the energy

$$E = \int u dn = 8\pi N m\left(\frac{\beta}{2\pi m}\right)^{3/2} \int_0^\infty \left(\frac{p^2}{2m}\right)^2 e^{-\beta p^2/2m} dp = \frac{3N}{2\beta}. \tag{11.3.22}$$

By comparison with the kinetic theory we now know that $\beta = 1/kT$. Further comparison also shows that $\alpha = -\beta\mu$, where μ is the chemical potential.

Thus we have recovered the Maxwell Boltzmann distribution. Our only physical inputs have been the conservation of particle number and total energy. The next question is this: how can these methods be expanded to describe indistinguishable particles? If we have N indistinguishable particles then there is *only one* way to distribute them into energy cells so that n_1 is in cell "1", n_2 in cell "2", etc. However, care must be taken in accounting for an additional degeneracy within each cell. We deal with this problem exactly as we dealt with the harmonic oscillators, by considering distinguishable arrangements of n_j indistinguishable particles among g_j possible sub-cells, which will be

$$\Omega_j = \frac{(n_j + g_j - 1)!}{n_j!(g_j - 1)!} \tag{11.3.23}$$

(compare this with $g_j^{n_j}$ for n_j distinguishable particles) and so the total number of states is

$$\Omega = \prod_j \frac{(n_j + g_j - 1)!}{n_j!(g_j - 1)!}. \tag{11.3.24}$$

As before we are interested in the distribution that maximizes Ω subject to (11.3.12), so we consider the function

$$f(n_1, \ldots, n_K; \alpha, \beta) \quad = \quad \ln\Omega - \alpha(N - \sum_j n_j) + \beta(E - \sum_j n_j u_j)$$

$$= \sum_j [(n_j + g_j - 1)\ln(n_j + g_j - 1) - n_j \ln n_j - (g_j - 1)\ln(g_j - 1)] \\ + \alpha(N - \sum_j n_j) + \beta(E - \sum_j n_j u_j) \qquad (11.3.25)$$

instead and set its variation to zero to find

$$\ln(n_j + g_j - 1) - \ln n_j - \alpha - \beta u_j = 0 \Rightarrow n_j^{\mathrm{B}} = \frac{g_j}{e^{\alpha+\beta u_j} - 1}. \qquad (11.3.26)$$

This is the distribution appropriate for Bosons. When $\beta u_i \gg -a$ the distribution approximates to

$$n_i^{\mathrm{B}} \approx e^{-\alpha-\beta u_i}, \qquad (11.3.27)$$

which compares with the Maxwell-Boltzmann distribution if $\beta = 1/kT$ and $\alpha = -\beta\mu$, where μ is the chemical potential. As before, α can be recovered by summing over all occupation numbers.

The number distribution appropriate for Fermions can be obtained similarly. The particles continue to be distinguishable, but this time no more than *one* particle may occupy any particular sub-cell. As before the number of ways in which N particles may be distributed so that n_1 particles lie in cell "1", n_2 in cell "2" etc., is still one because they are indistinguishable, but we must account for the degeneracy within each cell. Since no state in the cell may have more than a single fermion, the number of particles in any cell cannot be larger than the degeneracy associated with that cell ($n_j \leq g_j$) and we can think of the sub-cells as either occupied or empty. In all there will be n_j occupied sub-cells and $(g_j - n_j)$ empty ones. We determine the number of distinguishable states (within each cell) by counting all possible arrangements of n_j "occupied" sub-cells and $(g_j - n_j)$ empty sub-cells,

$$\Omega_j = \frac{g_j!}{n_j!(g_j - n_j)!} \qquad (11.3.28)$$

Performing the same steps as before we find

$$n_j^{\mathrm{F}} = \frac{g_j}{e^{\alpha+\beta u_j} + 1}. \qquad (11.3.29)$$

Again, when $\beta u_i \gg -a$, the distribution approximates to

$$n_j^{\mathrm{F}} \approx e^{-\alpha-\beta u_j}, \qquad (11.3.30)$$

which compares with the Maxwell-Boltzmann distribution if $\beta = 1/kT$ and $\alpha = -\beta\mu$, where μ is the chemical potential. Both the Bose and the Fermi distributions approach the Maxwell Boltzmann distribution at sufficiently high temperature.

11.4 The Partition Function

As we saw in the combinatoric analyses above, each state of a gas is a particular distribution of particles between available energy levels. If we call the energies of these levels ε_i then a typical state is of the form $\{n_1, n_2, \ldots, n_j, \ldots\}$, where n_j particles have energy ε_j. If the particles are distinguishable, then each state has a degeneracy of

$$g(n_1, n_2, \ldots, n_j, \ldots) = \frac{N!}{n_1! n_2! \ldots n_j! \ldots} \tag{11.4.1}$$

and if they are indistinguishable, then

$$g(n_1, n_2, \ldots, n_j, \ldots) = 1. \tag{11.4.2}$$

We will refer to the set of all states (distinguishable distributions) by $\aleph$, then the following relations must be hold

$$\begin{aligned} N_\aleph &= \sum_i n_i \\ E_\aleph &= \sum_i n_i \varepsilon_i \end{aligned} \tag{11.4.3}$$

and the partition function can be written as

$$\Xi(\beta, \mu, \vec{X}) = \sum_\aleph e^{-\beta(E_\aleph - \mu N_\aleph)}, \tag{11.4.4}$$

where μ is the chemical potential. Writing this out explicitly,

$$\Xi(\beta, \mu, \vec{X}) = \sum_N \sum_{n_1, n_2, \ldots, n_j, \ldots} g(n_1, n_2, \ldots, n_j, \ldots) e^{-\beta \sum_j n_j(\varepsilon_j - \mu)}, \tag{11.4.5}$$

where $\sum_j n_j = N$. Then using a property of the exponential we turn the sum in the exponent into a product, expressing it in the more useful form

$$\Xi(\beta, \mu, \vec{X}) = \sum_N \sum_{n_1, n_2, \ldots, n_j, \ldots} g(n_1, n_2, \ldots, n_j, \ldots) \prod_j e^{-\beta n_j(\varepsilon_j - \mu)}. \tag{11.4.6}$$

To see that this makes sense, we first address the case of distinguishable particles, for which we have some familiarity. In this case, $g(n_1, \ldots)$ is given in (11.4.1) and

$$\Xi^{\mathrm{M}}(\beta, \mu, \vec{X}) = \sum_N \sum_{n_1, n_2, \ldots, n_j, \ldots} \frac{N!}{n_1! n_2! \ldots n_j! \ldots} e^{-\beta n_1(\varepsilon_1 - \mu)} e^{-\beta n_2(\varepsilon_2 - \mu)} \ldots e^{-\beta n_j(\varepsilon_j - \mu)} \ldots \tag{11.4.7}$$

By the multinomial theorem this is just

$$\begin{aligned}\Xi^{\mathrm{M}}(\beta,\mu,\vec{X}) &= \sum_N \left(e^{-\beta n_1(\varepsilon_1-\mu)} + e^{-\beta n_2(\varepsilon_2-\mu)} + \ldots + e^{-\beta n_j(\varepsilon_j-\mu)} + \ldots +\right)^N \\ &= \sum_N \left(\sum_j e^{-\beta(\varepsilon_j-\mu)}\right)^N = \sum_N e^{\beta\mu N} Z_N \qquad (11.4.8)\end{aligned}$$

where Z_N is the canonical partition function for N particles. Alternatively, since $Z_N = Z_1^N$, where Z_1 is the *single particle* partition function,

$$\Xi^{\mathrm{M}}(\beta,\mu,\vec{X}) = \sum_N (e^{\beta\mu} Z_1)^N = \frac{1}{1-e^{\beta\mu}Z_1} = \frac{1}{1-\sum_j e^{-\beta(\varepsilon_j-\mu)}} \qquad (11.4.9)$$

The answer is somewhat different if we take into account Gibb's correction, for then

$$\Xi^{\mathrm{M}}(\beta,\mu,\vec{X}) = \sum_N \frac{(e^{\beta\mu}Z_1)^N}{N!} = \exp\left(e^{\beta\mu}Z_1\right) \qquad (11.4.10)$$

and so

$$\Xi^{\mathrm{M}}(\beta,\mu,\vec{X}) = \exp\left(\sum_j e^{-\beta(\varepsilon_j-\mu)}\right) = \prod_j \exp\left(e^{-\beta(\varepsilon_j-\mu)}\right) \qquad (11.4.11)$$

when the particles are classically indistinguishable.

For Bosons, $g(n_1,\ldots) = 1$ and we end up with

$$\Xi^{\mathrm{B}}(\beta,\mu,\vec{X}) = \sum_{n_1,n_2,\ldots,n_j,\ldots} \prod_j e^{-\beta n_j(\varepsilon_j-\mu)} \equiv \prod_j \sum_{n_j=0}^{\infty} e^{-\beta n_j(\varepsilon_j-\mu)}. \qquad (11.4.12)$$

We have interchanged the product and sum above and allowed the occupation numbers to run all the way to infinity. Thus we get

$$\Xi^{\mathrm{B}}(\beta,\mu,\vec{X}) = \prod_j \left(1-e^{-\beta(\varepsilon_j-\mu)}\right)^{-1} \qquad (11.4.13)$$

for the partition function for a gas of Bosons.

A Fermi gas can be treated similarly, except that n_j in the sum can only take values zero and one. Thus

$$\Xi^{\mathrm{F}}(\beta,\mu,\vec{X}) = \prod_j \left(1+e^{-\beta(\varepsilon_j-\mu)}\right) \qquad (11.4.14)$$

is the partition function that describes Fermions.

Let us now check that these partition functions yield the number distributions that we derived earlier. From the defining equation in (11.4.5) we could obtain the average distribution from

$$\langle n_j \rangle = -\frac{1}{\beta}\frac{\partial \ln \Xi}{\partial \varepsilon_j} \tag{11.4.15}$$

in each case. Thus, for particles obeying Maxwell-Boltzmann statistics and (classical or Gibb's) indistinguishability,

$$\langle n_j^{\mathrm{M}} \rangle = -\frac{1}{\beta}\frac{\partial}{\partial \varepsilon_j}\sum_i e^{-\beta(\varepsilon_i-\mu)} = \sum_i \delta_{ij} e^{-\beta(\varepsilon_i-\mu)} = e^{-\beta(\varepsilon_j-\mu)}. \tag{11.4.16}$$

For Bosons,

$$\langle n_j^{\mathrm{B}} \rangle = -\frac{1}{\beta}\frac{\partial}{\partial \varepsilon_j}\sum_i \ln(1-e^{-\beta(\varepsilon_i-\mu)}) = \sum_i \frac{\delta_{ij} e^{-\beta(\varepsilon_i-\mu)}}{1-e^{-\beta(\varepsilon_i-\mu)}} \tag{11.4.17}$$

and simplifying

$$\langle n_j^{\mathrm{B}} \rangle = \frac{1}{e^{\beta(\varepsilon_j-\mu)}-1} \tag{11.4.18}$$

as we had before. Finally, for Fermions

$$\langle n_j^{\mathrm{F}} \rangle = -\frac{1}{\beta}\frac{\partial}{\partial \varepsilon_j}\sum_i \ln(1+e^{-\beta(\varepsilon_i-\mu)}) = \sum_i \frac{\delta_{ij} e^{-\beta(\varepsilon_i-\mu)}}{1+e^{-\beta(\varepsilon_i-\mu)}} \tag{11.4.19}$$

or

$$\langle n_j^{\mathrm{F}} \rangle = \frac{1}{e^{\beta(\varepsilon_j-\mu)}+1}. \tag{11.4.20}$$

In each case, we should find that

$$\langle N \rangle = \sum_j \langle n_j \rangle = \frac{1}{\beta}\frac{\partial \ln \Xi}{\partial \mu}, \tag{11.4.21}$$

where $\langle N \rangle$ refers to the average total number of particles. We now want to discuss some physical properties of the distributions.

11.5 Physical consequences of the Distributions

Although all distributions asymptotically approach the Maxwell-Boltzmann distribution in the limit of high temperature, it is worth analyzing their behavior is detail. There are three possible distributions,

$$\langle n_i^{\mathrm{M}} \rangle = g_i e^{-\beta(\varepsilon_i-\mu)}$$

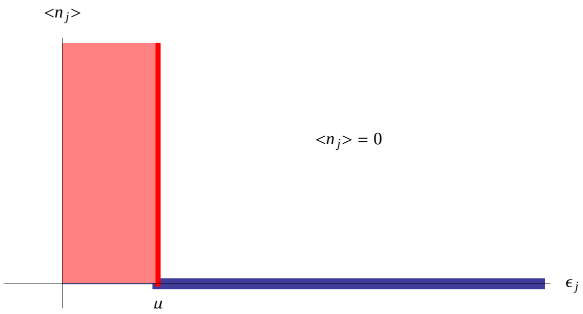

Figure 11.1: Maxwell-Boltzmann distribution at $T = 0$

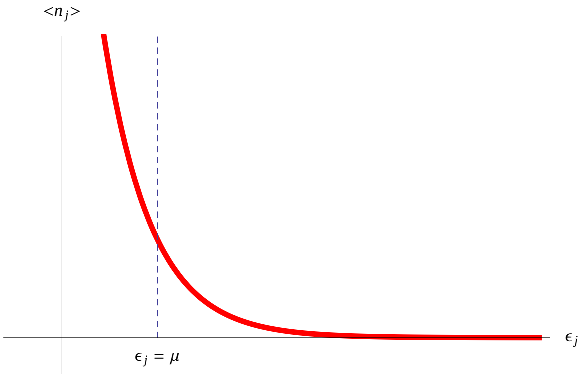

Figure 11.2: Maxwell-Boltzmann distribution when $T > 0$

$$\begin{aligned}\langle n_i^{\mathrm{B}} \rangle &= \frac{g_i}{e^{\beta(\varepsilon_i - \mu)} - 1} \\ \langle n_i^{\mathrm{F}} \rangle &= \frac{g_i}{e^{\beta(\varepsilon_i - \mu)} + 1},\end{aligned} \tag{11.5.1}$$

written in terms of the chemical potential, $a = -\beta\mu$, which we wish to compare and contrast.

11.5.1 Maxwell-Boltzmann distribution

At low temperatures, as $T \to 0$, the number of Maxwell-Boltzmann particles in energy levels for which $\varepsilon_j < \mu$ approaches infinity,

$$\langle n_i^{\mathrm{M}} \rangle \xrightarrow{T \to 0} \infty \tag{11.5.2}$$

whereas it approaches zero in energy levels for which $\varepsilon_j > \mu$,

$$\langle n_i^{\mathrm{M}} \rangle \xrightarrow{T \to 0} 0 \tag{11.5.3}$$

so that *all* Maxwell-Boltzmann particles tend to distribute themselves in energy levels with $\varepsilon_j < \mu$ at $T = 0$. Two distinct cases arise for $T > 0$:

1. When $\varepsilon_j < \mu$
   (a) low temperature: $|\varepsilon_j - \mu| \gg kT \Rightarrow \langle n_i^{\mathrm{M}} \rangle \sim e^{-\beta(\varepsilon_j - \mu)} \to \infty$

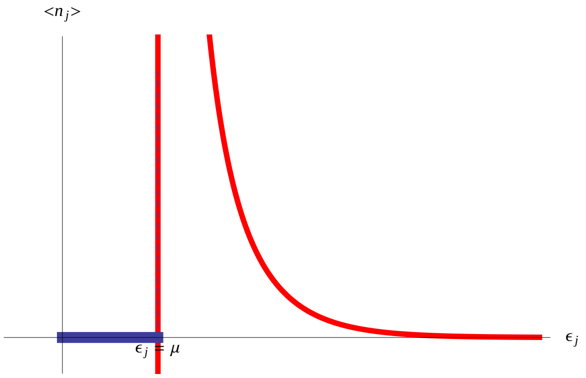

Figure 11.3: Bose-Einstein distribution for $T > 0$

   (b) high temperature: $|\varepsilon_j - \mu| \ll kT \Rightarrow \langle n_i^{\mathrm{M}} \rangle \sim e^{-\beta(\varepsilon_j - \mu)} \to 1$

2. When $\varepsilon_j > \mu$
   (a) low temperature: $|\varepsilon_j - \mu| \gg kT \Rightarrow \langle n_i^{\mathrm{M}} \rangle \sim e^{-\beta(\varepsilon_j - \mu)} \to 0$
   (b) high temperature: $|\varepsilon_j - \mu| \ll kT \Rightarrow \langle n_i^{\mathrm{M}} \rangle \sim e^{-\beta(\varepsilon_j - \mu)} \to 1$

Thus we get the following picture: as $T \to 0$ all particles tend to occupy only energy levels below the chemical potential. When $T > 0$ the the level occupancy of a state exponentially decreases with its energy. This behavior is shown in figures 11.1 and 11.2.

11.5.2 Bose-Einstein distribution

Particles in the Bose-Einstein distribution may *never* occupy energy levels below the chemical potential because for them $\langle n_j \rangle < 0$, which is nonsense. So we consider only states with $\varepsilon_j \geq \mu$ and note that for any temperature $\langle n_j \rangle \to \infty$ as $\varepsilon_j \to \mu$. Furthermore, at $T = 0$ no states may occupy energy levels above the chemical potential since $\langle n_j \rangle \to 0$, therefore as $T \to 0$ all Bosons tend to fall into just one energy level, the one with $\varepsilon_j = \mu$. As the temperature rises two possibilities emerge:

1. low temperature: $\beta(\varepsilon_j - \mu) \ll 1 \Rightarrow \langle n_j^{\mathrm{B}} \rangle \to \infty$, and
2. high temperature: $\beta(\varepsilon_j - \mu) \gg 1 \Rightarrow \langle n_j^{\mathrm{B}} \rangle \to e^{-\beta(\varepsilon_j - \mu)}$, which is the Maxwell-Boltzmann distribution.

We can summarize the behavior of Bosons in the following way: energy levels below the chemical potential can never be occupied. At zero temperature all Bosons “condense”

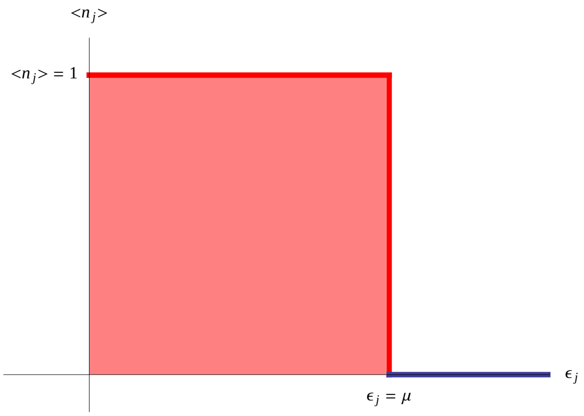

Figure 11.4: Fermi-Dirac distribution at $T = 0$

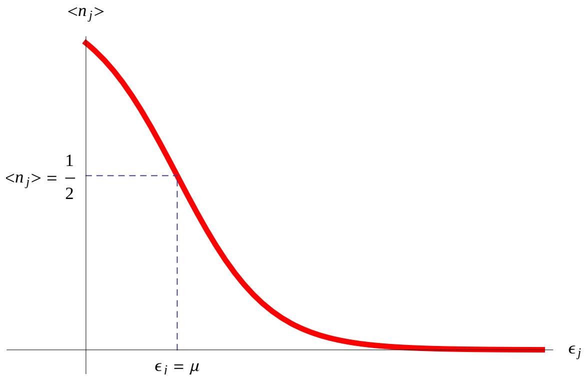

Figure 11.5: Fermi-Dirac distribution when $T > 0$

into the level whose energy is precisely the chemical potential. As the temperature rises energy levels above the chemical potential begin to be occupied, with the distribution approaching the Maxwell-Boltzmann distribution as $\beta|\varepsilon_j - \mu|$ gets smaller. This behavior is shown in figure 11.3.

11.5.3 Fermi-Dirac distribution

The Fermi-Dirac distribution behaves somewhat differently from both of the distributions described above. For $T = 0$,

1. if $\varepsilon_j < \mu \Rightarrow \langle n_j^{\mathrm{F}} \rangle \to 1$, and
2. if $\varepsilon_j > \mu \Rightarrow \langle n_j^{\mathrm{F}} \rangle \to 0$,

so at very low temperature Fermions will distribute themselves in the energy levels below the chemical potential, no two Fermions occupying a single particle state, and all the levels above μ are empty. At temperatures above absolute zero,

1. If $\varepsilon_j < \mu$ then
   (a) low temperature: $\beta|\varepsilon_j - \mu| \gg 1 \Rightarrow \langle n_j^{\mathrm{F}} \rangle \approx 1$, and
   (b) high temperature: $\beta|\varepsilon_j - \mu| \ll 1 \Rightarrow \langle n_j^{\mathrm{F}} \rangle \approx \frac{1}{2}$
2. If $\varepsilon_j > \mu$ then

(a) low temperature: $\beta|\varepsilon_j - \mu| \gg 1 \Rightarrow \langle n_j^{\mathrm{F}} \rangle \approx e^{-\beta(\varepsilon_j - \mu)}$, *i.e.,* the Maxwell-Boltzmann distribution, and

(b) high temperature: $\beta|\varepsilon_j - \mu| \ll 1 \Rightarrow \langle n_j^{\mathrm{F}} \rangle \approx \frac{1}{2}$

and so we get the following picture: at very low temperatures, only energy levels below the chemical potential will be occupied. As the temperature rises, energy levels above the chemical potential begin to be occupied, with the distribution approaching the Maxwell-Boltzmann distribution as $\beta|\varepsilon_j - \mu|$ gets smaller (see figures 11.4 and 11.5).

In all cases, the chemical potential will depend on the total number of particles, the temperature and other thermodynamic properties of the system and should be computed first. We will now embark upon a study of some elementary applications of these distributions and the new statistics implied by them.

Chapter 12

Quantum Gases

We will now consider some simple applications of quantum statistics, paying special attention to the central role played by indistinguishability. We begin by treating the simplest of all quantum systems, but an important one, the photon gas. Then we turn to the Bose and Fermi gases of massive particles and examine some consequences of quantum statistics.

12.1 The Photon Gas

A photon gas is a gas-like collection of photons and can be described by the same thermodynamic variables as an ordinary gas of particles, such as pressure, temperature and entropy. Because the energy of a photon, $E = hf$, where h is Planck's constant, is a function of the frequency and because the frequency itself varies smoothly from zero, photons of arbitrary small energy it can be created and added to the gas. As a consequence the chemical potential is identically zero and the photon number is not conserved. We think of f as labeling the energy level of a photon. In an ordinary gas, equilibrium is achieved by particle collisions with one another. Photons do not, however, interact so equilibrium is achieved by other means, *i.e.,* by the interaction of the photons with the matter in the bounding container or cavity, so the equilibriation time will be on the order of $\tau = L/c$, where L is the characteristic length dimension of the container. The thermodynamics of a photon gas in equilibrium at a temperature T is obtained via the Bose partition function in (11.4.12)

$$Z^{\mathrm{ph}}(T,V) = \prod_f (1 - e^{-\beta hf})^{-1} \tag{12.1.1}$$

where the product is over all frequencies. Photons obey Bose statistics and the number of photons of frequency f is given by the distribution function

$$\langle n^{\text{ph}} \rangle = \frac{1}{e^{\beta h f} - 1} \tag{12.1.2}$$

and we may compute the internal energy of the gas from the sum (dropping the superscript "ph" from now on)

$$\langle E \rangle = \sum_f \frac{hf}{e^{\beta h f} - 1}. \tag{12.1.3}$$

The sum over the number of states goes over to an integral in phase space

$$\sum_f \cdots \to \frac{g}{h^3} \left(\int_V d^3\vec{r} \right) \int d^3\vec{p} \ldots = \frac{4\pi g V}{h^3} \int dp\, p^2 \ldots \tag{12.1.4}$$

where g is the degeneracy associated with each phase-space cell. This can be re-written in terms of an integral over frequencies by using the dispersion relation $E = pc$. The degeneracy, g, counts the two polarizations of the photon and we find

$$\frac{8\pi V}{h^3} \int dp\, p^2 \ldots \quad = \quad \frac{8\pi V}{c^3} \int df\, f^2 \ldots \tag{12.1.5}$$

and the internal energy at temperature T is

$$\langle E \rangle = \frac{8\pi h V}{c^3} \int_0^\infty \frac{f^3 df}{e^{\beta h f} - 1}. \tag{12.1.6}$$

Transforming to the dimensionless variable $x = \beta h f$, allows us to extract the temperature dependence of the internal energy

$$\langle E \rangle = \frac{8\pi h V}{c^3 (\beta h)^4} \int_0^\infty \frac{x^3 dx}{e^x - 1}, \tag{12.1.7}$$

which evidently goes as T^4. Indeed, calling the integral (which is just a number) I_1 we have

$$\langle E \rangle = \frac{8\pi h V}{c^3} \left(\frac{kT}{h} \right)^4 I_1, \tag{12.1.8}$$

where

$$I_1 = \int_0^\infty \frac{x^3 dx}{e^x - 1} = \frac{\pi^2}{15}. \tag{12.1.9}$$

From these expressions we can derive Stefan's and Wien's laws of black body radiation quite easily. Define the **spectral** energy density as the energy density of photons (of both polarizations) with frequency between f and $f + df$ as

$$\mathcal{E}(f)df = \frac{8\pi h}{c^3}\frac{f^3 df}{e^{\beta hf} - 1} \tag{12.1.10}$$

and let $d\vec{S}$ represent an infinitesimal opening in a cavity, pointing (for convenience) in the $z-$direction. According to (10.2.13) and (12.1.10), the average radiation energy passing through the opening per unit time per unit area, with frequency between f and $f + df$, will be

$$\mathcal{F}(f)df = \frac{\langle d\Phi\rangle}{dS} = \langle c_z\rangle\mathcal{E}(f)df = \frac{8\pi h}{c^3}\langle c_z\rangle\frac{f^3 df}{e^{\beta hf} - 1}, \tag{12.1.11}$$

where $\langle c_z\rangle$ is the average value of the $z-$component of the photon velocity (in the positive $z-$direction). It is given by[1]

$$\langle c_z\rangle = c\langle\cos\theta\rangle = \frac{c}{4\pi}\int_0^{2\pi} d\phi \int_0^{\pi/2} d\theta \sin\theta\cos\theta = \frac{c}{4}, \tag{12.1.12}$$

so the radiation flux at frequencies lying between f and $f + df$ is

$$\mathcal{F}(f)df = \frac{2\pi h}{c^2}\frac{f^3 df}{e^{\beta hf} - 1}. \tag{12.1.13}$$

The function $\mathcal{F}(f)$ is called the **spectral radiancy** and is shown in figure 12.1 Several things are noteworthy about the curves shown: (i) they all have the same "shape", (ii) each peaks at a frequency characteristic *only* of the temperature and (iii) the area under each curve depends only on the temperature. Characteristics (ii) and (iii) are qualitative statements of Wien's displacement law and Stefan's law respectively. To see that the spectral radiancy peaks at a frequency that depends only on the temperature we note that the maximum of $\mathcal{F}(f)$ occurs at

$$f_{\max} = \frac{3 + \mathcal{W}(-3e^{-3})}{h\beta} \tag{12.1.14}$$

where $\mathcal{W}(x)$ is the Lambert "W" function, defined as the solution to the equation,[2]

$$x = \mathcal{W}(x)e^{\mathcal{W}(x)} \tag{12.1.15}$$

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[1] In this integral, $\theta \in [0, \pi/2]$ because we are only interested in the radiation flowing *out* of the cavity, which is assumed to open in the positive $z-$direction, so we count only half the solid angle.

[2] The Lambert function is single valued only when $x \geq 0$. Although it is real in the interval $x \in [-1/e, \infty)$, it is double valued when $x \in [-1/e, 0)$.

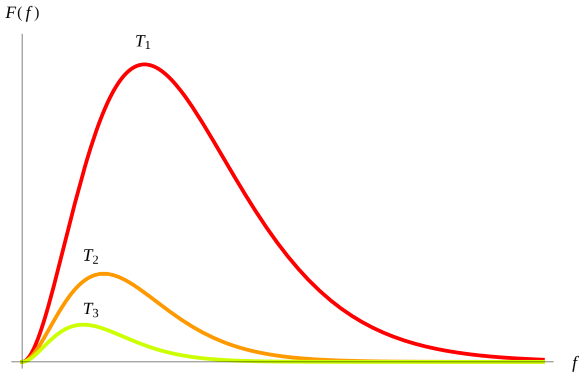

Figure 12.1: The photon radiation spectrum for temperatures $T_1 > T_2 > T_3$.

Numerically, we find

$$f_{\text{max}} \approx 5.87 \times 10^{10}\, T \ \ \text{Hz/K}. \tag{12.1.16}$$

The area under each spectral radiancy curve represents the total energy flux, which is

$$F = \int_0^\infty \mathcal{F}(f) df = \frac{2\pi h}{c^2} \int_0^\infty \frac{f^3 df}{e^{\beta h f} - 1} \tag{12.1.17}$$

and we could extract the temperature dependence by defining the dimensionless variable $x = \beta h f$, as before, but we already know the value of the integral so we determine Stefan's constant σ,

$$F = \sigma T^4, \quad \sigma = \frac{2\pi^5 k^4}{15 c^2 h^3}, \tag{12.1.18}$$

in terms of the fundamental constants. Numerically, Stefan's constant evaluates to $\sigma \approx 5.67 \times 10^{-8}\ \text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-4}$.

The entropy of the photon gas is calculated from the relation

$$\begin{aligned} S &= k(\ln Z + \beta\langle E\rangle) = k \sum_f \left[\ln(1 - e^{-\beta h f})^{-1} + \frac{\beta h f}{e^{\beta h f} - 1}\right] \\ &= \frac{8\pi k V}{c^3} \int_0^\infty df\, f^2 \left[-\ln(1 - e^{\beta h f}) + \frac{\beta h f}{e^{\beta h f} - 1}\right]. \end{aligned}$$

While both integrals can be evaluated exactly, it is possible to extract the temperature dependence of the entropy from both integrals by the same substitution we made earlier *i.e.,* $x = \beta h f$, without evaluating them. We find

$$S = \frac{8\pi k V}{c^3} \left(\frac{kT}{h}\right)^3 (I_2 - I_1) \tag{12.1.19}$$

where

$$\begin{aligned} I_1 &= \int_0^\infty dx\ x^2 \ln(1-e^{-x}) = -\frac{\pi^4}{45} \\ I_2 &= \int_0^\infty \frac{x^3 dx}{e^x - 1} = \frac{\pi^4}{15} \end{aligned}$$

It has the behavior that is expected by the third law as $T \to 0$. Further, using the expression for the internal energy in (12.1.8) we determine the free energy

$$F = \frac{8\pi h V}{c^3}\left(\frac{kT}{h}\right)^4 I_1 \tag{12.1.20}$$

and the pressure exerted by the gas of photons,

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = -\frac{8\pi h}{c^3}\left(\frac{kT}{h}\right)^4 I_1 = -\frac{I_2}{I_1}\frac{\langle E\rangle}{V} \equiv \frac{1}{3}\frac{\langle E\rangle}{V}, \tag{12.1.21}$$

which is seen to be positive and proportional to the energy density.

12.2 Non-relativistic Bose Gas

Except for photons it is a good practice to first determine the chemical potential in terms of the number of particles and the temperature. This can be done from the defining equation,

$$\sum_j \langle n_j \rangle = N = \sum_j \frac{1}{e^{\beta(\varepsilon_j - \mu)} - 1}. \tag{12.2.1}$$

Let us first consider a gas of bosonic particles in a cubic box of side L. The energy levels of a gas of free, non-relativistic particles, are quantized according to elementary quantum mechanics,

$$\varepsilon_{\vec{n}} = \frac{\pi^2\hbar^2}{2mL^2}(n_x^2 + n_y^2 + n_z^2) \tag{12.2.2}$$

where n_x, n_y and n_z are independent integers, each representing the quantization of momentum in one dimension. The two equations of interest,

$$\begin{aligned} N &= \sum_{\vec{n}} \frac{1}{e^{\beta(\varepsilon_{\vec{n}} - \mu)} - 1} \\ \langle E \rangle &= \sum_{\vec{n}} \frac{\varepsilon_{\vec{n}}}{e^{\beta(\varepsilon_{\vec{n}} - \mu)} - 1} \end{aligned} \tag{12.2.3}$$

are difficult to solve. Let us simplify the problem by restricting our attention to a one-dimensional box, say in the $x-$direction, and drop the suffix x, then we have

$$N = \sum_{n=0}^{\infty} \frac{1}{e^{\beta(qn^2-\mu)} - 1} \tag{12.2.4}$$

where $q = \pi^2\hbar^2/2mL^2$. We now introduce the **fugacity**, $\lambda = e^{\beta\mu}$ (if the ground state energy were not zero, but ε_0, then we would define the fugacity as $\lambda = e^{\beta(\mu-\varepsilon_0)}$) and re-express N in terms of λ as

$$N = \frac{\lambda}{1-\lambda} + \sum_{n=1}^{\infty} \frac{\lambda}{e^{\beta qn^2} - \lambda} \tag{12.2.5}$$

The second term represents all the particles in "excited" energy levels ($n \geq 1$) so the first term must represent the number of particles in the ground state. We call it N_0,

$$N_0 = \frac{\lambda}{1-\lambda} \tag{12.2.6}$$

and the remaining particles we call N_{ex} (for "excited")

$$N_{\text{ex}} = \sum_{n=1}^{\infty} \frac{\lambda}{e^{\beta qn^2} - \lambda} \tag{12.2.7}$$

so $N = N_0 + N_{\text{ex}}$ and we try to evaluate N_{ex} first. Clearly the fugacity must be less than one ($\mu < 0$), othewise (12.2.6) would make no sense. Therefore let us write

$$\sum_{n=1}^{\infty} \frac{\lambda}{e^{\beta qn^2} - \lambda} = \sum_{n=1}^{\infty} e^{-\beta qn^2} \frac{\lambda}{1 - \lambda e^{-\beta qn^2}} \tag{12.2.8}$$

and expand in a Maclaurin series to get

$$N_{\text{ex}} = \sum_{n=1}^{\infty}\sum_{r=1}^{\infty} \lambda^r e^{-\beta qn^2 r} \tag{12.2.9}$$

The best way to evaluate sums of this type is via the Mellin-Barnes representation of the exponential function by a integration in the complex plane (see the appendix)

$$e^{-\alpha} = \frac{1}{2\pi i} \int_{\tau-i\infty}^{\tau+i\infty} dt\ \Gamma(t)\alpha^{-t} \tag{12.2.10}$$

where $\Re(\alpha) > 0$ and the integral is over a line lying parallel with the imaginary axis and such that $\Re(\tau) > 0$. This formula is easily proved by closing the path in the left half of the plane. (Since there is no contribution from the part of the contour that lies at infinity, the integral is determined only by the poles of the $\Gamma-$function, which lie at $\{0, -1, -2, \ldots\}$.)

With this representation, our sums can be written as

$$N_{\rm ex} = \sum_{n=1}^{\infty}\sum_{r=1}^{\infty} \frac{1}{2\pi i}\int_{\tau-i\infty}^{\tau+i\infty} dt\ \frac{\Gamma(t)\lambda^r}{(\beta q n^2 r)^t} \tag{12.2.11}$$

and then, after interchanging them with the integral, re-expressed in terms of the Riemann $\zeta-$function and the Polylogarithm function,

$$\begin{aligned} \zeta(s) &= \sum_{n=1}^{\infty} \frac{1}{n^s} \\ {\rm Li}_t(x) &= \sum_{r=1}^{\infty} \frac{x^r}{r^t}. \end{aligned} \tag{12.2.12}$$

This is only possible if the sums are absolutely convergent, which can be achieved by taking τ to lie sufficiently to the right. We find $N_{\rm ex}$ as an integral in the complex plane

$$N_{\rm ex} = \frac{1}{2\pi i}\int_{\tau-i\infty}^{\tau+i\infty} dt\ \frac{\Gamma(t)\zeta(2t){\rm Li}_t(\lambda)}{(\beta q)^t} \tag{12.2.13}$$

instead of the double infinite sum, provided that $\tau > 1/2$. The integral may be closed in the left half plane; as before there will be no contribution from the portion of the contour that lies at infinity. The advantage in this integral representation lies in the fact that, assuming $\beta q \ll 1$, the integral is dominated by the simple pole in the $\zeta-$function at $t = 1/2$. All other poles (of the $\Gamma-$function) would contribute non-negative powers of βq, which are negligible in comparison. So we get

$$N_{\rm ex} \approx \frac{\Gamma(\frac{1}{2}){\rm Li}_{1/2}(\lambda)}{2(\beta q)^{1/2}} = \sqrt{\frac{\pi}{4\beta q}}\ {\rm Li}_{1/2}(\lambda) \tag{12.2.14}$$

and therefore

$$N = \frac{\lambda}{1-\lambda} + \sqrt{\frac{\pi}{4\beta q}}\ {\rm Li}_{1/2}(\lambda) \tag{12.2.15}$$

which, at least in principle, can be solved for λ to find it as a function of (N, β). The behavior of the fugacity as a function of the inverse temperature β is shown in figure 12.2. Notice that as $\beta \to 0$ ($T \to \infty$) the fugacity approaches zero *i.e.,* the chemical potential becomes large and negative. As $\beta \to \infty$ ($T \to 0$) the fugacity approaches unity and the chemical potential approaches zero. We can still consider this limit (of very low

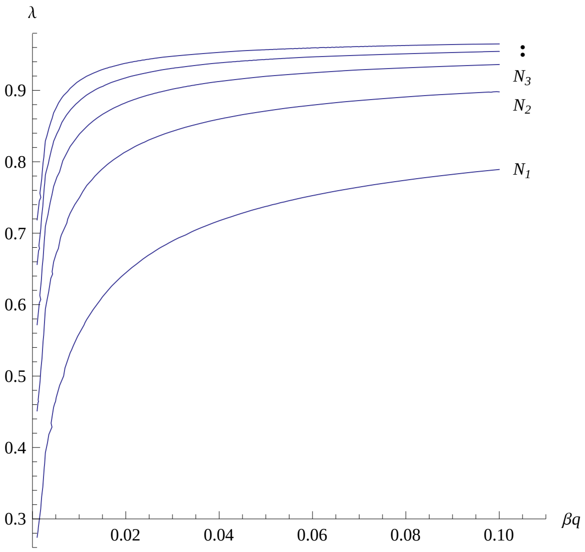

Figure 12.2: The fugacity as a function of β for $N_1 < N_2 < N_3 < \ldots$

temperatures) within our approximation so long as the condition that $\beta q \ll 1$ continues to hold.[3]

A significant number of particles can exist in the ground state only if $\lambda \approx 1$, so put $\lambda = 1 - y$ ($y > 0$) and expand the expression for N about $y = 0$. The Polylogarithm has the Maclaurin expansion

$$\mathrm{Li}_{1/2}(1-y) = \frac{\sqrt{\pi}}{\sqrt{y}} + \zeta(1/2) + \mathcal{O}(\sqrt{y}) \tag{12.2.16}$$

so retaining only the first term, letting $N+1 \approx N$ and calling $a = \pi/\sqrt{4q\beta}$ we get

$$\frac{1}{\sqrt{y}} = \frac{1}{2}\left[-a + \sqrt{a^2 + 4N}\right]. \tag{12.2.17}$$

The only way for y to be small is for

$$a^2 \ll 4N \Rightarrow \frac{\pi^2}{4q\beta} \ll 4N \Rightarrow \beta \gg \frac{\pi^2}{16qN} = \frac{m\pi^2 L^2}{2h^2 N} \tag{12.2.18}$$

---

[3] With $q = \pi^2\hbar^2/2mL^2$, taking $m \sim m_p$ and $L \sim 1$, gives the condition $T \gg 10^{-18}$ K for the validity of our approximation ($\beta q \ll 1$). The lower bound of 10^{-18} K is very far below what is achievable in any experimental setting.

then $y \approx N^{-1}$ and

$$\lambda \approx 1 - \frac{1}{N} \tag{12.2.19}$$

This is evidently the *low temperature* behavior, since there is a lower bound on the inverse temperature determined by Planck's constant, the size of the box and the number of particles.

On the other hand, most of the molecules occupy the excited states when $\lambda \approx 0$, for then $N_0 \approx 0$. In this case

$$\mathrm{Li}_{1/2}(\lambda) = \lambda + \frac{\lambda^2}{\sqrt{2}} + \mathcal{O}(\lambda^3), \tag{12.2.20}$$

so, ignoring terms of order λ^2 and higher, we have

$$\lambda \approx \frac{N}{1+a} \tag{12.2.21}$$

For this to be small $a \gg N$, so putting $a + 1 \approx a$ we get

$$\lambda \approx N\sqrt{\frac{4q\beta}{\pi}} = \frac{Nh}{L(2\pi mkT)^{1/2}} \tag{12.2.22}$$

and the condition for smallness translates into

$$\beta \ll \frac{\pi}{4qN^2} = \frac{mL^2}{h^2N^2}, \tag{12.2.23}$$

which means that this is a *high temperature* behavior since the validity of our expansion requires an upper bound on the inverse temperature.

We define the **critical temperature** to be that temperature at which $\lambda \approx 1$ *and* $N \approx N_{\text{ex}}$. If we compare this definition with the expression (12.2.13) for the number of excited moelcules, it would mean that at the critical temperature, T_c, is given by

$$N = \frac{1}{2\pi i}\int_{\tau-i\infty}^{\tau+i\infty} dt\ \frac{\Gamma(t)\zeta(2t)\zeta(t)}{(\beta_c q)^t} \tag{12.2.24}$$

where we replace $\mathrm{Li}_t(\lambda \approx 1)$ by $\zeta(t)$ according to the definition of the polylogarithm in (12.2.12) and β by $\beta_c = 1/kT_c$. The integral is dominated by two simple poles, one at $t = \frac{1}{2}$ and the other at $t = 1$ (as before we will ignore all the poles at $t \leq 0$) and so we get

$$N \approx \frac{\Gamma(\frac{1}{2})\zeta(\frac{1}{2})}{(\beta_c q)^{1/2}} + \frac{\Gamma(1)\zeta(2)}{\beta_c q} = \frac{\sqrt{\pi}\zeta(1/2)}{(\beta_c q)^{1/2}} + \frac{\pi^2}{6\beta_c q} \tag{12.2.25}$$

Now $\zeta(1/2) \approx -1.46$ (is negative) so β_c should satisfy

$$\beta_c \lesssim \frac{\pi^3}{36|\zeta(1/2)|^2 q}. \tag{12.2.26}$$

because the left hand side cannot be less than zero. For large N, the last term on the right hand side of (12.2.25) will dominate and to leading order we find,

$$\beta_c \approx \frac{\pi^2}{6qN} \tag{12.2.27}$$

and therefore the critical temperature *increases with increasing number of bosons.* Moreover, the thermal de Broglie wavelength given in (6.4.3) at the critical temperature is of the same order of magnitude as the average spacing between the molecules, which is the length of the box divided by the number of molecules, $d = L/N$. If we also define the **condensate fraction** to be the ratio of molecules in the ground state to the total number of molecules

$$f_C = \frac{N_0}{N} = 1 - \frac{N_{\text{ex}}}{N} \tag{12.2.28}$$

then a significant fraction of the molecules will be found in the ground state and f_C approaches unity at temperatures below the critical temperature. The gas is then said to be in a **condensed** state. In fact, putting together the expression for the number of excited molecules in (12.2.14) together with the expression in (12.2.27) for the critical temperature, we see that the condensate fraction behaves as

$$f_C \approx 1 - \sqrt{\frac{T}{T_c}} \tag{12.2.29}$$

for temperatures below T_c. Naturally, above the critical temperature, most molecules are in excited states and the condensate fraction rapidly approaches zero.

What can be said about the average energy of the system? This is given by the second equation in (12.2.3),

$$\langle E\rangle = \frac{\pi^2\hbar^2}{2mL^2}\sum_{n=1}^{\infty}\frac{n^2}{e^{\beta(qn^2-\mu)}-1}. \tag{12.2.30}$$

Expanding as we did before and using the Mellin-Barnes representation of the exponential function, we are able to write the following integral expression for the internal energy

$$\langle E\rangle = \frac{\pi^2\hbar^2}{2mL^2}\frac{1}{2\pi i}\int dt\ \frac{\Gamma(t)\mathrm{Li}_t(\lambda)\zeta(2t-2)}{(\beta q)^t} \tag{12.2.31}$$

which has a simple pole at $t = 3/2$ and we find

$$\langle E\rangle = \frac{\pi^2\hbar^2}{2mL^2}\frac{\Gamma(3/2)\mathrm{Li}_{3/2}(\lambda)}{2(\beta q)^{3/2}} = \frac{1}{2}\sqrt{\frac{\pi}{4\beta q}}\frac{1}{\beta}\ \mathrm{Li}_{3/2}(\lambda) \tag{12.2.32}$$

Let us examine this expression at temperatures well above the critical temperature, for which $\lambda \ll 1$. In this case, the Pologarithm has the following expansion in λ

$$\mathrm{Li}_{3/2}(\lambda) \approx \lambda + \frac{\lambda^2}{2^{3/2}} + \frac{\lambda^3}{3^{3/2}} + \ldots + \tag{12.2.33}$$

Also recall the expression for the number of molecules in (12.2.15). Neglecting the first term because we are interested in high temperatures, we have

$$N \approx \sqrt{\frac{\pi}{4\beta q}}\mathrm{Li}_{1/2}(\lambda) \approx \sqrt{\frac{\pi}{4\beta q}}\left(\lambda + \frac{\lambda^2}{2^{1/2}} + \frac{\lambda^2}{3^{1/2}} + \ldots +\right) \tag{12.2.34}$$

and the energy *per particle* becomes

$$\begin{aligned} \frac{\langle E\rangle}{N} &\approx \frac{\sqrt{\pi}}{4\sqrt{\beta^3 q}}\sqrt{\frac{4\beta q}{\pi}}\left(\lambda + \frac{\lambda^2}{2^{3/2}} + \ldots +\right)\left(\lambda + \frac{\lambda^2}{2^{1/2}} + \ldots +\right)^{-1} \\ &\approx \frac{1}{2}kT\left(1 + \frac{\lambda}{2^{3/2}} + \ldots +\right)\left(1 - \frac{\lambda}{2^{1/2}} + \ldots +\right) \\ &\approx \frac{1}{2}kT\left(1 - \frac{\lambda}{2^{3/2}} + \ldots +\right) \\ &\approx \frac{1}{2}kT\left(1 - \frac{Nh}{4L(\pi mkT)^{1/2}} + \ldots +\right) \end{aligned} \tag{12.2.35}$$

Notice that the average energy per molecule is *less than* the average energy of molecules obeying Boltzmann statistics and that the extent to which this energy is less depends on the number of particles. This corresponds to the fact that the probability of the molecules being in the same state is enhanced over the probability of two molecules obeying Boltzmann statistics doing the same. The degree of enhancement depends on the number of particles, as we have seen before.

At temperatures well below the critical temperature, $\lambda \approx 1 - N^{-1}$ and the polylogarithm has the expansion

$$\mathrm{Li}_{3/2}(1-x) \approx \zeta(3/2) - 2\sqrt{\pi}x^{1/2} - \zeta(1/2)x + \cdots +, \tag{12.2.36}$$

so to leading order

$$\langle E\rangle = \frac{\sqrt{\pi}\,\zeta(3/2)}{4\sqrt{\beta^3 q}} \tag{12.2.37}$$

The (constant volume) heat capacity at low temperatures is then

$$C_L = -k\beta^2\frac{d}{d\beta}\langle E\rangle = \frac{3k\sqrt{\pi}\,\zeta(3/2)}{8\sqrt{q}}\beta^{-1/2} \tag{12.2.38}$$

and satisfies the condition required by the third law. At any temperature, the constant volume heat capacity is given by

$$C_L = -k\beta^2\frac{d}{d\beta}\langle E\rangle = \frac{1}{4}k\beta^{-1/2}\sqrt{\frac{\pi}{q}}\left[\frac{3}{2}\mathrm{Li}_{3/2}(\lambda) - \beta\ \mathrm{Li}_{1/2}(\lambda)\frac{d\ln\lambda}{d\lambda}\right] \tag{12.2.39}$$

where we used the following property of the Polylogarithm function[4]

$$\frac{d}{dx}\mathrm{Li}_t(x) = \frac{1}{x}\mathrm{Li}_{t-1}(x) \tag{12.2.40}$$

One can solve this equation in conjunction with (12.2.15) numerically to obtain the heat capacity as a function of temperature everywhere.

Let us turn to the entropy and free energy. For this we must compute the partition function,

$$\ln \Xi = -\sum_{n=1}^{\infty} \ln\left(1 - \lambda e^{-\beta q n^2}\right) = \sum_{n=1}^{\infty}\sum_{r=1}^{\infty} \frac{\lambda^r}{r} e^{-\beta q n^2 r} \tag{12.2.41}$$

and again, employing the Mellin-Barnes representation of the exponential function,

$$\ln \Xi = \frac{1}{2\pi i}\int_{\tau - i\infty}^{\tau + i\infty} \int dt\, \frac{\Gamma(t)\zeta(2t)\mathrm{Li}_{t+1}(\lambda)}{(\beta q)^t} \tag{12.2.42}$$

and the integral has a simple pole at $t = \frac{1}{2}$. Therefore

$$\ln \Xi = \frac{\Gamma\left(\frac{1}{2}\right)\mathrm{Li}_{3/2}(\lambda)}{2\sqrt{\beta q}} = \frac{\sqrt{\pi}\ \mathrm{Li}_{3/2}(\lambda)}{2\sqrt{\beta q}} \tag{12.2.43}$$

and the free energy is

$$F = -\frac{1}{\beta}\ln \Xi = -\frac{\sqrt{\pi}\ \mathrm{Li}_{3/2}(\lambda)}{2\sqrt{\beta^3 q}}. \tag{12.2.44}$$

Combining this with the result for the average energy in (12.2.37) and simplifying, first in the limit of high temperature, $\lambda \ll 1$, we have

$$S \approx k(\ln \Xi + \beta\langle E\rangle - \beta\mu\langle N\rangle) = kN\left[\ln\frac{L}{N} + \frac{1}{2}\ln T + \frac{1}{2}\ln\frac{2\pi m k e^3}{h^2}\right] \tag{12.2.45}$$

which should be compared with (6.4.17), taking into account that our box is one dimensional, that $g = 1$ and that the ground state is not degenerate. On the other hand, in the limit of low temperatures, when $T \ll T_c$ and $\lambda \approx 1$, we will get

$$S(T) \approx \frac{3\sqrt{3}}{2\sqrt{2}}\frac{\zeta(3/2)}{\sqrt{\pi}} k\sqrt{N}\left(\frac{T}{T_c}\right)^{1/2} \approx 2.707 k\sqrt{N}\left(\frac{T}{T_c}\right)^{1/2}. \tag{12.2.46}$$

This is precisely

$$S(T) = \int_0^T \frac{C_L(T)}{T}\, dT \tag{12.2.47}$$

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[4] Problem: Verify this identity using the definition of the Polylogarithm in (12.2.12)

where $C_L(T)$ is given in (12.2.38).

The generalization to a three dimensional box is now straightforward. A similar expansion to the one performed for the one dimensional system will lead to

$$N = \frac{\lambda}{1-\lambda} + \left(\frac{\pi}{4\beta q}\right)^{3/2} \mathrm{Li}_{3/2}(\lambda) \tag{12.2.48}$$

and

$$\langle E\rangle = \frac{3}{2}\left(\frac{\pi}{4\beta q}\right)^{3/2} \frac{1}{\beta}\mathrm{Li}_{5/2}(\lambda) \tag{12.2.49}$$

The critical temperature is a bit more tricky to compute, so we shall do so explicitly. Recall that the condition for $\beta = \beta_c$ is $N = N_{\mathrm{ex}}$ and $\lambda \approx 1$, so

$$N = \sum_{\vec{n}=1}^{\infty} \frac{1}{e^{\beta_c \vec{n}^2} - 1} = \sum_{\vec{n}=1}^{\infty}\sum_{r=1}^{\infty} e^{-\beta_c \vec{n}^2 r} \tag{12.2.50}$$

where we have used the short-hand $\vec{n} = 1$ to signify that each of n_x, n_y and n_z begin at unity. Then according to the Mellin Barnes representation of each of the three exponential functions in the sum, we should have

$$N = \frac{1}{(2\pi i)^3}\int ds \int dt \int du \frac{\Gamma(s)\Gamma(t)\Gamma(u)\zeta(2s)\zeta(2t)\zeta(2u)\zeta(s+t+u)}{(\beta_c q)^{s+t+u}}, \tag{12.2.51}$$

where each integral runs from $\tau - i\infty$ to $\tau + i\infty$. Performing the s integration, we recognize that there are two simple poles, one at $s = \frac{1}{2}$ and the other at $s = 1 - t - u$, so

$$\begin{aligned} N &= \frac{1}{(2\pi i)^2}\int dt \int du \frac{\Gamma(1/2)\Gamma(t)\Gamma(u)\zeta(2t)\zeta(2u)\zeta(1/2+t+u)}{2(\beta_c q)^{1/2+t+u}} \\ &\quad + \frac{1}{(2\pi i)^2}\int dt \int du \frac{\Gamma(1-t-u)\Gamma(t)\Gamma(u)\zeta(2[1-t-u])\zeta(2t)\zeta(2u)}{2(\beta_c q)} \end{aligned} \tag{12.2.52}$$

The t integration also involves two simple poles, one at $t = \frac{1}{2}$ and the other at $t = \frac{1}{2} - u$, therefore

$$\begin{aligned} N &= \frac{1}{2\pi i}\int du \frac{\Gamma^2(1/2)\Gamma(u)\zeta(2u)\zeta(1+u)}{4(\beta_c q)^{1+u}} \\ &\quad + \frac{1}{2\pi i}\int du \frac{\Gamma(1/2-u)\Gamma(1/2)\Gamma(u)\zeta(1-2u)\zeta(2u)}{4(\beta_c q)} \\ &\quad + \frac{1}{2\pi i}\int du \frac{\Gamma(1/2)\Gamma(1/2-u)\Gamma(u)\zeta(1-2u)\zeta(2u)}{4(\beta_c q)} \end{aligned}$$

$$+\frac{1}{2\pi i}\int du\frac{\Gamma(1/2)\Gamma(1/2-u)\Gamma(u)\zeta(1-2u)\zeta(2u)}{4(\beta_c q)} \tag{12.2.53}$$

The first integral has a single pole at $u=\frac{1}{2}$, its value is

$$\frac{\Gamma^3(1/2)\zeta(3/2)}{(4\beta_c q)^{3/2}}=\left(\frac{\pi}{4\beta_c q}\right)^{3/2}\mathrm{Li}_{3/2}(\lambda\approx 1). \tag{12.2.54}$$

The last three integrals are all the same, having a double pole at $u=\frac{1}{2}$. Their contribution is therefore

$$3\left(\frac{\Gamma(1/2)\Gamma(u)\zeta(1-2u)}{4(\beta q)}\right)'_{u=\frac{1}{2}}=\frac{3}{\beta q}\left[\pi\ln 2\pi-\frac{\pi}{2}\psi(1/2)\right] \tag{12.2.55}$$

where $\psi(z)$ is the digamma function. The dominant contribution to N therefore comes from the first integral and we compute β_c from

$$N\approx\left(\frac{\pi}{4\beta_c q}\right)^{3/2}\zeta(3/2)\Rightarrow\beta_c\approx\frac{\pi}{4q}\left(\frac{\zeta(3/2)}{N}\right)^{2/3} \tag{12.2.56}$$

showing clearly that the critical temperature rises with the number of Bosons present. This result could have been directly obtained from (12.2.48) by setting $N=N_{\text{ex}}$ and $\lambda\approx 1$. It is now not difficult to see that, in three dimensions, the condensate fraction behaves for $T\ll T_c$ as

$$f_C=1-\left(\frac{T}{T_c}\right)^{3/2} \tag{12.2.57}$$

Let us now turn to the heat internal energy, heat capacity and entropy of the gas at low temperature.[5]

At very low temperatures, $T\ll T_c$ and $\lambda\approx 1-N^{-1}$, the Polylogarithm function has the expansion

$$\mathrm{Li}_{5/2}(1-x)\approx\zeta(5/2)-\zeta(3/2)x+\frac{4}{3}\pi x^{3/2}+\ldots+ \tag{12.2.58}$$

so retaining only the first term we get

$$\langle E\rangle\approx\frac{3}{2}\left(\frac{\pi}{4\beta q}\right)^{3/2}\frac{1}{\beta}\zeta(5/2) \tag{12.2.59}$$

and the heat capacity is

$$C_V=-k\beta^2\frac{d\langle E\rangle}{d\beta}=\frac{15}{4}\frac{\zeta(5/2)}{\zeta(3/2)}Nk\left(\frac{T}{T_c}\right)^{3/2}\approx 1.93Nk\left(\frac{T}{T_c}\right)^{3/2}. \tag{12.2.60}$$

---

[5] Problem: Show that at high temperature the internal energy is $\langle E\rangle\approx\frac{3}{2}\frac{N}{\beta}$ and that the entropy is given by the standard expression from thermodynamics in (6.4.17).

Similar calculations should also yield the entropy of the Bose gas

$$S = \frac{5}{2}k\left(\frac{\pi}{4\beta q}\right)^{3/2}\mathrm{Li}_{5/2}(\lambda) - Nk\ln\lambda \tag{12.2.61}$$

whose low temperature behavior ($T \ll T_c$ and $\lambda \approx 1 - N^{-1}$) is

$$S \approx \frac{5}{2}\frac{Nk}{\zeta(3/2)}\left(\frac{T}{T_c}\right)^{3/2} \approx 0.96Nk\left(\frac{T}{T_c}\right)^{3/2} \tag{12.2.62}$$

At low temperatures the last term's contribution to the entropy is negligible because $\lambda \approx 1$. On the contrary, at high temperatures the dominant contribution comes from the last term because λ rapidly approaches zero.

The methods indicated above are quite general and can be applied at any temperature. However, at high temperatures a simpler formulation is possible if we recall that when the spacing between energy levels is much less than kT then thermal fluctuations will effectively turn the discrete spectrum into a continuum. If, for example, we imagine increasing n_x by one keeping n_y and n_z fixed, then the spacing is

$$\Delta\varepsilon_{\vec{n}} = \frac{(2n_x+1)\pi^2\hbar^2}{2mL^2} \tag{12.2.63}$$

and T should be high enough that $\Delta\varepsilon_{\vec{n}} \ll kT$. Since this means that we can approximate the sum by the integral

$$\sum_{\vec{n}} \to \frac{1}{h_0^3}\int d^3\vec{r}d^3\vec{p} \tag{12.2.64}$$

and assuming that the gas is isotropic so $d^3\vec{p} = 4\pi p^2 dp$ we can replace the sum by

$$\sum_{\vec{n}} \to \frac{4\pi V}{h_0^3}\int dp\, p^2. \tag{12.2.65}$$

Again because the energy of a free particle is related to its momentum by $\epsilon = p^2/2m$ we have

$$p^2 dp = \frac{1}{2}(2m)^{3/2}\sqrt{\epsilon}d\epsilon \tag{12.2.66}$$

and therefore

$$N = \frac{2\pi V(2m)^{3/2}}{h_0^3}\int_0^\infty \frac{\lambda\sqrt{\epsilon}d\epsilon}{e^{\beta\epsilon}-\lambda} \tag{12.2.67}$$

With $x = \beta\epsilon$, we can write the expression for N as

$$N = \frac{2\pi V(2m/\beta)^{3/2}}{h_0^3}\int_0^\infty \frac{\lambda\sqrt{x}dx}{e^x-\lambda} \tag{12.2.68}$$

where the value of the integral is

$$\int_0^\infty \frac{\lambda\sqrt{x}dx}{e^x-\lambda} = \frac{1}{2}\sqrt{\pi}\mathrm{Li}_{3/2}(\lambda) \tag{12.2.69}$$

Expanding the polylogarithm in λ,

$$N = \frac{V(2\pi m/\beta)^{3/2}}{h_0^3}\sum_{n=0}^\infty (1+n)^{-3/2}\lambda^{n+1} \tag{12.2.70}$$

or, explicitly,

$$N = \left(\frac{2\pi m}{\beta h_0^2}\right)^{3/2} V\left[\lambda + \frac{\lambda^2}{2^{3/2}} + \frac{\lambda^3}{3^{3/2}} + \ldots\right], \tag{12.2.71}$$

which is precisely (12.2.48) in the limit in which all the molecules are excited. Since $\epsilon \gg \mu$, we can ignore all higher powers of λ and arrive at the approximate fugacity

$$\lambda \approx \frac{Nh_0^3}{(2\pi mkT)^{3/2}V} \tag{12.2.72}$$

which is the three dimensional equivalent of (12.2.22). Likewise,

$$\begin{aligned}\langle E\rangle &= \frac{2\pi V(2m)^{3/2}}{h_0^3}\int_0^\infty \frac{\lambda\epsilon^{3/2}d\epsilon}{e^{\beta\epsilon}-\lambda} \\ &= \frac{2\pi V(2m/\beta)^{3/2}}{h_0^3\beta}\int_0^\infty \frac{dx\lambda x^{3/2}}{e^x-\lambda} \\ &\overset{\text{def}}{=} \frac{2\pi V(2m/\beta)^{3/2}}{h_0^3\beta} I_1(\lambda) \end{aligned} \tag{12.2.73}$$

where

$$I_1(\lambda) = \frac{3}{4}\sqrt{\pi}\mathrm{Li}_{5/2}(\lambda). \tag{12.2.74}$$

Thus the energy turns out to be precisely (12.2.49). Expanding the polylogarithm as before

$$\langle E\rangle = \left(\frac{2\pi m}{\beta h_0^2}\right)^{3/2}\frac{3}{2\beta}V\sum_{n=0}^\infty (1+n)^{-5/2}\lambda^{n+1} \tag{12.2.75}$$

or explicitly,

$$\langle E\rangle = \left(\frac{2\pi m}{\beta h_0^2}\right)^{3/2}\frac{3}{2\beta}V\left[\lambda + \frac{\lambda^2}{2^{5/2}} + \frac{\lambda^3}{3^{5/2}} + \ldots\right] \tag{12.2.76}$$

and the energy per particle is then calculated exactly as we did before (at high temperature)

$$\frac{\langle E\rangle}{N} \approx \frac{3}{2}kT\left[1-\frac{Nh_0^3}{(2\pi mkT)^{3/2}V}+\ldots\right] \tag{12.2.77}$$

which is the three dimensional equivalent of (12.2.35). The entropy and free energy are computed as integrals in this limit as well. Note that

$$\ln\Xi \to \frac{2\pi V(2m)^{3/2}}{h_0^3}\int d\epsilon\sqrt{\epsilon}\;\ln(1-\lambda e^{-\beta\epsilon}) \tag{12.2.78}$$

can be expressed as

$$\begin{aligned}\ln\Xi &= -\frac{2\pi V(2m/\beta)^{3/2}}{h_0^3}\int dx\sqrt{x}\;\ln(1-\lambda e^{-x})\\ &\overset{\text{def}}{=} -\frac{2\pi V(2m/\beta)^{3/2}}{h_0^3}I_2(\lambda)\end{aligned} \tag{12.2.79}$$

and

$$I_2 = -\frac{1}{2}\sqrt{\pi}\mathrm{Li}_{5/2}(\lambda) \tag{12.2.80}$$

so that the entropy at high temperature can be written in terms of the two integrals, $I_1(\lambda)$ and $I_2(\lambda)$ as

$$\begin{aligned}S &= \frac{2\pi kV(2m/\beta)^{3/2}}{h_0^3}[-I_2(\lambda)+I_1(\lambda)] - Nk\ln\lambda\\ &\approx \frac{5}{2}k\frac{V(2\pi m/\beta)^{3/2}}{h_0^3}\mathrm{Li}_{5/2}(\lambda) - Nk\ln\lambda\end{aligned} \tag{12.2.81}$$

which is precisely (12.2.61).

12.3 Bosonic Harmonic Oscillators

Let us now consider a system of Bosonic harmonic oscillators, first in one dimension and next in three dimensions as we have done above. This problem is actually easier to solve analytically than the previous one. The grand partition function for a one dimensional system of Bosonic oscillators is

$$\Xi(\beta,\mu) = \prod_j (1-e^{-\beta(\varepsilon_j-\mu)})^{-1} \tag{12.3.1}$$

where the energy levels are given by the well-known result from elementary quantum theory,

$$\varepsilon_j = \left(j + \frac{1}{2}\right)\hbar\omega, \tag{12.3.2}$$

ω being the angular frequency, which we take for simplicity to be the same for all oscillators. $\varepsilon_0 = \hbar\omega/2$ is the ground state energy. We will define the fugacity by

$$\lambda = e^{\beta(\mu-\varepsilon_0)} \tag{12.3.3}$$

and call $\Delta\varepsilon_j = \varepsilon_j - \varepsilon_0 = n\hbar\omega$, then

$$\Xi(\beta,\lambda) = \prod_j \frac{1}{1-\lambda e^{-\beta\Delta\varepsilon_j}} \tag{12.3.4}$$

whereas the level occupation number is given by

$$\langle N_j\rangle = -\frac{1}{\beta}\frac{\partial \ln \Xi}{\partial \Delta\varepsilon_j} = \frac{\lambda}{e^{\beta\Delta\varepsilon_j} - \lambda} \tag{12.3.5}$$

Therefore the total number of particles, obtained either by summing over all levels or by differentiation w.r.t. μ, becomes

$$N = \frac{\lambda}{1-\lambda} + \sum_{j=1}^{\infty} \frac{\lambda}{e^{\beta\Delta\varepsilon_j} - \lambda} \tag{12.3.6}$$

where the first term on the right represents the occupation of the ground state as usual and the sum represents the number of excited particles, which we called N_{ex}. Let's follow the same analysis we used in the case of molecules in a box. Expanding the denominator of the sum as a power series,

$$N = \frac{\lambda}{1-\lambda} + \sum_{j=1}^{\infty}\sum_{r=1}^{\infty} \lambda^r e^{-\beta\hbar\omega jr} \tag{12.3.7}$$

and using the Mellin-Barnes representation of the exponential function we arrive at

$$N = \frac{\lambda}{1-\lambda} + \frac{1}{2\pi i}\int_{\tau-i\infty}^{\tau+i\infty} dt \frac{\Gamma(t)\zeta(t)\mathrm{Li}_t(\lambda)}{(\beta\hbar\omega)^t} \tag{12.3.8}$$

For $\lambda < 1$ this integral is governed by the simple pole of the $\zeta-$function at $t = 1$, therefore

$$N = \frac{\lambda}{1-\lambda} + \frac{\mathrm{Li}_1(\lambda)}{\beta\hbar\omega} = \frac{\lambda}{1-\lambda} - \frac{1}{\beta\hbar\omega}\ln(1-\lambda) \tag{12.3.9}$$

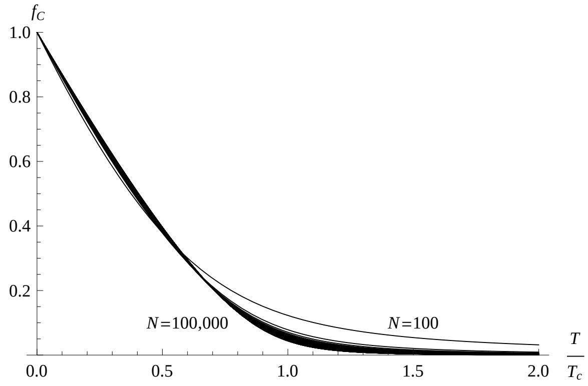

Figure 12.3: Behavior of the condensate fraction, f_C with x for fixed N.

where we used the fact that

$$\mathrm{Li}_1(\lambda) = -\ln(1-\lambda) \tag{12.3.10}$$

Unlike the situation we encountered for molecules in a box, (12.3.9) can be solved explicitly for λ and we recover the fugacity as a function of the temperature and number of particles as

$$\lambda(\beta, N) = 1 - \frac{\beta\hbar\omega}{\mathcal{W}(\beta\hbar\omega e^{(N+1)\beta\hbar\omega})} \tag{12.3.11}$$

where $\mathcal{W}(x)$ is the Lambert $W-$function, obviously defined as the solution of the equation $(y = W(x))$

$$x = ye^y \tag{12.3.12}$$

The Lambert function is double valued in the interval $(-1/e, 0)$ and single valued for $x \in (0, \infty)$, with $W(0) = 0$ and $W(e) = 1$.

We can now write down the condensate fraction as

$$f_C = \frac{\lambda}{N(1-\lambda)} = \frac{\mathcal{W}(\beta\hbar\omega e^{(N+1)\beta\hbar\omega})}{N\beta\hbar\omega} - \frac{1}{N} \tag{12.3.13}$$

but, as always, it will be much more illuminating to express the condensate fraction not in terms of the temperature but in terms of the ratio of T to the critical temperature, T_c, which we recall is defined to be that temperature at which $\lambda \approx 1$ and all the bosons are in excited, *i.e.,* $N_{\text{ex}} \approx N$. Once again, the Mellin Barnes representation of the exponential function will play a key role. We can write

$$N \approx N_{\text{ex}} = \frac{1}{2\pi i}\int_{\tau-i\infty}^{\tau+i\infty} dt \frac{\Gamma(t)\zeta^2(t)}{(\beta_c\hbar\omega)^t} \tag{12.3.14}$$

and the integral admits a double pole at $t = 1$ via the zeta function. Therefore

$$N = \left(\frac{\Gamma(t)}{(\beta_c\hbar\omega)^t}\right)' = -\frac{1}{\beta_c\hbar\omega}\ln(e^{\gamma}\beta_c\hbar\omega) \tag{12.3.15}$$

where γ is the Euler-Mascheroni constant. Now this equation is solved exactly by

$$\beta_c\hbar\omega = \frac{1}{N}\mathcal{W}(e^{-\gamma}N) \tag{12.3.16}$$

and after a little algebra we can express the condensate fraction, f_C in terms of the ratio $x = T/T_c$ as

$$f_C(x, N) = \frac{x}{\mathcal{W}_N}\mathcal{W}\left(\frac{\mathcal{W}_N}{Nx}e^{\frac{(N+1)\mathcal{W}_N}{Nx}}\right) - \frac{1}{N} \tag{12.3.17}$$

where $\mathcal{W}_N = W(e^{-\gamma}N)$. At temperatures very much above the critical temperature $(x \to \infty)$ the condensate fraction behaves as

$$f_C \approx \frac{\mathcal{W}_N}{Nx} + \mathcal{O}(x^{-2}) \tag{12.3.18}$$

and so becomes vanishingly small for large N. On the other hand, at temperatures below the critical temperature $(x \to 0)$ we will find that

$$f_C \approx 1 - \frac{\ln N}{\mathcal{W}_N}\, x + \mathcal{O}(x^2) \tag{12.3.19}$$

showing that the condensate fraction approaches unity. This behavior is shown in figure 12.3. The thing to note is that for large enough N the condensate fraction increases slowly with decreasing x so long as $x \gtrsim 1$, but when $x \lesssim 1$ it increases very rapidly until all bosons are condensed at $x = 0$.

Let us now turn to the average energy of the system. This is given by

$$\begin{aligned}\langle E\rangle &= \sum_{j=0}\varepsilon_j\langle N_j\rangle = \frac{1}{2}N\hbar\omega + \sum_{j=1} j\hbar\omega\langle N_j\rangle \\ &= \frac{1}{2}N\hbar\omega + \frac{\hbar\omega}{2\pi i}\int_{\tau-i\infty}^{\tau+i\infty} dt\frac{\Gamma(t)\mathrm{Li}_t(\lambda)\zeta(t-1)}{(\beta\hbar\omega)^t}\end{aligned} \tag{12.3.20}$$

and, for $\lambda < 1$ there is only a simple pole coming from the $\zeta-$function at $t = 2$, so the average energy can now be given by

$$\langle E\rangle = \frac{1}{2}N\hbar\omega + \frac{\mathrm{Li}_2(\lambda)}{\beta^2\hbar\omega} \tag{12.3.21}$$

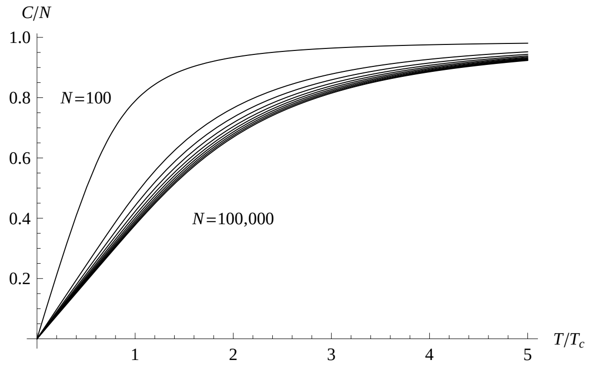

Figure 12.4: Behavior of the heat capacity per boson with x for fixed N.

so the heat capacity at constant "volume" is

$$C_L(\beta, N) = \frac{2\mathrm{Li}_2(\lambda)}{\beta\hbar\omega} - \frac{\mathrm{Li}_2'(\lambda)}{\hbar\omega}\left(\frac{\partial\lambda}{\partial\beta}\right)_N \tag{12.3.22}$$

where the prime on the polylogarithm represents a derivative with respect to λ. The constant volume heat capacity can be expressed in terms of the ratio x as well. We find

$$C_L(x, N) = \frac{2xN\mathrm{Li}(\lambda)}{\mathcal{W}_N} - \frac{x^2 N}{\lambda\mathcal{W}_N}\ln(1-\lambda)\left(\frac{\partial\lambda}{\partial\beta}\right)_N \tag{12.3.23}$$

The heat capacity per boson is shown in figure 12.4 as a function of x. Now for $x \ll 1$ (and $\lambda \approx 1 - N^{-1}$) we find

$$c_L = \frac{C_L}{N} \approx \frac{\pi^2 kT}{3N\hbar\omega} \tag{12.3.24}$$

whereas when $x \gg 1$ the heat capacity per boson approaches unity. From the figure it is clear that there is no phase transition in this system. Similar calculations will also yield the entropy of the gas

$$S = \ln\Xi + \beta\langle E\rangle - \mu\beta N = \frac{2xN}{\mathcal{W}_N}\mathrm{Li}_2(\lambda) - \ln(1-\lambda) + N\ln\lambda. \tag{12.3.25}$$

In the limit of vanishing x we find

$$S \approx \frac{\pi^2}{2\beta\hbar\omega} + \ln N + 1 \tag{12.3.26}$$

which is not vanishing as $x \to 0$. This is not really a problem because the specific entropy, S/N does vanish in the thermodynamic limit $N \to \infty$ and so the result is consistent with a generalized version of the third law of thermodynamics.

All our methods for studying one dimensional oscillators can be easily extended to higher dimensions as we did for the bosonic gas and we urge the reader to pursue these calculations to their fullest.

12.4 Phonons and Rotons

Essential to the program of computing the the partition function is a knowledge of the complete set of eigenstates of the system. In general it is a very difficult problem to list the energy eigenstates of any *interacting* many body system. However, it is often possible to develop the statistical mechanics in terms of a dilute gas of non-interacting elementary excitations or **quasiparticles**. These are low energy excitations of the system about some ground state according to

$$E = E_g + \sum_k n_{\vec{p}} \varepsilon_{\vec{p}} \tag{12.4.1}$$

where E_g is the energy of the ground state and the sum represents the contribution by the excitations: $n_{\vec{p}} = 0, 1, 2, \ldots$ for Bosonic excitations and $n_{\vec{p}} = 0, 1$ for Fermionic ones. The energy spectrum in (12.4.1) is not an exact calculation of the energy levels of the interacting many body system and the quasiparticles are not in general true eigenstates of the many body problem. Therefore, if we wait a long enough time the particle state will decay into more complicated states, so the approach only makes sense if the lifetime of the quasiparticle states is long enough for the energy to be well defined, by the uncertainty principle $\tau_{\vec{p}} \gg \hbar/\varepsilon_{\vec{p}}$. This must be shown either empirically or theoretically but it is often true at low temperatures simply because there are not many states for the quasiparticles to decay into. The partition function becomes

$$\Xi = e^{-\beta E_g} \sum_{\{n_{\vec{p}}\}} e^{-\beta \sum_{\vec{p}} n_{\vec{p}} \varepsilon_{\vec{p}}} = e^{-\beta E_g} \prod_{\vec{p}} \sum_{n_{\vec{p}}} e^{-\beta n_{\vec{p}} \varepsilon_{\vec{p}}} \tag{12.4.2}$$

The quasiparticle concept is useful in the description of solids and of certain liquids at very low temperatures. For example, atoms or molecules in solids are packed closely together and are unable to move freely. Thermal excitations cause the atoms to vibrate about their mean positions, setting up vibrations in the lattice. The ability of the lattice to store energy in vibrations contributes to the thermal properties of the material, as we have seen in Debye's treatment of the heat capacity of solids. Another example is liquid He II at very low temperatures. It exhibits superfluid properties and is a candidate for a Bose-Einstein condensate. In the 1940's, Landau developed a description of its thermodynamic properties by treating it as a mixture of two components. One of these components is a non-interacting gas of quasiparticles, which are elementary excitations about the other component, a quiescent ground state which in turn represents the superfluid. At $T = 0$ there are no excitations and the liquid exists exclusively in the superfluid state.

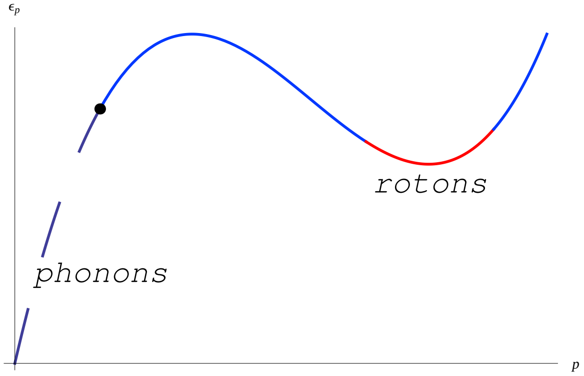

Figure 12.5: Energy spectrum of quasiparticles in He II when $0 < T < T_\lambda$.

Between $T = 0$ and a critical temperature called the $\lambda-$point the fluid is an admixture of the superfluid background and the gas of quasiparticles. Above the $\lambda-$point, the liquid behaves like a normal fluid, known as He I. The thermal properties of liquid He II are due to the quasiparticles and their spectrum was originally deduced by Landau via careful fitting to the measured thermodynamic properties of liquid He II. It is shown schematically in figure 12.5.

The quasiparticles are known as **Phonons** or **Rotons** depending on the dispersion relation that is satisfied. Phonons are the low energy, long wavelength (compared with the distance between the atoms) excitations and the dispersion relation for them is linear in the momentum,

$$\varepsilon = pc \tag{12.4.3}$$

where c is the speed of sound. At short wavelengths the dispersion relation is more complicated and there is a minimum in the dispersion curves caused by atomic interactions. Elementary excitations around this minimum are the Rotons. The Roton dispersion relation may be written as

$$\varepsilon = \Delta + \frac{(p - p_0)^2}{2m_*} \tag{12.4.4}$$

where m_* is the effective mass of the rotons ($\sim 10^{-27}$ kg) and $\Delta \sim E_F$. At low T the density of these quasiparticles is low and they barely interact.

The grand canonical partition function for phonons is similar to that for photons ($\mu = 0$) and can be written in the continuum limit as

$$\ln \Xi_{\text{ph}} = -\frac{4\pi V}{h^3}\int_0^\infty dp\, p^2\ \ln(1 - e^{-\beta pc}) = \frac{4\pi^5 V}{45(hc)^3}(kT)^3 \tag{12.4.5}$$

The case of the roton is similarly directly dealt with, at least around the minimum

$$\begin{aligned}\ln \Xi_{\rm rot} &= -\frac{4\pi V}{h^3}\int_0^\infty dp\; p^2\;\ln(1-e^{-\beta\Delta-\beta(p-p_0)^2/2m_*}) \\ &\approx \frac{4\pi V}{h^3}\sqrt{\frac{2\pi m_*}{\beta}}\left(p_0^2+\frac{m_*}{\beta}\right)e^{-\beta\Delta} \qquad (12.4.6)\end{aligned}$$

and from these expressions we can calculate all the relevant thermodynamical quantities.

12.5 Bulk motion of Phonons

Let's consider a gas of phonons in bulk motion within a solid. Since the number of phonons is indefinite we must set the chemical potential, μ, to zero as we did in the case of photons. However, if the gas is in bulk motion, with a momentum $\vec{p}$, then we now have a new constraint on the system, which is that the total momentum is fixed. Thus the partition function for the phonon gas becomes

$$\Xi = \prod_j \left(1-e^{-\beta\varepsilon_j-\vec{\gamma}\cdot\vec{p}_j}\right)^{-1} \qquad (12.5.1)$$

where the sum is over all states and the vector $\vec{\gamma}$ is a Lagrange multiplier that enforces the conservation of momentum. To determine $\vec{\gamma}$ we must determine the drift velocity of the bulk motion, but since c is the velocity of sound, the velocity of the individual phonons will be $\vec{v} = c\hat{n}$ where $\hat{n}$ is the direction of their propagation. Each individual phonon's motion will make some angle, θ, with the bulk motion, which we can take to be in the z direction. By symmetry, we require $\vec{\gamma}$ to be either parallel or antiparallel to the direction of bulk motion, *i.e.* we set $\vec{\gamma}\cdot\vec{p} = \gamma p\cos\theta$. Therefore we find

$$\begin{aligned}\ln\Xi(\beta,\gamma) &= -\sum_j \ln\left(1-e^{-\beta\varepsilon_j-\gamma p_j\cos\theta_j}\right) \\ &= -\frac{2\pi g V}{h^3}\int_0^\infty dp p^2\int_0^\pi d\theta\sin\theta\ln\left(1-e^{-\beta pc-\gamma p\cos\theta}\right) \\ &= \frac{4\pi^5 c g V\beta}{45h^3(\beta^2c^2-\gamma^2)^2} \qquad (12.5.2)\end{aligned}$$

provided that $\beta c > \gamma$.

Now, the bulk velocity can be associated with the mean value of the phonon velocities

$$v = c\;\langle\cos\theta\rangle \qquad (12.5.3)$$

To compute the expectation value of $\cos\theta$, we write it as

$$\langle\cos\theta\rangle = \frac{\sum_j \langle n_j\rangle \cos\theta_j}{\sum_j \langle n_j\rangle} \tag{12.5.4}$$

where $\langle n_j\rangle$ is the distribution function of phonons,

$$\langle n_j\rangle = \frac{1}{e^{\beta\varepsilon_j + \gamma p_j \cos\theta_j} - 1}. \tag{12.5.5}$$

Thus

$$\langle\cos\theta\rangle = \frac{\int_0^\infty dpp^2 \int_0^\pi d\theta \sin\theta\cos\theta \left(e^{\beta pc + \gamma p\cos\theta} - 1\right)^{-1}}{\int_0^\infty dpp^2 \int_0^\pi d\theta \sin\theta \left(e^{\beta\varepsilon + \gamma p\cos\theta} - 1\right)^{-1}} = -\frac{\gamma}{\beta c} \tag{12.5.6}$$

and we find

$$v = c\,\langle\cos\theta\rangle = -\frac{\gamma}{\beta} \Rightarrow \vec{\gamma} = -\beta\vec{v} \tag{12.5.7}$$

giving, for the partition function

$$\ln\Xi|_{\gamma=-\beta v} = \frac{4\pi^5 g V \beta^{-3}}{45 c^3 h^3 \left(1 - \frac{v^2}{c^2}\right)^2}, \tag{12.5.8}$$

First, we note that the bulk velocity cannot be larger than c, as expected. Second, the average energy and the bulk momentum can be computed directly from the partition function. They are, respectively,

$$\langle E\rangle = -\left.\frac{\partial\ln\Xi(\beta,\gamma)}{\partial\beta}\right|_{\gamma,V} = \sum_j \langle n_j\rangle p_j c = \frac{4\pi^5 g V\beta^{-4}}{15 c^3 h^3} \frac{1 + \frac{1}{3}\frac{v^2}{c^2}}{\left(1 - \frac{v^2}{c^2}\right)^3} \tag{12.5.9}$$

and

$$\langle P\rangle = -\left.\frac{\partial\ln\Xi(\beta,\gamma)}{\partial\gamma}\right|_{\beta,V} = \sum_j \langle n_j\rangle p_j \cos\theta_j = \frac{16\pi^5 g V\beta^{-4}(v/c^2)}{45 h^3 c^3 \left(1 - \frac{v^2}{c^2}\right)^3} \tag{12.5.10}$$

so one can associate

$$M = \frac{\langle P\rangle}{v} = \frac{16\pi^5 g V\beta^{-4}}{45 h^3 c^5 \left(1 - \frac{v^2}{c^2}\right)^3} \tag{12.5.11}$$

with the "inertial mass" of the phonon gas.

To understand the extent to which M can be interpreted as an "inertial mass", let's get a closer look at the thermodynamics. Because the partition function is a natural function of $\{\beta, \gamma, V\}$, can write

$$\begin{aligned} d\ln\Xi &= \left(\frac{\partial \ln\Xi}{\partial\beta}\right)_{\gamma,V} d\beta + \left(\frac{\partial \ln\Xi}{\partial\gamma}\right)_{\beta,V} d\gamma + \left(\frac{\partial \ln\Xi}{\partial V}\right)_{\beta,\gamma} dV \\ &= -\langle E\rangle d\beta - \langle P\rangle d\gamma + \beta p dV \end{aligned} \tag{12.5.12}$$

where we defined

$$p = \frac{1}{\beta}\left(\frac{\partial \ln\Xi}{\partial V}\right)_{\beta,\gamma} \tag{12.5.13}$$

Therefore

$$d[\ln\Xi + \beta\langle E\rangle + \gamma\langle P\rangle] = \beta d\langle E\rangle + \gamma\langle P\rangle + \beta p dV \tag{12.5.14}$$

or

$$T dS_{\text{ph}} = d\langle E\rangle + \mathcal{F} d\langle P\rangle + p dV \tag{12.5.15}$$

where $\mathcal{F} = \gamma/\beta$ and p are generalized forces conjugate to the extensive variables $\langle P\rangle$ and V respectively and

$$S_{\text{ph}}/k = \ln\Xi + \beta\langle E\rangle + \gamma\langle P\rangle = \frac{16\pi^5 c g V\beta}{45h^3\left(\beta^2c^2 - \gamma^2\right)^2} \tag{12.5.16}$$

We easily compute

$$\mathcal{F} = \frac{\gamma}{\beta} = -v, \quad p = \frac{4\pi^5 c g}{45h^3(\beta^2c^2 - \gamma^2)^2} = \frac{4\pi^5 g\beta^{-4}}{45h^3c^3\left(1 - \frac{v^2}{c^2}\right)^2} \tag{12.5.17}$$

Therefore the work term associated with a change in the bulk momentum of the phonon gas is (henceforth dropping angular brackets)

$$đW_{\text{ph}} = -v dP \tag{12.5.18}$$

It should be interpreted as the the work done *by* the system, so

$$đW = v dP \tag{12.5.19}$$

is the work that must be done *on* the system to achieve a change in its bulk momentum. Note that

$$đW = v dP = v\frac{dP}{dz}dz = F_z dz \tag{12.5.20}$$

implies that

$$F_z = v\frac{dP}{dz} = \frac{dP}{dt} \tag{12.5.21}$$

is then the external force applied. This is precisely Newton's second law of motion, whence the interpretation of M.

12.6 Fermi Gases

Noting that the Fermi-Dirac distribution requires *all* fermions to be distributed in the levels below μ, there is a simple way to estimate the chemical potential of a Fermi gas at zero temperature. Consider

$$N = \lim_{\beta\to\infty} \left[\sum_{\varepsilon_j \text{ upto } \mu} \frac{1}{e^{\beta(\varepsilon_j - \mu)} + 1} \right] \tag{12.6.1}$$

Consider a quasi-classical situation in which the spacing between energy levels is small compared with the energies of the levels themselves (for example, imagine that the dimensions of the box are very large), then replace the sum by the density of states we had used earlier for a non-relativistic gas in (12.2.67)

$$N = \lim_{\beta\to\infty} \frac{2\pi(2m)^{3/2}}{h^3} V \int_0^\mu \frac{\sqrt{\epsilon} d\epsilon}{e^{\beta(\epsilon-\mu)} + 1} \tag{12.6.2}$$

Of course, since $\epsilon < \mu$, the limit as $\beta \to \infty$ eliminates the exponential in the denominator and we have

$$N = \frac{2\pi(2m)^{3/2}}{h^3} V \int_0^\mu \sqrt{\epsilon} d\epsilon = \frac{4\pi(2m)^{3/2} V}{3h^3} \mu^{3/2}. \tag{12.6.3}$$

Solving for μ then gives

$$\mu(T = 0) = \frac{h^2}{2m} \left(\frac{3n}{4\pi} \right)^{2/3} \tag{12.6.4}$$

where n is the number density of the fermions.[6] The chemical potential at zero temperature is usually called the **Fermi energy**, E_F, of the system. In a typical metal, the number density of electrons can be estimated via the metal density and atomic mass assuming that each atom donates a few electrons to the conduction band. For copper, whose density is $\rho = 8920$ kg/m^3 and atomic mass is 63.5, each atom donates a single electron and we have $n \approx 8.4 \times 10^{28}$ m^{-3}. This then gives $E_F = 13.6 \times 10^{-19}$ J or 8.5 eV, which is on the order of typical atomic binding energies. It corresponds to a Fermi temperature of roughly 10^5 K, which is well above the metal's melting point, so we expect the zero temperature approximation to be excellent for metals *i.e.,* in metals at room temperature, the electrons are effectively distributed in the energy levels below μ. The total energy of the Fermi gas at $T = 0$ is likewise easy to come by since now we will have

$$\langle E\rangle = \frac{2\pi(2m)^{3/2}}{h^3}V\int_0^{E_F}\epsilon^{3/2}d\epsilon = \frac{3}{5}\frac{4\pi(2m)^{3/2}V}{3h^3}E_F^{5/2} = \frac{3}{5}NE_F. \tag{12.6.5}$$

But how does the chemical potential depend on the temperature? Let us continue to work in the continuum approximation, calling $\lambda = e^{\beta\mu}$ as before, then[7]

$$N = \frac{2\pi(2m)^{3/2}}{h^3}V\int_0^{\infty}\frac{\sqrt{\epsilon}d\epsilon}{\lambda^{-1}e^{\beta\epsilon}+1} = -\frac{V}{h^3}\left(\frac{2\pi m}{\beta}\right)^{3/2}\mathrm{Li}_{3/2}(-\lambda) \tag{12.6.6}$$

---

[6] It is interesting to realize that this could be obtained directly from the uncertainty principle. Assume that the average momentum, p_i of the fermions is typically zero, then

$$\Delta p \approx \frac{\hbar}{\Delta x} = \hbar n^{1/3}$$

where we have used the fact that $n^{-1/3} = (V/N)^{1/3}$ provides a good estimate of the distance between the fermions in the gas. Assuming that $\Delta p = p_{\rm rms}$, we find the r.m.s. speed,

$$p_{\rm rms} = mv_{\rm rms} \Rightarrow v_{\rm rms} = \frac{\hbar n^{1/3}}{m}$$

and the pressure exerted by the Fermi gas will be

$$P = \frac{1}{3}mnv_{\rm rms}^2 = \frac{\hbar^2 n^{5/3}}{3m}$$

Now, using the ideal gas equation of state, $P = nkT_F$ and taking $\mu = \frac{3}{2}kT_F$, we find

$$P = \frac{2}{3}n\mu = \frac{\hbar^2 n^{5/3}}{m} \Rightarrow \mu \approx \frac{3\hbar^2 n^{2/3}}{2m}$$

[7] A generalization of the integral in (12.6.6) is known as the Fermi-Dirac integral:

$$F_s(t) = \frac{1}{\Gamma(s+1)}\int_0^{\infty}\frac{x^s dx}{e^{x-t}+1} = -\mathrm{Li}_{s+1}(-e^t)$$

and serves as an alternate definition of the Polylogarithm function.

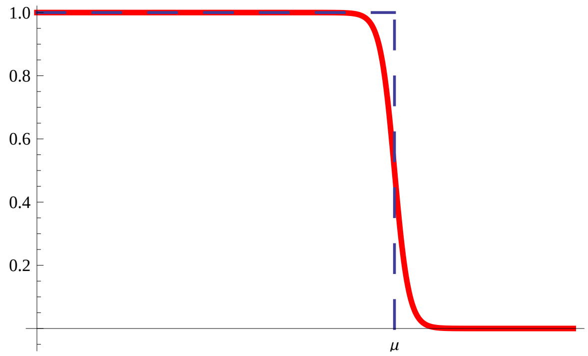

Figure 12.6: The low temperature Fermi distribution.

Now

$$\lim_{\lambda\to\infty} \mathrm{Li}_s(-\lambda) = -\frac{(\ln\lambda)^s}{\Gamma(s+1)}, \tag{12.6.7}$$

provided s is not a negative integer, which returns (12.6.4) when inserted into (12.6.6). In fact, the polylogarithm has the asymptotic expansion

$$\mathrm{Li}_s(-\lambda) = -\frac{(\ln\lambda)^s}{\Gamma(s+1)}\left[1+\sum_{k=2,4,\ldots} 2s(s-1)\ldots(s-k+1)\left(1-\frac{1}{2^{k-1}}\right)\frac{\zeta(k)}{(\ln\lambda)^k}\right] \tag{12.6.8}$$

At low temperatures compared to the Fermi temperature, the polylogarithm may be approximated by the first few terms in the asymptotic expansion in (12.6.8) and this gives

$$\begin{aligned} N &= -\frac{V}{h^3}\left(\frac{2\pi m}{\beta}\right)^{3/2}\mathrm{Li}_{3/2}(-\lambda) \\ &\approx \frac{4\pi(2m)^{3/2}}{3h^3}V\mu^{3/2}\left[1+\frac{\pi^2}{8}\left(\frac{kT}{\mu}\right)^2+\frac{7\pi^4}{640}\left(\frac{kT}{\mu}\right)^4+\ldots\right], \end{aligned} \tag{12.6.9}$$

which can in principle be inverted to recover the chemical potential, as a function of the temperature and number of particles. To lowest order in the temperature we find the zero temperature expression in (12.6.4), but we now want to find a perturbative expansion for the chemical potential, $\mu(n,T)$. This is not difficult to do. We must expand $\mu(n,T)$ about its solution at zero temperature, which of course will be meaningful only for small enough temperatures. What we mean by "small" must be made precise, so we proceed as follows. If μ_0 represents the zero temperature solution then the parameter $\lambda = \frac{kT}{\mu_0}$ is dimensionless and can serve as an expansion parameter provided that $\lambda \ll 1$ or $\mu_0 \gg kT$. Now replacing

$kT = \mu_0\lambda$ and setting $\mu = \sum_{j=0}^{\infty} \lambda^j \mu_j$ in (12.6.9) we find

$$E_F^{3/2} = \mu_0^{3/2} + \frac{3\lambda}{2}\mu_0\mu_1 + \frac{\lambda^2}{8}\frac{\pi^2\mu_0^2 + 3(\mu_1^2 + 4\mu_0\mu_2)}{\sqrt{\mu_0}} + \ldots \tag{12.6.10}$$

and this may be solved order by order to find the non-vanishing coefficients

$$\mu_0 = E_F, \quad \mu_2 = -\frac{\pi^2\mu_0}{12}, \quad \mu_4 = -\frac{\pi^4\mu_0}{80}, \quad \ldots \tag{12.6.11}$$

and so on. Therefore, up to fourth order,

$$\mu = E_F\left[1 - \frac{\pi^2}{12}\left(\frac{kT}{E_F}\right)^2 - \frac{\pi^4}{80}\left(\frac{kT}{E_F}\right)^4 \ldots\right] \tag{12.6.12}$$

and of course one may proceed to as high an order as one pleases.

The average energy will be

$$\langle E\rangle = \frac{2\pi(2m)^{3/2}}{h^3}V\int_0^\infty \frac{\epsilon^{3/2}d\epsilon}{e^{\beta(\epsilon-\mu)}+1} = -\frac{3}{2}\frac{V}{h^3\beta}\left(\frac{2\pi m}{\beta}\right)^{3/2} \mathrm{Li}_{5/2}(-\lambda) \tag{12.6.13}$$

and expanding the polylogarithm according to (12.6.8) gives

$$\langle E\rangle = \frac{4\pi}{5}\frac{(2m)^{3/2}}{h^3}V\mu^{5/2}\left[1 + \frac{5\pi^2}{8}\left(\frac{kT}{\mu}\right)^2 - \frac{7\pi^4}{384}\left(\frac{kT}{\mu}\right)^4 + \ldots\right] \tag{12.6.14}$$

Combining the expansions of $\langle E\rangle$ and N, we can express $\langle E\rangle$ as

$$\begin{aligned}\langle E\rangle &= \frac{3}{5}N\mu\left[1 + \frac{\pi^2}{2}\left(\frac{kT}{\mu}\right)^2 - \frac{11\pi^4}{120}\left(\frac{kT}{\mu}\right)^4 + \ldots\right] \\ &= \frac{3}{5}NE_F\left[1 + \frac{5\pi^2}{12}\left(\frac{kT}{E_F}\right)^2 - \frac{\pi^4}{16}\left(\frac{kT}{E_F}\right)^4 + \ldots\right]\end{aligned} \tag{12.6.15}$$

so that the heat capacity of a Fermi gas is given by the expansion

$$C_V = \left.\frac{\partial\langle E\rangle}{\partial T}\right|_{N,V} \approx \frac{\pi^2}{2}Nk\left(\frac{kT}{E_F}\right)\left[1 - \frac{3\pi^2}{10}\left(\frac{kT}{E_F}\right)^2 + \ldots\right]. \tag{12.6.16}$$

Its leading behavior is seen to be linear in the temperature and so at low temperatures it is much smaller than the classical heat capacity at constant volume of a monatomic gas, which is $3Nk/2$.

Consider the entropy of a Fermi gas,

$$S = k[\ln \Xi + \beta\langle E\rangle - \beta\mu N]. \tag{12.6.17}$$

We have already evaluated $\langle E\rangle$ and N, so it remains to evaluate the partition function. In the continuum approximation,

$$\ln \Xi = \frac{2\pi(2m/\beta)^{3/2}}{h^3} V \int_0^\infty dx\sqrt{x}\ln\left(1+\lambda e^{-x}\right) = -\frac{V}{h^3}\left(\frac{2\pi m}{\beta}\right)^{3/2} \mathrm{Li}_{5/2}(-\lambda) \tag{12.6.18}$$

where we have set $x = \beta\epsilon$. Combining all the results obtained,

$$\begin{aligned} S &= -\frac{kV}{2h^3}\left(\frac{2\pi m}{\beta}\right)^{3/2}\left[5\mathrm{Li}_{5/2}(-\lambda) - 2\beta\mu\mathrm{Li}_{3/2}(-\lambda)\right] \\ &= \frac{2k}{3}\left(\frac{2\pi^2 m}{h^2}\right)^{3/2} V\mu^{3/2}\left(\frac{kT}{\mu}\right)\left[1 - \frac{7\pi^2}{120}\left(\frac{kT}{\mu}\right)^2 + \ldots\right] \\ &= \frac{\pi^2}{2}Nk\left(\frac{kT}{E_F}\right)\left[1 - \frac{\pi^2}{10}\left(\frac{kT}{E_F}\right)^2 + \ldots\right] \end{aligned} \tag{12.6.19}$$

which is consistent with the third law. At high temperatures, compared with the Fermi temperature, the polylogarithm functions can be directly expanded according to their definitions in (12.2.12). We leave this as an exercise.

12.7 Electrons in Metals

Atoms in a metal are closely packed, which causes their outer shell electrons to break away from the parent atoms and move "freely" through the solid. The set of electron energy levels for which they are more or less "free" to move in the solid is called the **conduction band**. Energy levels below the conduction band form the "valence" band and electrons at energies below that are strongly bound to the atoms. This is shown graphically in figure 12.7. The "work function", W, is the energy that an electron must acquire to "evaporate" from the metal. We've already seen that at room temperature $E_F \gg kT$. Now electrons at energies close to the Fermi energy (~ 8.5 eV) have a very high velocity. Equating the Fermi energy to the kinetic energy we have

$$v_F = \sqrt{\frac{2E_F}{m_e}} \approx 1.7 \times 10^6 \text{ m/s}. \tag{12.7.1}$$

(This is only about 0.6% of the speed of light and justifies the use of the Newtonian expression for the kinetic energy.) It is nevertheless very fast for material particles. When

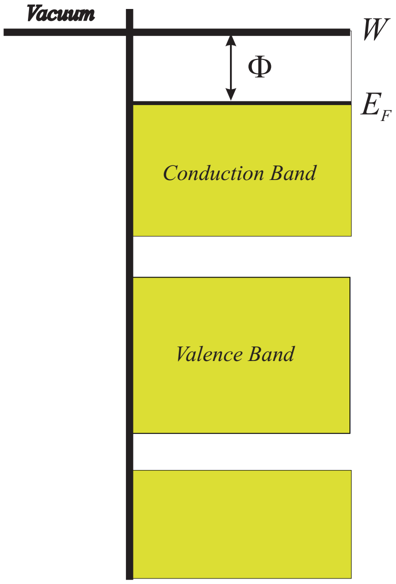

Figure 12.7: Electron states in a metal. E_F is the Fermi energy and W is the "work function".

an electric potential difference is applied across the metal, the electrons in the conduction band begin to flow toward the positive terminal, acquiring an *average* speed that is very much smaller (for reasonable potential differences, about 2×10^{-4} m/s) than this speed, so v_F refers to the speed *between* collisions. This difference between the average speed and the actual speed between collisions clearly implies that the collision rate between the electrons and the atomic lattice is very high and, indeed it is about 10^{14} collisions/s. Now v_F is the speed between collisions only of electrons *at* the Fermi energy. On the average, an electron carries an energy $\langle E\rangle \approx \frac{3}{5}E_F$ and so its velocity is smaller, but not by much. The thermal velocity leads to a pressure that will be exerted by the electron gas and from the kinetic theory we find

$$P = \frac{1}{3}nm_e\langle v^2\rangle = \frac{2}{5}nE_F \tag{12.7.2}$$

where n is their number density. This is called the Fermi or **degeneracy** pressure. If we take $n \sim 8.4 \times 10^{28}$ /m^3 then we find $P \approx 4.6 \times 10^{10}$ Pa or 4.5×10^5 atm! In metals this enormous pressure is balanced by the Coulomb interaction with the ions.

The heat capacity of the electron gas was shown earlier to grow linearly in the temperature. On the other hand, the phonon heat capacity was shown to grow as the third power of the temperature and therefore at ordinary temperatures (small, compared to the Fermi temperature) it is the lattice vibrations that contribute primarily to the specific heat of a metal. However, as the temperature decreases the phononic heat capacity decreases more rapidly than the electronic heat capacity and a temperature is reached when they are both comparable in value. Below this temperature, at very low temperatures, the electronic heat capacity will dominate.

12.7.1 DC Conductivity

Let's consider how we may describe steady state (DC) conduction in metals. As electrons move through a solid conductor we may safely expect that they undergo collisions. In principle these collisions will be between the electrons among themselves, or between the electrons and atoms or between the electrons and defects in the lattice structure or between the electrons and phonons in the conductor but, as we will later see, the first two options are wrong. There will be collisions, however, and at each collision a given electron will experience a force, which we'll call the "collision force". Apart from the collision force there will also be an external force due to an applied electric field. Therefore, applying Newton's second law,

$$\frac{d\vec{p}}{dt} = \vec{F}^{\text{ext}}(t) + \vec{F}^{\text{col}}(t) \tag{12.7.3}$$

We will be interested in the *average* momentum of the electron,

$$\frac{d\langle\vec{p}\rangle}{dt} = \langle\vec{F}^{\text{ext}}\rangle + \langle\vec{F}^{\text{col}}\rangle \tag{12.7.4}$$

Suppose an electron enters a particular collision with momentum $\vec{p}_i$ and exits with momentum $\vec{p}_f$ then we may say that on the average

$$\langle F^{\text{col}}\rangle = \frac{\langle\vec{p}_f - \vec{p}_i\rangle}{\tau} \tag{12.7.5}$$

where we have introduced the **relaxation time**, τ, which can be thought of as the mean time between collisions. Now, if the collisions occur randomly, we can make two approximations: (a) take $\langle p_f\rangle = 0$ and (b) $\langle\vec{p}_i\rangle = \langle\vec{p}\rangle$. Then

$$\langle F^{\text{col}}\rangle = -\frac{\langle\vec{p}\rangle}{\tau} \tag{12.7.6}$$

and so

$$\frac{d\langle\vec{p}\rangle}{dt} = \langle\vec{F}^{\text{ext}}\rangle - \frac{\langle\vec{p}\rangle}{\tau} \tag{12.7.7}$$

This is the **Drude** equation of motion. All the information that survives of the collisions is contained in the relaxation time. In the steady state, $d\langle\vec{p}\rangle/dt = 0$ so

$$\langle\vec{p}\rangle = \langle F^{\text{ext}}\rangle\tau = -e\vec{E}\tau \tag{12.7.8}$$

where $-e$ is the electronic charge and $\vec{E}$ is the electric field within the conductor. Therefore the drift velocity of the electrons through the conductor will be

$$\vec{v} = \frac{\langle\vec{p}\rangle}{m_e} = -\frac{e\vec{E}\tau}{m_e} \tag{12.7.9}$$

which gives a current density that agrees with Ohm's law,

$$\vec{j} = \frac{ne^2\tau}{m_e}\,\vec{E} = \sigma\vec{E} \tag{12.7.10}$$

where σ is the DC conductivity of the material. The resistivity of the conductor is

$$\rho = \frac{1}{\sigma} = \frac{m_e}{ne^2\tau}. \tag{12.7.11}$$

This is the basic idea behind the **Drude** model. The number density of electrons can be estimated directly from the number density of atoms/ions in the metal as each atom will donate one or two electrons to the conduction band. The relaxation time, τ, is an undetermined quantity here because no detailed microscopic analysis has been made. Such an analysis would be required to determine τ. However, the Drude model can be used to obtain the relaxation time from an experimental determination of the resistivity of any material. A typical resistivity of 10^{-8} Ω·m leads to $\tau \approx 10^{-14}$ s. Now if we take the average speed of the electrons to be about $v \sim 10^6$ m/s, this would imply a mean free path of roughly $l = v\tau \sim 10^{-8}$ m, or 100 Angstroms, which is roughly 50 times the atomic separation! We can conclude that, in metals, collisions of electrons do not occur principally between electrons and atoms. In fact it turns out that in a fully quantum treatment, scattering of electrons by a periodic array of atoms or ions does not occur. Scattering in pure metals occurs primarily between electrons and ions that are displaced from their equilibrium position due to thermal vibrations. Such thermal vibrations of the atomic lattice are phonons and the resistivity of conductors at normal temperatures is due to electron-phonon scattering. In alloys, scattering may also occur between electrons and impurities and defects. Below estimate the relaxation time τ for each kind of scattering.

We can re-express the relaxation time by relating it to the mean free path of electrons

$$\tau = \frac{l}{v_F} = \frac{1}{n_s\Sigma_s v_F} \tag{12.7.12}$$

where n_s is the number density of scattering centers and Σ_s the cross-section of scattering at each center. We have used the Clausius relation of (2.3.22). It remains therefore to estimate the number density of scatterers, n_s, and the cross-section, Σ_s. Let us determine the dependence of τ on the temperature, which can only arise due to the combination $n_s\Sigma_s$.

Vibrations of the ions may be considered as simple harmonic motion. Then using the equipartition theorem we can equate the mean potential energy of the vibrations to the temperature by

$$\frac{1}{2}m_a\omega^2\langle x^2\rangle = \frac{1}{2}kT \qquad (12.7.13)$$

where ω is the angular frequency of the oscillations. This gives an r.m.s. displacement of any atom from its mean lattice position as

$$x_{\text{r.m.s.}} = \sqrt{\frac{kT}{m_a\omega^2}} \qquad (12.7.14)$$

If we now take $\Sigma_s \sim x^2_{\text{r.m.s.}}$ and take n_s to be constant, we find

$$\tau = \frac{C}{T} \qquad (12.7.15)$$

where C is a constant. Substituting this into the expression for the resistivity in (12.7.11) we should find that ρ grows linearly with the temperature, $\rho = AT$, for constant A. If we consider scattering by impurities (and defects) then n_s should be replaced by n_d, the number density of impurities, and Σ_s by the cross-section for electron scattering off an impurity, Σ_d. Both of these quantities should be independent of the temperature and so the resistivity will also end up being independent of the temperature, $\rho = D$. D is called the **residual resistivity**.

In general several mechanisms for scattering may be present in any particular sample and it is worth knowing how the contributions from them add up to an effective resistivity. This is given by **Mathhiessen's Rule**, which states that the effective relaxation time for multiple scattering processes is

$$\frac{1}{\tau_{\text{eff}}} = \sum_k \frac{1}{\tau_k} \qquad (12.7.16)$$

Of course, this means that the effective resistivity can be expressed as a sum over resistivities, each originating in one of the scattering processes,

$$\rho_{\text{eff}} = \sum_k \rho_k \qquad (12.7.17)$$

If only scattering by impurities and vibrations are included, we get $\rho_{\text{eff}} = D + CT$. Most metals and alloys will exhibit different behaviors as different forms of scattering dominate at different temperatures.

12.7.2 AC conductivity

If the electric field is oscillating, take

$$\vec{E} = \Re\left[\vec{E}_\omega e^{-i\omega t}\right] \tag{12.7.18}$$

and assume that the solution of the Drude equation of motion is also oscillatory,

$$\vec{p} = \Re\left[\vec{p}_\omega e^{-i\omega t}\right] \tag{12.7.19}$$

then the Drude equation reads

$$-i\omega\vec{p}_\omega = -e\vec{E}_\omega - \frac{\vec{p}_\omega}{\tau} \Rightarrow \vec{p}_\omega = \frac{e\tau}{i\omega\tau - 1}\vec{E}_\omega \tag{12.7.20}$$

where we have dropped the angular brackets. The drift velocity can now be approximated by

$$\vec{v} = \frac{\vec{p}}{m_e} = -\Re\left[\frac{e\tau\vec{E}_\omega e^{-i\omega t}}{1 - i\omega\tau}\right] \tag{12.7.21}$$

If we define the current density as $\vec{j} = \Re(\vec{j}_\omega e^{-i\omega t})$ then $\vec{j}_\omega = \sigma(\omega)\vec{E}_\omega$, with the AC conductivity defined as

$$\sigma(\omega) = \frac{ne^2\tau}{m_e(1 - i\omega\tau)} = \frac{\sigma}{1 - i\omega\tau} \tag{12.7.22}$$

where σ is the DC conductivity. Notice that when $\sigma\tau \ll 1$ the AC conductivity approaches the DC conductivity, but when $\omega\tau \gg 1$ (*i.e.,* when the frequency of the electric field oscillations is much greater than the collision frequency) then $\sigma(\omega)$ becomes independent of τ.

12.7.3 Hall Effect

12.7.4 Thermionic Emission

While electrons move around more or less freely inside a metal they must still acquire a certain amount of energy to escape from the metal itself. The energy that must be acquired by an electron to “evaporate” from the metal is called the **work function**, Φ. Only electrons with energy greater than a certain amount, W, may expect to appear outside the metal and at normal temperatures, electrons that possess this amount of energy are few. However if the metal is heated the number of electrons possessing enough energy to escape may become significant and the metal can serve as an electron emitter. This is the idea behind some older electronic devices, the “valves” used in older amplifiers and logic circuits. This effect is called the **thermionic** or **Richardson effect**.

Consider then a metallic surface, which for convenience we take to lie in the $x-y$ plane. The number of electrons emitted per unit time per unit area of the surface will be

$$R = \sum_j \langle n_j \rangle u_{z,j} \to \frac{1}{h^3} \int_{\sqrt{2mW}}^{\infty} dp_z \int_{-\infty}^{\infty} d^2\vec{p}_\perp \frac{p_z/m}{e^{\beta(\epsilon(\vec{p})-\mu)}+1} \tag{12.7.23}$$

where the energy of the electrons is given by

$$\epsilon(\vec{p}) = \frac{\vec{p}_\perp^2}{2m} + \frac{p_z^2}{2m} \tag{12.7.24}$$

and the momentum in the $z-$direction is required to be larger than $\sqrt{2mW}$ (see figure 12.7) for escape. Thus we get

$$R = \frac{2\pi}{\beta h^3} \int_{\sqrt{2mW}}^{\infty} dp_z \; p_z \ln\left[1 + e^{-\beta(p_z^2/2m-\mu)}\right] \tag{12.7.25}$$

which can be put in a simpler form by simply making the change of variables $\varepsilon_z = p_z^2/2m$,

$$R = \frac{2\pi m}{\beta h^3} \int_W^{\infty} d\varepsilon_z \ln\left[1 + e^{-\beta(\varepsilon_z-\mu)}\right] \tag{12.7.26}$$

Now the temperatures of interest are generally such that the exponential term inside the logarithm is much smaller than unity. Therefore, we could replace $\ln(1+x) \approx x$ in the integral and we find

$$R \approx \frac{2\pi m}{\beta^2 h^3} \; e^{\beta(\mu-W)} \tag{12.7.27}$$

which gives the thermionic current density as (e is the electronic charge)

$$J = eR \approx \frac{2\pi m e k^2}{h^3} T^2 \lambda(n,T) e^{-\beta W} \tag{12.7.28}$$

where $\lambda(n,T)$ is the fugacity in (12.6.6). In the classical limit, at very high temperature and low density we have

$$\lambda(n,T) \approx \frac{nh^3}{(2\pi mkT)^{3/2}} \tag{12.7.29}$$

and

$$J \approx ne \left(\frac{kT}{2\pi m}\right)^{1/2} e^{-\beta W} \tag{12.7.30}$$

but at high density and low temperature (compared to the Fermi energy) the chemical potential is almost constant, $\mu \approx E_F$ and so $\lambda \approx e^{\beta E_F}$, giving

$$J \approx \frac{2\pi m e k^2}{h^3} T^2 e^{-\beta\Phi} \tag{12.7.31}$$

where $\Phi = W - E_F$ is the work function. The difference between the two formulas for J is striking. Naturally, for normal metals at normal operating temperatures the second formula applies.

12.8 Pauli Paramagnetism

Let us consider a gas of free spin $\frac{1}{2}$ particles in the presence of an external magnetic field. The energy of each particle will be

$$\varepsilon = \epsilon(\vec{k}) - \vec{m}_B \cdot \vec{B} \tag{12.8.1}$$

where $\epsilon(\vec{k})$ represents the kinetic energy of the particles, $\vec{m}_B$ is their magnetic moment and $-\vec{m}_B \cdot \vec{B}$ represents the energy it acquires by interacting with the external magnetic field. Let $n_\pm(\vec{k})$ represent the particles carrying momentum $\vec{k}$ and which are parallel (+) and antiparallel (−) with the field. Evidently, $n_\pm(\vec{k}) = 0, 1$ and the partition function can be written as

$$\Xi = \sum_{n_\pm(\vec{k})} \exp\left[-\beta \sum_{\pm,\vec{k}} \left\{ n_{+\vec{k}}[\epsilon(\vec{k}) - m_B B - \mu^+] + n_{-\vec{k}}[\epsilon(\vec{k}) + m_B B - \mu^-] \right\}\right] \tag{12.8.2}$$

where we have introduced two chemical potentials, one for the particles oriented parallel to the magnetic field and one for those oriented antiparallel to it. Since the sum over $n_\pm(\vec{k})$ breaks up, using $n_\pm(\vec{k}) = 0, 1$ we can write

$$\Xi = \prod_k \left(1 + e^{-\beta(\epsilon(\vec{k}) - m_B B - \mu^+)}\right)\left(1 + e^{-\beta(\epsilon(\vec{k}) + m_B B - \mu^-)}\right) \tag{12.8.3}$$

so the system neatly breaks up into two mutually non-interacting pieces and the number of parallel spins or antiparallel spins will be

$$N^+ = \sum_k \left(e^{\beta(\epsilon(\vec{k}) - m_B B - \mu^+)} + 1\right)^{-1}, \quad N^- = \sum_k \left(e^{\beta(\epsilon(\vec{k}) + m_B B - \mu^-)} + 1\right)^{-1} \tag{12.8.4}$$

and the magnetization of the system will be $M = m(N^+ - N^-)$. Now the parallel and antiparallel particles will be in equilibrium when $\mu^+ = \mu^- = \mu$. Then let us compute the magnetization, first at zero temperature. We have

$$N^\pm = \lim_{\beta \to \infty} \frac{2\pi(2m)^{3/2}V}{h^3} \int_0^\infty \frac{\sqrt{\epsilon}\, d\epsilon}{e^{\beta(\epsilon \mp m_B B - \mu)} + 1} \tag{12.8.5}$$

or

$$N^\pm = \frac{2\pi(2m)^{3/2}V}{h^3} \int_0^{\mu \pm mB} \sqrt{\epsilon}\, d\epsilon = \frac{4\pi(2m)^{3/2}V}{3h^3}(\mu \pm m_B B)^{3/2} \tag{12.8.6}$$

We will assume that $mB \ll \mu$, then expanding in powers of mB/μ we find

$$N = N^+ + N^- = \frac{8(2m)^{3/2}\pi V}{3h^3}\mu^{3/2}\left[1 + \frac{3}{8}\left(\frac{m_B B}{\mu}\right)^2 + \dots\right], \tag{12.8.7}$$

which shows that to lowest order the chemical potential is given by the Fermi energy in the absence of the external magnetic field. Moreover,

$$M = m(N^+ - N^-) = \frac{4\pi(2m)^{3/2}V}{h^3}(\sqrt{\mu}\ m_B^2 B)\left[1 - \frac{1}{3}\left(\frac{m_B B}{\mu}\right)^2 + \ldots\right] \tag{12.8.8}$$

and it is easy to see that

$$M = \frac{3}{2}N\frac{m_B^2 B}{\mu}\left[1 - \frac{5}{12}\left(\frac{m_B B}{\mu}\right)^2 + \ldots\right] \tag{12.8.9}$$

giving the susceptibility per unit volume as

$$\chi = \lim_{B\to 0}\frac{M}{VB} = \frac{3}{2}\frac{n^2}{\mu} \tag{12.8.10}$$

at zero temperature, where n is the number density of particles.

It's worth comparing the result for the susceptibility above with the classical result, in (9.2.19), which can be stated as $M = Nm_B\tanh(\beta m_B B)$. At low temperatures $\tanh(\beta m_B B) \to 1$ and all spins are aligned. In the quantum case, however, we have (12.8.9), which is smaller by a factor of $3m_B B/2\mu \ll 1$. Again, at room temperature, the corrections in the quantum case become negligible, and the magnetization stays more or less independent of T, which is not so for the classical result. The quantum result is smaller than the classical by a factor of $3kT/2\mu$.

At non-zero temperature, the situation is similar to what we had in he previous sections. All those results can be applied to this situation with the replacement $\lambda_\pm \to e^{\beta(\mu\pm mB)}$. Thus, for example,

$$N^+ = \sum_k \frac{\lambda_+}{e^{\beta\epsilon(\vec{k})} + \lambda_+} = -\frac{V}{h^3}\left(\frac{2\pi m}{\beta}\right)^{3/2}\mathrm{Li}_{3/2}(-\lambda_+) \tag{12.8.11}$$

and

$$N^- = \sum_k \frac{\lambda_-}{e^{\beta\epsilon(\vec{k})} + \lambda_-} = -\frac{V}{h^3}\left(\frac{2\pi m}{\beta}\right)^{3/2}\mathrm{Li}_{3/2}(-\lambda_-) \tag{12.8.12}$$

give the numbers of particles aligned parallel and antiparallel to the magnetic field respectively. The magnetization is

$$M = m(N^+ - N^-) = -\frac{V}{h^3}\left(\frac{2\pi m}{\beta}\right)^{3/2}\left[\mathrm{Li}_{3/2}(-\lambda_+) - \mathrm{Li}_{3/2}(-\lambda_-)\right] \tag{12.8.13}$$

from where its low and high temperature behavior can be analyzed as we have done earlier.

12.9 White Dwarfs and Neutron Stars

A star that has consumed all its nuclear fuel will undergo gravitational collapse, but may end up in a stable state as a white dwarf or a neutron star provided that the mass that remains in the core after the outer layers are blown away during its death throes does not exceed a particular limit, called the **Chandrashekar** limit. Stars that succeed in forming such stable remnants owe their existence to the high degeneracy pressure exerted by electrons in the first case and neutrons in the second.

A typical white dwarf would hold about one solar mass in a volume equal to that of the earth. Thus it is an object whose density is approximately

$$\rho_{\text{wd}} = \frac{3M_\odot}{4\pi R_{\text{earth}}^3} \approx 1.8 \times 10^9 \text{ kg/m}^3 \tag{12.9.1}$$

At such densities virtually all the electrons are stripped from their nuclei and form a degenerate fermi gas in the star. The pressure exerted by this electron gas is given by (12.7.2),

$$P_e = \left(\frac{3}{4\pi}\right)^{2/3} \frac{h^2 n_e^{5/3}}{5m_e} \tag{12.9.2}$$

where the number density of electrons is now equal to the number density of protons, assuming that the core is neutral. Neglecting the electrons because their mass is much smaller than that of the proton and taking the mass of the neutron to be approximately that of the proton, the density of the core is $\rho = (n_p + n_n)m_p$, where n_p and n_n refer respectively to the number density of protons and neutrons in the core. Let Z be the average atomic number and A the average atomic mass number of the atoms constituting the core, then $n_p = Zn$ and $n_n = (A - Z)n$, where n is the density of atoms. Therefore

$$\frac{n_n}{n_p} = \left(\frac{A}{Z} - 1\right) \Rightarrow n_n + n_p = \frac{A}{Z} n_p \tag{12.9.3}$$

and therefore we have $n_e = n_p = (Z\rho/Am_p)$.[8] Substituting this in (12.9.2) we get

$$P_e \approx \left(\frac{3}{4\pi}\right)^{2/3} \frac{h^2}{5m_e} \left(\frac{Z\rho}{Am_p}\right)^{5/3} = \left(\frac{3}{4\pi}\right)^{2/3} \frac{h^2}{5m_e} \left(\frac{3ZM}{8\pi Am_p R^3}\right)^{5/3} \tag{12.9.4}$$

where M is the mass of the white dwarf and R is its radius. At or close to the center of the core the gravitational component of the pressure may be estimated purely by dimensional analysis. Since we assume spherical symmetry, the only properties of the star upon which

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[8] For the density in (12.9.1) and taking $Z/A \approx 0.5$, the electron density is $n_e \approx 5.4 \times 10^{35}$ m^{-3}.

the gravitational pressure may depend are M and R. Since the pressure is due to the weight of all the layers of the star, we easily find that at the center

$$P_g = \alpha \frac{GM^2}{R^4} \tag{12.9.5}$$

where α is some dimensionless quantity that only a sound numerical calculation can give. The (outward) electron degeneracy pressure can balance the (inward) gravitational pressure at the center if and only if

$$\left(\frac{3}{4\pi}\right)^{2/3} \frac{h^2}{5m_e} \left(\frac{3ZM}{8\pi A m_p R^3}\right)^{5/3} = \alpha \frac{GM^2}{R^4} \tag{12.9.6}$$

Simplifying, we find the radius of the white dwarf as a function of its mass,

$$R = \frac{3}{40\pi} \left(\frac{9}{32\pi^2}\right)^{2/3} \frac{h^2 M_\odot^{-1/3}}{\alpha G m_e} \left(\frac{Z}{A m_p}\right)^{5/3} \left(\frac{M}{M_\odot}\right)^{-1/3}. \tag{12.9.7}$$

Thus the larger the mass the smaller the white dwarf gets. This is easy to understand because larger mass cores require a higher degeneracy pressure to balance the inward pull of gravity. The star achieves this by making the core smaller to increase the density of electrons and cause them to acquire higher mean speeds. The process of getting smaller with increasing mass cannot go on forever; at some point the electrons become relativistic and the relationship between the pressure they exert and their speeds softens.[9] For ultrarelativistic electrons, we can take $v_{\rm rms} = c$ and find

$$P_e = \frac{1}{3} n_e v_{\rm rms} p_{\rm rms} \approx \frac{c}{3} n_e p_{\rm rms} \tag{12.9.8}$$

But what is the average energy of a Fermi gas in the extreme relativistic limit? We find this by beginning with the expression for the number density (still at low temperature and in the continuum limit)

$$N = \lim_{\beta \to \infty} \frac{2\pi V}{h^3} \int_0^\mu \frac{p^2 dp}{e^{\beta(\epsilon - \mu)} + 1} \tag{12.9.9}$$

keeping in mind that in the ultrarelativistic limit the dispersion relation is $p = \epsilon/c$. Thus

$$N \approx \frac{2\pi V}{h^3 c^3} \int_0^\mu \epsilon^2 d\epsilon = \frac{2\pi V \mu^3}{3h^3 c^3} \Rightarrow \mu = hc \left(\frac{3n}{2\pi}\right)^{1/3} \equiv E_F \tag{12.9.10}$$

and the average energy is

$$\langle E \rangle = \frac{2\pi V}{h^3 c^3} \int_0^\mu \epsilon^3 d\epsilon = \frac{\pi V \mu^4}{2h^3 c^3} = \frac{3}{4} N E_F. \tag{12.9.11}$$

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[9] Problem: Estimate the density of electrons for which they become relativistic.

It follows that $p_{\rm rms} \approx 3E_f/4c$ giving

$$P_e = \left(\frac{3}{2\pi}\right)^{1/3} \frac{hcn_e^{4/3}}{4} = \left(\frac{3}{2\pi}\right)^{1/3} \frac{hc}{4} \left(\frac{3ZM}{8\pi Am_p R^3}\right)^{4/3} \tag{12.9.12}$$

Once again, equating this to the gravitational pressure and solving for M we find,

$$M_{\rm Ch} = \left(\frac{3}{4\pi}\right)^{5/2} \left(\frac{hc}{8\alpha G}\right)^{3/2} \left(\frac{Z}{Am_p}\right)^2 \tag{12.9.13}$$

which is the absolute maximum mass that can be supported by electron degeneracy. Notice that it depends only on the fundamental constants and that it is independent of the electron mass. If this mass is exceeded, electron degeneracy is no longer capable of supporting the star against gravitational collapse and the star continues to collapse. Within a tenth of a second the electrons combine with the protons to form neutrons according to the reaction

$$p^+ + e^- \to n + \nu_e \tag{12.9.14}$$

The neutrino cross-section is so small that they do not significantly interact with matter until densities on the order of the nuclear density are achieved. They simply pass through the core leaving behind the neutrons. The collapsing inner regions send out waves that rapidly become shock waves and tear the outer layers off. The star goes **"supernova"**, leaving behind, if anything, a neutron star.

What would the density of a neutron star be? As a first approximation we could suggest the density of a neutron. Take the "size" of the neutron to be just its Compton wavelength, $h/m_n c$, and get $\sim 10^{-15}$ m, or 1 Fermi. The neutron packs a mass of $\sim 1.67 \times 10^{-27}$ kg in a volume which is about the volume of a sphere of radius 1 Fermi, so its density is on the order of 4×10^{17} kg/m^3. This is eight orders of magnitude greater than the density of a white dwarf. A neutron star of $M_\odot$ would have a radius of just 10.5 km! As long as the neutrons remain non-relativistic, the relationship between the radius of the neutron star and its mass is similar to (12.9.7) with the electron mass replaced by the neutron mass and Z/A replaced by unity. The neutron possesses roughly 1800 times the electron mass so the star is now smaller by roughly that factor. However, for sufficiently large stars the neutrons may also become ultrarelativistic, and the Chandrashekar limit may be exceeded.[10] When this happens, neutron degeneracy pressure is not able to counteract gravity and we know of no force that can keep the star from collapsing into a black hole.

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[10] Problem‘: Estimate the density at which neutrons become relativistic.

Chapter 13

The Density Matrix

In this chapter we aim to formalize the heuristic considerations of Chapter 12. Quantum Mechanics as we generally learn it is designed for isolated or "closed" systems, *i.e.,* systems that do not interact in any significant way with their environment. Such systems are highly idealized and excellent for demonstrating some of the most intriguing features of the quantum theory, however most systems that are encountered in the laboratory do possess some interactions with their environment. We will begin by employing some of the most basic features of the quantum theory to reformulate it in terms of the so-called **density matrix**. Then we'll argue that the reformulation applies even when the quantum system that we are considering is not isolated. We will see that the most effective way to describe an "open" system, *i.e.,* systems that interact with the rest of the universe, is via a generalization of the density matrix. We'll examine its properties in some detail.

13.1 Closed Quantum systems

A closed quantum system is one that does not interact with the enviroment. If $\widehat{\mathcal{H}}$ is the Hamiltonian operator of such a system then the wave function describing it will obey Schroedinger's equation

$$i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = \widehat{\mathcal{H}}|\psi(t)\rangle \tag{13.1.1}$$

If, moreover, $\widehat{\mathcal{H}}$ is time independent then the wave function can always be written as a linear combination of stationary states,

$$|\psi_\alpha(t)\rangle = e^{-iE_\alpha t}|\alpha\rangle \tag{13.1.2}$$

where $|\alpha\rangle$ are the (complete set of) eigenstates of the Hamiltonian with eigenvalues E_α. Writing

$$|\psi(t)\rangle = \sum_\alpha c_\alpha e^{-iE_\alpha t}|\alpha\rangle \tag{13.1.3}$$

and assuming that the eigenstates of the Hamiltonian are normalized we find that $|\psi(t)\rangle$ is normalized if and only if the coefficients c_α satisfy the constraint

$$\sum_\alpha c_\alpha^* c_\alpha = \sum_\alpha |c_\alpha|^2 = 1. \tag{13.1.4}$$

In fact these expressions can be extended to *any* complete set of states, $|\alpha\rangle$, even if they are not eigenstates of the Hamiltonian, for then we write

$$|\psi(t)\rangle = \sum_\alpha c_\alpha(t)|\alpha\rangle \tag{13.1.5}$$

and again assuming that the complete set of states is normalized, we get

$$\sum_\alpha c_\alpha^*(t) c_\alpha(t) = \sum_\alpha |c_\alpha(t)|^2 = 1. \tag{13.1.6}$$

The expectation value of any operator $\widehat{A}$ is given by

$$\langle \widehat{A} \rangle = \langle \psi(t)|\widehat{A}|\psi(t)\rangle = \sum_{\alpha,\beta} c_\alpha^*(t) c_\beta(t) \langle \alpha|\widehat{A}|\beta\rangle = \sum_{\alpha,\beta} c_\alpha^*(t) c_\beta(t) A_{\alpha\beta} \tag{13.1.7}$$

so if we introduce the operator $\widehat{\rho}$, with matrix elements defined via its transpose, $\widehat{\rho}^T$ as

$$\langle \alpha|\widehat{\rho}^T|\beta\rangle \overset{\text{def}}{=} \rho_{\alpha\beta}^T = c_\alpha^*(t) c_\beta(t) \tag{13.1.8}$$

then it follows from (13.1.6) that $\widehat{\rho}$ is a Hermitean projection operator of unit trace,

$$\widehat{\rho}^\dagger = \widehat{\rho}, \quad \widehat{\rho}^2 = \widehat{\rho}, \quad \mathrm{Tr}(\widehat{\rho}) = 1 \tag{13.1.9}$$

and furthermore, from (13.1.7), that the expectation value of $\widehat{A}$ is given by

$$\langle \widehat{A} \rangle = \mathrm{Tr}(\widehat{\rho A}) \tag{13.1.10}$$

The matrix $\widehat{\rho}$ is called the density matrix.

Now $\widehat{\rho}$ can be diagonalized because it is Hermitean so let $|i\rangle$ be a complete, orthonormal set of eigenvectors of $\widehat{\rho}$ then the operator can be wriiten as

$$\widehat{\rho} = \sum_i w_i |i\rangle\langle i| \tag{13.1.11}$$

where w_i are the eigenvalues of $\widehat{\rho}$. The average value of any operator $\widehat{A}$ can be given in the new basis as well and reads

$$\mathrm{Tr}(\widehat{\rho A}) = \sum_{i,j} w_i \langle j|i\rangle\langle i|\widehat{A}|j\rangle = \sum_i w_i \langle i\widehat{A}|i\rangle = \sum_i w_i A_{ii} \tag{13.1.12}$$

which says that the eigenvalue w_i of $\widehat{\rho}$ should be interpreted as the probability that the system is in the state $|i\rangle$, because A_{ii} is the expectation value of the operator $\widehat{A}$ in that state. For such an interpretation to be possible, however, one should show in general that $\sum_j w_j = 1$ and that $w_j \geq 0$ for all i. Fortunately, this is quite straightfoward since

$$\mathrm{Tr}(\widehat{\rho}) = 1 \Rightarrow \sum_i w_i = 1 \tag{13.1.13}$$

and if we take $\widehat{A} = |j\rangle\langle j|$ then

$$w_j = \mathrm{Tr}(\widehat{\rho A}) = \langle \widehat{A} \rangle = \langle \psi(t)|\widehat{A}|\psi(t)\rangle = \langle \psi(t)|j\rangle\langle j|\psi(t)\rangle = |\langle \psi(t)|j\rangle|^2 \geq 0 \tag{13.1.14}$$

which says that $w_j \geq 0$ for every j. But there is yet another important property of the w_j's that holds for closed systems: all but *one* of the w_j are exactly zero. This is a consequence of the fact that $\widehat{\rho}$ is a projection operator, therefore

$$\mathrm{Tr}\widehat{\rho}^2 = \mathrm{Tr}\widehat{\rho} \Rightarrow \sum_j w_j(1 - w_j) = 0 \tag{13.1.15}$$

and since the left hand side of the second equation is a sum of non-negative terms, each term should be identically zero, which is possible if and only if $w_j = 0$ or $w_j = 1$ for every j. Again, since $\sum_j w_j = 1$ it follows that all w_j but one are zero.

13.2 Open Quantum Systems

An open quantum system is one that interacts with another quantum system, generally called the environment. It can be viewed as a part of a larger *closed* quantum system, the other part being the environment. As we will see, most of our discussion above is valid for open quantum systems as well. However the density operator will not necessarily be a projection operator and the relaxation of this condition will turn out to have very important consequences. Let us first see how one describes an open quantum system.

Suppose that "our" system interacts with the environment in such a way that the quantum state of the entire universe (our system plus the environment) can be written as the linear superposition of a complete set of normalized eigenstates, each of which is a tensor product,

$$|\psi(t)\rangle = \sum_{\alpha,a} c_{\alpha a}(t)|\alpha\rangle|a\rangle \tag{13.2.1}$$

where α and a refer to the system we're interested in ("our" system) and the environment respectively. The eigenstates are assumed orthonormal, therefore

$$\langle a|\langle\alpha|\beta\rangle|b\rangle = \delta_{\alpha\beta}\delta_{ab} \tag{13.2.2}$$

and, if we will assume that $|\psi(t)\rangle$ is normalized, we will have

$$\langle\psi(t)|\psi(t)\rangle = 1 \Rightarrow \sum_{\alpha,a} c^*_{\alpha a} c_{\alpha a} = \sum_{\alpha,a} |c_{\alpha a}|^2 = 1. \tag{13.2.3}$$

The average value of an operator that acts *only* on our system will be

$$\langle\widehat{A}\rangle = \langle\psi(t)|\widehat{A}|\psi(t)\rangle = \sum_{\alpha,a,\beta,b} c^*_{\alpha a} c_{\beta b} \langle a|(\langle\alpha|\widehat{A}|\beta\rangle)|b\rangle = \sum_{\alpha,\beta,a} c^*_{\alpha a} c_{\beta a} A_{\alpha\beta} \tag{13.2.4}$$

and so, by analogy with our treatment of closed systems we define the density operator via its transpose

$$\langle\alpha|\widehat{\rho}^T|\beta\rangle = \rho^T_{\alpha\beta} = \sum_a c^*_{\alpha a} c_{\beta a} \tag{13.2.5}$$

so that

$$\langle\widehat{A}\rangle = \mathrm{Tr}(\widehat{\rho A}) \tag{13.2.6}$$

in keeping with our desire to have $\widehat{\rho}$ compute averages of operators that act only on the system.

The density operator as defined above is obviously Hermitean and of unit trace since by (13.2.3)

$$\mathrm{Tr}(\widehat{\rho}) = \sum_a c^*_{\alpha a} c_{\alpha a} = 1 \tag{13.2.7}$$

but it is not a projection operator as can be seen by simply computing $\widehat{\rho}^2$,

$$\widehat{\rho}^2 = \sum_{\gamma,a,b} c^*_{\gamma a} c_{\alpha a} c^*_{\beta b} c_{\gamma b} \neq \widehat{\rho}. \tag{13.2.8}$$

Therefore, two of the three conditions met by the density operator of closed systems are met also by the density operator of open systems. As before, we may introduce an eigenbasis for the density operator and express $\widehat{\rho}$ in terms of it

$$\widehat{\rho} = \sum_i w_i |i\rangle\langle i| \tag{13.2.9}$$

where w_i are the eigenvalues of $\widehat{\rho}$. If $\widehat{A}$ acts only on our system and not on the environment then its expectation value

$$\langle\widehat{A}\rangle = \mathrm{Tr}(\widehat{\rho A}) = \sum_{j,i} w_i \langle j|i\rangle\langle i|\widehat{A}|j\rangle = \sum_i w_i A_{ii} \tag{13.2.10}$$

indicates as before, that the eigenvalue w_i of $\widehat{\rho}$ represents the probability of finding the system in the eigenstate $|i\rangle$. To strengthen this interpretation, we note also that

$$\mathrm{Tr}(\widehat{\rho}) = \sum_{i,j} w_i \langle j|i\rangle\langle i|j\rangle = \sum_i w_i = 1 \tag{13.2.11}$$

and if we take $\widehat{A} = |j\rangle\langle j|$ then

$$w_j = \mathrm{Tr}(\widehat{\rho A}) = \langle \widehat{A} \rangle = \langle \psi(t)|\widehat{A}|\psi(t)\rangle = \langle \psi(t)|j\rangle\langle j|\psi(t)\rangle = \sum_i |\langle \psi(t)|j\rangle|^2 \geq 0 \qquad (13.2.12)$$

so the two necessary conditions are indeed met.

To summarize, every quantum mechanical system can be described by a density matrix (operator), $\widehat{\rho}$ satisfying the following four properties:

- $\widehat{\rho}$ is Hermitean
- $\mathrm{Tr}(\widehat{\rho}) = 1$
- The expectation value of any operator that acts only on the system can be given by $\langle \widehat{A} \rangle = \mathrm{Tr}(\widehat{\rho A})$
- If the quantum system is closed, *i.e.,* if it does not interact with its environment, then $\widehat{\rho}$ is a projection operator. Otherwise $\widehat{\rho}$ is not a projection operator.

The distinction between an open system and a closed system is contained in the fourth statement above. States for which the density operator is a projection operator are called **pure states**. States for which the density operator is not a projection operator are called **mixed states**. In quantum statistics we are generally concerned with mixed states. While pure states are excellent for describing peculiarly quantum mechanical phenomena such as interference, they are idealizations that cannot actually be prepared in the laboratory.

Let's consider a simple example of pure and mixed states in a two state system. Consider a spin $\frac{1}{2}$ particle, whose quantum states may be specified in the $\widehat{s}_z$ basis of "spin up" and "spin down" states

$$|+\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |-\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \qquad (13.2.13)$$

Suppose that the particle is interacting with the environment, whose states we represent by $|y_i\rangle$. The general state of the universe (particle plus its environment) will be a linear superposition of the form,

$$|\psi\rangle = \sum_i (c_{+i}|+\rangle + c_{-i}|-\rangle)|y_i\rangle \qquad (13.2.14)$$

and normalization of this state is equivalent to restriction

$$\sum_i (|c_{+i}|^2 + |c_{-i}|^2) = 1. \qquad (13.2.15)$$

The average value of any operator acting only on the particle (eg. $\widehat{s}_x$) would be

$$\langle \widehat{A} \rangle \quad = \quad \sum_{i,j} \langle y_j|(c^*_{+j}\langle +| + c^*_{-j}\langle -|)\widehat{A}(c_{+i}|+\rangle + c_{-i}|-\rangle)|y_i\rangle$$

$$= \sum_i (|c_{+i}|^2 A_{++} + c_{+i}^* c_{-i} A_{+-} + c_{+i} c_{-i}^* A_{-+} + |c_{-i}|^2 A_{--}) \tag{13.2.16}$$

Therefore, if we call,

$$\sum_i |c_{+i}|^2 = a, \quad \sum_i c_{+i}^* c_{-i} = b, \quad \sum_i |c_{-i}|^2 = c \tag{13.2.17}$$

then $a + c = 1$ and the density matrix corresponding to this state will be of the form

$$\widehat{\rho} = \begin{pmatrix} a & b \\ b^* & c \end{pmatrix} \tag{13.2.18}$$

Clearly, $\widehat{\rho}$ is a Hermitean matrix of unit trace. For $\widehat{\rho}$ to be a projection operator as well, the following conditions should hold

$$a^2 + |b|^2 = a, \quad c^2 + |b|^2 = c \tag{13.2.19}$$

Of course the equations are not independent: because $a + c = 1$, the second equation implies the first and vice-versa. The first equation tells us that $|b|^2 = a - a^2$. Since a is real, we set $a = ss^*$, for some complex s of magnitude less than or equal to unity. Then $|b|^2 = |s|^2(1 - |s^2|) = |sr^*|^2$, where r is another complex number of magnitude is less than or equal to unity and such that $|s|^2 + |r|^2 = 1$. This gives $c = |r|^2$ and, modulo a phase, $b = sr^*$, so $\widehat{\rho}$ has the form

$$\widehat{\rho} = \begin{pmatrix} |s|^2 & sr^* \\ s^* r & |r|^2 \end{pmatrix} \tag{13.2.20}$$

which is precisely the density matrix we would derive from the pure state

$$|\psi\rangle = s|+\rangle + r|-\rangle \tag{13.2.21}$$

In general, however, $\widehat{\rho}$ is not a projection operator. For example, the density matrix with $a = \cos^2\theta$, $c = \sin^2\theta$ and $b = 0$

$$\widehat{\rho} = \begin{pmatrix} \cos^2\theta & 0 \\ 0 & \sin^2\theta \end{pmatrix} \tag{13.2.22}$$

represents a mixed state, not a pure state, so long as θ is not an integer or half-integer multiple of π. Its eigenvalues are $\cos^2\theta$ and $\sin^2\theta$, with eigenvectors $|+\rangle$ and $|-\rangle$ respectively and it can be written as

$$\widehat{\rho} = \cos^2\theta |+\rangle\langle+| + \sin^2\theta |-\rangle\langle-| \tag{13.2.23}$$

This tells us that the probability of finding “spin up” is $\cos^2\theta$ and “spin down” is $\sin^2\theta$. Furthermore, a little computation shows that both the x and y components of the spin,

$$\widehat{s}_x = |+\rangle\langle-| + |-\rangle\langle+|$$

$$\widehat{s}_y = i(|+\rangle\langle-| - |-\rangle\langle+|) \tag{13.2.24}$$

have vanishing expectation values.

On the other hand, the density matrix

$$\widehat{\rho} = \begin{pmatrix} \cos^2\theta & e^{i\Delta\phi}\sin\theta\cos\theta \\ e^{-i\Delta\phi}\sin\theta\cos\theta & \sin^2\theta \end{pmatrix} \tag{13.2.25}$$

represents the pure state

$$|\psi\rangle = \cos\theta|+\rangle + e^{-i\Delta\phi}\sin\theta|-\rangle \tag{13.2.26}$$

and, as expected, its eigenvalues are 1 and 0 with eigenvectors

$$|1\rangle = \begin{pmatrix} \cos\theta \\ e^{-i\Delta\phi}\sin\theta \end{pmatrix}, \quad |0\rangle = \begin{pmatrix} -\sin\theta \\ e^{-i\Delta\phi}\cos\theta \end{pmatrix} \tag{13.2.27}$$

respectively. Thus $\widehat{\rho} = |1\rangle\langle 1|$ and whereas the expectation values of $\widehat{s}_x$ and $\widehat{s}_y$ are non-vanishing in this pure state,

$$\langle\widehat{s}_x\rangle = \sin 2\theta\cos\Delta\phi, \quad \langle\widehat{s}_y\rangle = \sin 2\theta\sin\Delta\phi, \tag{13.2.28}$$

they are vanishing in the mixed state considered earlier.[1],

Thus it is an experiment that measures the x (or y) components of the spin that distinguishes the mixed state from the pure state and not an experiment that measures the z component, since in both cases the probability for spin up is $\cos^2\theta$ and the probability for spin down is $\sin^2\theta$.

13.3 Additional Properties of the Density Matrix

From the definition of the density operator,

$$\widehat{\rho} = \sum_i w_i|i\rangle\langle i| \tag{13.3.1}$$

it is easy to see that

$$\widehat{\rho}^n = \sum_i w_i^n|i\rangle\langle i| \tag{13.3.2}$$

and therefore any analytic function of the density operator can be written as

$$f(\widehat{\rho}) = \sum_i f(w_i)|i\rangle\langle i| \tag{13.3.3}$$

---

[1] Problem: Show this.

Again, because each w_i represents the probability for finding the system in state $|i\rangle$, we can define the Gibbs entropy of the system,

$$S = -\sum_i w_i \ln w_i = \mathrm{Tr}(\widehat{\rho} \ln \widehat{\rho}). \tag{13.3.4}$$

For a pure state the entropy will be identically zero, but it will not be zero for a mixed state.

What about the time evolution of the density matrix? Starting from the definition of $\widehat{\rho}$ and taking a time derivative

$$\begin{aligned} i\hbar \frac{\partial \widehat{\rho}}{\partial t} &= i\hbar \sum_i w_i \frac{\partial}{\partial t}(|i\rangle\langle i|) = \sum_i w_i(\widehat{\mathcal{H}}|i\rangle\langle i| - |i\rangle\langle i|\widehat{\mathcal{H}}) = [\widehat{\mathcal{H}}, \widehat{\rho}] \\ \Rightarrow \qquad i\hbar \frac{\partial \widehat{\rho}}{\partial t} &+ [\widehat{\rho}, \widehat{\mathcal{H}}] = 0 \end{aligned} \tag{13.3.5}$$

because each state evolves according to Schoredinger's equation. Note that the equation of motion for $\widehat{\rho}$ differs from the usual Heisenberg equation by a minus sign. This is because it is constructed from state vectors, so it is not an observable like other hermitian operators and there is no reason to expect that its time evolution will be the same. It follows that $\widehat{\rho}$ is independent of time if and only if it commutes with the Hamiltonian. This means that in equilibrium statistical mechanics we will be interested only in density matrices that are constant or commute with the Hamiltonian.

Recall how in classical statistical mechanics the microcanonical ensemble was defined by requiring the probability of finding a member of the ensemble in all available microstates to be the same. Thus if $\Omega(E, N, X_\alpha)$ represents the number of microstates accessible to the system we write the distribution function as

$$\rho(\vec{p}, \vec{q}) = \frac{1}{\Omega(E, N, X_\alpha)} \delta(\mathcal{H}(q,p) - E)\delta(N(q,p) - N). \tag{13.3.6}$$

The normalization of the density function determines $\Omega(E, N, X_\alpha)$,

$$\frac{1}{h^f N!} \int d^f q d^f p \; \rho(p,q) = 1, \tag{13.3.7}$$

where we have used Gibb's correction for indistinguishable particles. The average value of any operator $\widehat{A}$ is given by

$$\langle \widehat{A} \rangle = \frac{1}{h^f N!} \int d^f q d^f p \; \rho(q,p) A(q,p) \tag{13.3.8}$$

Quantum mechanically, the microcanonical ensemble for an isolated system with Hamiltonian $\mathcal{H}(q,p)$ and energy eigenstates E_α is defined by the density matrix

$$\widehat{\rho} = \frac{1}{\Omega} \sum_\alpha \delta_{E_\alpha, E} |\alpha\rangle\langle\alpha| \tag{13.3.9}$$

so that all the microstates whose energy equals the the total (fixed) energy E of the system contribute to the density matrix with equal weights.

In the canonical ensemble the density matrix takes the form

$$\widehat{\rho} = \sum_\alpha \frac{1}{Z} e^{-\beta E_\alpha} |\alpha\rangle\langle\alpha| = \frac{1}{Z} e^{-\beta \widehat{\mathcal{H}}} \tag{13.3.10}$$

where Z is obtained by the normalization condition, $\mathrm{Tr}(\widehat{\rho}) = 1$, which gives $Z = \mathrm{Tr}(e^{-\beta\widehat{\mathcal{H}}})$. Evidently, then, Z is the partition function we have used in the previous chapters.

In the grand canonical ensemble,

$$\widehat{\rho} = \sum_\alpha \frac{1}{Z} e^{-\beta(E_\alpha - \mu N_\alpha)} |\alpha\rangle\langle\alpha| = \frac{e^{-\beta(\widehat{\mathcal{H}} - \mu\widehat{N})}}{\mathrm{Tr}(e^{-\beta(\widehat{\mathcal{H}} - \mu\widehat{N})})} \tag{13.3.11}$$

where Z is again the partition function, now in the grand canonical ensemble. When the density matrix in the canonical ensemble is viewed as a function of the temperature, we find that it satisfies a very simple equation. Let $\widehat{\rho}_U$ be the unnormalized density matrix, $\widehat{\rho}_U = e^{-\beta\widehat{\mathcal{H}}}$, then

$$\frac{\partial \widehat{\rho}_U}{\partial \beta} = -\widehat{\mathcal{H}}\widehat{\rho}_U \tag{13.3.12}$$

with the initial condition $\rho_U(0) = 1$.

13.4 Density Matrix in the position representation

We will now perform some simple, one dimensional computations of the density matrix. Our emphasis will be in finding $\rho(x, x'; \beta)$ and computing the expectation values of simple operators with it.

13.4.1 One Dimensional Particle

The simplest system is the free particle, so it makes sense to begin with $\mathcal{H} = p^2/2m$. In the position representation, we could write the equation for $\widehat{\rho}_U$ as

$$\frac{\partial}{\partial \beta} \rho_U(x, x'; \beta) = \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \rho_U(x, x'; \beta) \tag{13.4.1}$$

where

$$\rho_U(x, x'; \beta) = \langle x'|e^{-\beta\widehat{\mathcal{H}}}|x\rangle = \sum_\alpha e^{-\beta E_\alpha} \langle x'|\alpha\rangle\langle\alpha|x\rangle = \sum_\alpha e^{-\beta E_\alpha} \psi^*_\alpha(x')\psi_\alpha(x) \tag{13.4.2}$$

where $\psi_\alpha(x)$ is an energy eigenstate. The equation for $\rho(x,x';\beta)$ is a diffusion equation and we are interested in solving it subject to the boundary condition

$$\lim_{\beta\to 0}\rho_U(x,x';\beta)=\delta(x-x'). \tag{13.4.3}$$

One way is to take

$$\rho_U(x,x';\beta)=\int_{-\infty}^{\infty}\frac{dk}{2\pi}\rho_U(k,\beta)e^{-ik(x-x')} \tag{13.4.4}$$

where $\lim_{\beta\to 0}\rho_U(k,\beta)=1$. Then

$$\frac{\partial}{\partial\beta}\rho_U(k,\beta)=-\frac{\hbar^2k^2}{2m}\rho_U(k,\beta) \tag{13.4.5}$$

gives

$$\rho_U(k,\beta)=e^{-\frac{\hbar^2k^2\beta}{2m}} \tag{13.4.6}$$

so, inserting this solution into (13.4.4) gives

$$\rho_U(x,x';\beta)=\int_{-\infty}^{\infty}\frac{dk}{2\pi}e^{-\frac{\hbar^2k^2\beta}{2m}}e^{-ik(x-x')}=\sqrt{\frac{m}{2\pi\beta\hbar^2}}e^{-\frac{m}{2\hbar^2\beta}(x-x')^2} \tag{13.4.7}$$

Of course we would get the same answer if we exploit (13.4.2), writing

$$\rho_U(x,x';\beta)=\int_{-\infty}^{\infty}\frac{dk}{2\pi}e^{-\frac{\hbar^2k^2\beta}{2m}}\psi_k^*(x')\psi_k(x) \tag{13.4.8}$$

where we have used $\langle k'|\widehat{\rho}_U|k\rangle=e^{-\frac{\beta\hbar^2k^2}{2m}}\delta(k-k')$ together with $\psi_k(x)=\langle x|k\rangle=e^{ikx}$.

If we imagine that the particle is confined in a one dimensional box of length L, then the trace of the density matrix, which is just the partition function, can be written as

$$\mathrm{Tr}(\widehat{\rho}_U)=\int_0^L dx\ \rho(x,x;\beta)=L\sqrt{\frac{m}{2\pi\beta\hbar^2}}, \tag{13.4.9}$$

and therefore the normalized density matrix is just

$$\rho(x,x';\beta)=\frac{1}{L}e^{-\frac{m}{2\hbar^2\beta}(x-x')^2}. \tag{13.4.10}$$

Let's first evaluate the expectation values of some typical quantities. For example,

$$\langle\widehat{x}\rangle=\mathrm{Tr}(\widehat{\rho x})=\int_0^L dx\ x\ \rho(x,x;\beta)=\frac{L}{2} \tag{13.4.11}$$

The expectation value of the momentum operator needs only a little more work. The definition of the expectation value

$$\langle\widehat{p}\rangle = \int dx \langle x|\widehat{p}\widehat{\rho}|x\rangle = \int dx dx' \langle x|\widehat{p}|x'\rangle\langle x'|\widehat{\rho}|x\rangle \tag{13.4.12}$$

together with the fact that

$$\langle x|\widehat{p}|x'\rangle = \frac{\hbar}{i}\frac{\partial}{\partial x}\delta(x-x') \tag{13.4.13}$$

imply that

$$\langle\widehat{p}\rangle = \int dx dx' \frac{\hbar}{i}\left[\frac{\partial}{\partial x}\delta(x-x')\right]\rho(x,x';\beta) = i\hbar\int_0^L dx \left[\frac{\partial}{\partial x}\rho(x,x';\beta)\right]_{x=x'} = 0 \tag{13.4.14}$$

where we have integrated by parts once. What about $\langle\widehat{p}^2\rangle$? We have to use

$$\langle x|\widehat{p}^2|x'\rangle = -\hbar^2\frac{\partial^2}{\partial x^2}\delta(x-x') \tag{13.4.15}$$

so

$$\begin{aligned} \langle x|\widehat{p}^2|x'\rangle &= \int dx dx' \left\{-\hbar^2\left[\frac{\partial^2}{\partial x^2}\delta(x-x')\right]\rho(x,x';\beta)\right\} \\ &= -\hbar^2\int_0^L dx \left[\frac{\partial^2}{\partial x^2}\rho(x,x';\beta)\right]_{x=x'} = \frac{m}{\beta} \end{aligned} \tag{13.4.16}$$

where we integrated twice in the second step. The average energy of the system is therefore $\langle\widehat{\mathcal{H}}\rangle = \langle\widehat{p}^2/2m\rangle = \frac{1}{2}kT$.

13.4.2 One Dimensional Harmonic Oscillator

The smallest step up from the free particle is the one dimensional harmonic oscillator with Hamiltonian

$$\mathcal{H} = \frac{p^2}{2m} + \frac{1}{2}m\omega^2x^2 \tag{13.4.17}$$

which gives the following equation for the density matrix

$$\frac{\partial}{\partial\beta}\rho(x,x';\beta) = \left[\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} - \frac{1}{2}m\omega^2x^2\right]\rho(x,x';\beta) \tag{13.4.18}$$

This is not easily solved by the method of Green functions. However, we can exploit the fact that we know the quantum states of the oscillator. Thus, from (13.4.2)

$$\langle x'|\widehat{\rho}_U|x\rangle = \sum_{n=0}^{\infty} e^{-\beta E_n}\varphi_n^*(x')\varphi_n(x), \tag{13.4.19}$$

where $\varphi_n(x)$ are eigenstates of $\widehat{\mathcal{H}}$ of energy $E_n = \left(n+\frac{1}{2}\right)\hbar\omega$. We have

$$\varphi_n(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n(\sqrt{\alpha}x) e^{-\frac{\alpha x^2}{2}} \tag{13.4.20}$$

where $\alpha = \frac{m\omega}{\hbar}$. Therefore

$$\langle x'|\widehat{\rho}_U|x\rangle = \left(\frac{\alpha}{\pi}\right)^{1/2} e^{-\frac{\alpha}{2}(x^2+x'^2)} \sum_{n=0}^{\infty} \frac{1}{2^n n!} e^{-\beta(n+\frac{1}{2})\hbar\omega} H_n(\sqrt{\alpha}x') H_n(\sqrt{\alpha}x) \tag{13.4.21}$$

This sum is by no means easy to do, but the answer can be obtained in closed form. It is

$$\begin{aligned} \rho_U(x,x';\beta) &= \sqrt{\frac{m\omega}{2\pi\hbar\sinh(\beta\hbar\omega)}} \times \\ & \exp\left[-\frac{m\omega}{4\hbar}\left\{(x+x')^2\tanh\left(\frac{\beta\hbar\omega}{2}\right) + (x-x')^2\coth\left(\frac{\beta\hbar\omega}{2}\right)\right\}\right] \end{aligned} \tag{13.4.22}$$

The trace of this matrix, or the partition function for this oscillator, is

$$\begin{aligned} \int_{-\infty}^{\infty} dx \rho_U(x,x;\beta) &= \sqrt{\frac{m\omega}{2\pi\hbar\sinh(\beta\hbar\omega)}} \int_{-\infty}^{\infty} dx \exp\left[-\frac{m\omega}{\hbar}x^2\tanh\left(\frac{\beta\hbar\omega}{2}\right)\right] \\ &= \left[2\sinh\left(\frac{\beta\hbar\omega}{2}\right)\right]^{-1} \end{aligned} \tag{13.4.23}$$

and now we may write the normalized density matrix as

$$\begin{aligned} \rho(x,x';\beta) &= \sqrt{\frac{m\omega}{\pi\hbar}\tanh\frac{\beta\hbar\omega}{2}} \times \\ & \exp\left[-\frac{m\omega}{4\hbar}\left\{(x+x')^2\tanh\left(\frac{\beta\hbar\omega}{2}\right) + (x-x')^2\coth\left(\frac{\beta\hbar\omega}{2}\right)\right\}\right] \end{aligned} \tag{13.4.24}$$

Taking expectation values as we did above for the free particle, we should find that the oscillator is, on the average, at the center, $\langle x\rangle = 0$, but

$$\langle x^2\rangle = \frac{\hbar}{2m\omega}\coth\left(\frac{\beta\hbar\omega}{2}\right) \tag{13.4.25}$$

and indeed, we see that $\rho(x,x;\beta)$ is a normalized Gaussian distribution with zero mean and variance equal to $\langle x^2\rangle$. Likewise, a simple calculation gives $\langle\widehat{p}\rangle = 0$ and

$$\langle\widehat{p}^2\rangle = \frac{1}{2}m\hbar\omega\coth\left(\frac{\beta\hbar\omega}{2}\right) \tag{13.4.26}$$

so we see that the mean energy of the oscillator is

$$\langle E\rangle = \frac{\langle \widehat{p}^2\rangle}{2m} + \frac{1}{2}m\omega^2\langle x^2\rangle = \frac{1}{2}\hbar\omega\coth\left(\frac{\beta\hbar\omega}{2}\right) \tag{13.4.27}$$

which compares with (9.2.26).

13.4.3 N Free Particles

Let us now turn to a system of N identical free particles. Assuming that the particles are identical but distinguishable, one could represent the wavefunction of the system by the product state

$$\psi(x_1, x_2, \ldots, x_N) = \prod_{i=1}^{N} \psi_{k_i}(x_i) \tag{13.4.28}$$

where k_i is the wave number associated with the particle i. To compute the matrix elements of the density matrix we need

$$\begin{aligned} \rho_U(x_1, \ldots, x_N; x_1', \ldots x_N'; \beta) &= \langle x_1', x_2', \ldots, x_N'|\widehat{\rho}_U|x_1, x_2, \ldots, x_N\rangle \\ &= \langle x_1', x_2', \ldots, x_N'|e^{-\beta\widehat{\mathcal{H}}}|x_1, x_2, \ldots, x_N\rangle \end{aligned} \tag{13.4.29}$$

and, inserting a complete set of energy eigenstates, we get

$$\begin{aligned} \rho_U(\vec{x}, \vec{x}'; \beta) &= \int_{-\infty}^{\infty} \prod_{\vec{k}', \vec{k}} \frac{d\vec{k}'}{(2\pi)^N} \frac{d\vec{k}}{(2\pi)^N} \langle \vec{x}'|\vec{k}'\rangle\langle\vec{k}'|e^{-\beta\widehat{\mathcal{H}}}|\vec{k}\rangle\langle\vec{k}|\vec{x}\rangle \\ &= \int_{-\infty}^{\infty} \prod_{\vec{k}} \frac{d\vec{k}}{(2\pi)^N} e^{i\vec{k}\cdot(\vec{x}-\vec{x}')} e^{-\frac{\beta\hbar^2\vec{k}^2}{2m}} \end{aligned} \tag{13.4.30}$$

where we have used $\vec{x} = \{x_1, \ldots, x_N\}$ and $\vec{k} = \{k_1, \ldots, k_N\}$. The integrals are all independent and may be evaluated to give

$$\rho_U(\vec{x}, \vec{x}'; \beta) = \left(\frac{m}{2\pi\beta\hbar^2}\right)^{N/2} e^{-\frac{m}{2\beta\hbar^2}(\vec{x}-\vec{x}')^2} \tag{13.4.31}$$

which generalizes the single particle density matrix in a trivial way.

Any interchange of the particles in (13.4.28) leads to a new wave function with physically different outcomes. If the particles are *indistinguishable* then (13.4.28) becomes inappropriate and we must ask for a wave function that remains invariant, or unchanged under exchanges or permutations of the particles amongst themselves. Of course because the particles don't interact and must obey Schroedinger's equation the wave function must end up being constructed as a linear superposition of wave functions of the form (13.4.28). There are $N!$ functions of this type and we want to ensure that

$$|\widehat{P}\psi|^2 = |\psi|^2 \tag{13.4.32}$$

This is only possible if ψ is either completely symmetric or completely antisymmetric under the action of the permutation group, *i.e.,*

$$\psi(x_1,\ldots,x_N) = \begin{cases} \psi_S(x_1,\ldots,x_N) = \frac{1}{\sqrt{N!}}\sum_\sigma \prod_i \psi_{k_i}(x_{\sigma_i}) \\ \\ \psi_A(x_1,\ldots,x_N) = \frac{1}{\sqrt{N!}}\sum_\sigma (-)^\sigma \prod_i \psi_{k_i}(x_{\sigma_i}) \end{cases} \tag{13.4.33}$$

where $\{\sigma\}$ is the set of all permutations of $\{1,\ldots,N\}$ and $\vec{\sigma} = \{\sigma_1,\ldots,\sigma_N\}$ is a particular permutation of $\{1,\ldots,N\}$ and

$$(-)^\sigma = \begin{cases} +1 & \vec{\sigma} \text{ is an even permutation} \\ \\ -1 & \vec{\sigma} \text{ is an odd permutation} \end{cases} \tag{13.4.34}$$

Let's begin by considering two indistinguishable particles. The energy eigenstates are

$$\psi_{k_1,k_2}(x_1,x_2) = \langle k_1,k_2|x_1,x_2\rangle = \frac{1}{\sqrt{2!(2\pi)}}\left[e^{i(k_1x_1+k_2x_2)} \pm e^{i(k_1x_2+k_2x_1)}\right] \tag{13.4.35}$$

where the positive sign applies to Bosons and the negative sign to Fermions. The eigenvalue of the Hamiltonian is

$$E = \frac{\hbar^2}{2m}(k_1^2+k_2^2)$$

so the density matrix is given by

$$\begin{aligned} \rho_U(\vec{x},\vec{x}';\beta) &= \int \frac{dk_1dk_2}{4\pi} e^{-\frac{\beta\hbar^2}{2m}(k_1^2+k_2^2)}\left[e^{i(k_1x_1+k_2x_2)} \pm e^{i(k_1x_2+k_2x_1)}\right] \times \\ &\qquad \times \left[e^{-i(k_1x_1'+k_2x_2')} \pm e^{-i(k_1x_2'+k_2x_1')}\right] \\ &= \left(\frac{m}{2\pi\beta\hbar^2}\right)\left[e^{-\frac{m}{2\beta\hbar^2}(\vec{x}-\vec{x}')^2} \pm e^{-\frac{m}{2\beta\hbar^2}[(x_1-x_2')^2+(x_2-x_1')^2]}\right] \end{aligned} \tag{13.4.36}$$

and using

$$(x_1-x_2')^2+(x_2-x_1')^2 = (\vec{x}-\vec{x}')^2 + 2(x_1-x_2)(x_1'-x_2') \tag{13.4.37}$$

we find that the density matrix can be represented by

$$\rho_U(\vec{x},\vec{x}';\beta) = \left(\frac{m}{2\pi\beta\hbar^2}\right) e^{-\frac{m}{2\beta\hbar^2}(\vec{x}-\vec{x}')^2}\left[1 \pm e^{-\frac{m}{\beta\hbar^2}x_{12}x_{12}'}\right] \tag{13.4.38}$$

Taking the trace of $\widehat{\rho}_U$ gives

$$\operatorname{Tr}(\widehat{\rho}_U) = \left(\frac{m}{2\pi\beta\hbar^2}\right)\int dx_1 dx_2 \left[1 \pm e^{-\frac{m}{\beta\hbar^2}x_{12}^2}\right] \tag{13.4.39}$$

Transform to the variables $x = x_1 + x_2$ (the center of mass) and $x_{12} = x_1 - x_2$ (the relative coordinate). The integral over x is simply the volume L to which the two particles are confined and we are left with

$$\begin{aligned}\operatorname{Tr}(\widehat{\rho}_U) &= \left(\frac{mL}{2\pi\beta\hbar^2}\right)\int_0^L dx_{12}\left[1 \pm e^{-\frac{m}{\beta\hbar^2}x_{12}^2}\right] \\ &= \left(\frac{mL^2}{2\pi\beta\hbar^2}\right)\left[1 + \frac{1}{2}\sqrt{\frac{\beta\pi\hbar^2}{mL^2}}\operatorname{erf}\left(\sqrt{\frac{m}{\beta\hbar^2}}\,L\right)\right] \approx \left(\frac{mL^2}{2\pi\beta\hbar^2}\right)\end{aligned} \tag{13.4.40}$$

where "erf" is the error function, which approaches unity as $L \to \infty$. So the normalized density matrix is approximately

$$\rho(\vec{x}, \vec{x}'; \beta) \approx \frac{1}{L^2}e^{-\frac{m}{2\beta\hbar^2}(\vec{x}-\vec{x}')^2}\left[1 \pm e^{-\frac{m}{\beta\hbar^2}x_{12}x'_{12}}\right]. \tag{13.4.41}$$

Notice the appearance of two particle correlations in the term in square brackets. These correlations arise purely out of the statistics. Since

$$\rho(\vec{x}, \vec{x}; \beta) = \frac{1}{L^2}\left[1 \pm e^{-\frac{mx_{12}^2}{\beta\hbar^2}}\right] \tag{13.4.42}$$

represents the probability of finding the two particles at $\vec{x} = (x_1, x_2)$ respectively, the probability that $x_1 \to x_2$ is enhanced for Bosons and diminished for Fermions over the corresponding probability for distinguishable particles.

We can treat this statistical correlation as an effective statistical interaction between classical particles. Introduce an effective potential with a pairwise interaction, $v(|x_{12}|)$ The probability of finding the two particles, one at x_1 and the other at x_2 at inverse temperature β is given by

$$P(x_1, x_2) = \frac{e^{-\beta v(|x_{12}|)}}{\int dx_1 dx_2 e^{-\beta v(|x_{12}|)}} = \frac{e^{-\beta v(|x_{12}|)}}{L\int dx_{12} e^{-\beta v(|x_{12}|)}} \tag{13.4.43}$$

where we've transformed to the variables $x = x_1 + x_2$ and $x_{12} = x_1 - x_2$. For large L and assuming that $v(|x_{12}|) \to 0$ as $|x_{12}| \to \infty$ we may set

$$\int dx_{12} e^{-\beta v(|x_{12}|)} \approx L \tag{13.4.44}$$

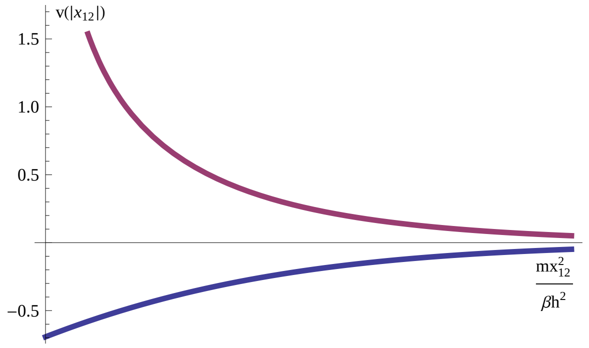

Figure 13.1: The effective two particle statistical potential.

so

$$P(x_1,x_2) = \frac{1}{L^2} e^{-\beta v(|x_{12}|)} \tag{13.4.45}$$

and comparing $P(x_1,x_2)$ to $\rho(\vec{x},\vec{x};\beta)$ we find the effective potential

$$v(|x_{12}|) \approx -\frac{1}{\beta} \ln \left[1 \pm e^{-\frac{mx_{12}^2}{\beta\hbar^2}} \right], \tag{13.4.46}$$

which is attractive for Bosons, repulsive for Fermions and significant when $|x_{12}| \lesssim \sqrt{\beta\hbar^2/m}$.

Let us now turn to an arbitrary number of particles. It should be clear that the integral expression for $\rho(\vec{x},\vec{x}';\beta)$ will be of the form

$$\rho_U(\vec{x},\vec{x}';\beta) = \sum_\sigma (\pm)^\sigma \int \frac{d\vec{k}}{(2\pi)^N N!} e^{-\frac{\beta\hbar^2\vec{k}^2}{2m}} e^{ik_i(x_i - x'_{\sigma_i})} \tag{13.4.47}$$

where the repeated index i is to be summed. The exponent factorizes and each integral can be evaluated as before

$$\rho_U(\vec{x},\vec{x}';\beta) = \left(\frac{m}{2\pi\beta\hbar^2}\right)^{N/2} \sum_\sigma (\pm)^\sigma e^{-\frac{m}{2\beta\hbar^2}(\vec{x}-\widehat{\sigma}\vec{x}')^2} \tag{13.4.48}$$

where $\widehat{\sigma}$ is the permutation operator that takes $x'_i \to [\widehat{\sigma}\vec{x}']_i = x'_{\sigma_i}$ and the sum is over all permutations. Consider the partition function,

$$\mathrm{Tr}(\widehat{\rho}_U) = \left(\frac{m}{2\pi\beta\hbar^2}\right)^{N/2} \sum_\sigma (\pm)^\sigma \int_0^L d\vec{x}\; e^{-\frac{m}{2\beta\hbar^2}(\vec{x}-\widehat{\sigma}\vec{x})^2} \tag{13.4.49}$$

The leading contribution comes from the identity permutation and it is just the classical result

$$\mathrm{Tr}(\widehat{\rho}_U) \approx L^N \left(\frac{m}{2\pi\beta\hbar^2}\right)^{N/2} \tag{13.4.50}$$

The next contribution comes from permutations that interchange a pair of particles. These are odd permutations and there will be $N(N-1)/2$ such terms,

$$\pm L^{N-2} \sum_{i<j} \int_0^L dx_i dx_j e^{-\frac{m}{2\beta\hbar^2}(x_i-x_j)^2}. \tag{13.4.51}$$

After the two particle interchanges we must consider the three particle interchanges, which involve two permutations of particles

$$+ L^{N-3} \sum_{i<j<k} \int_0^L dx_i dx_j dx_k e^{-\frac{m}{2\beta\hbar^2}[(x_i-x_j)^2+(x_j-x_k)^2+(x_k-x_i)^2]} \tag{13.4.52}$$

and so on. Thus the partition function has the expansion

$$\begin{aligned}\mathrm{Tr}(\widehat{\rho}_U) = \left(\frac{m}{2\pi\beta\hbar^2}\right)^{N/2} L^N \quad & \left[1 \pm \frac{1}{L^2} \sum_{i<j} \int_0^L dx_i dx_j e^{-\frac{m}{2\beta\hbar^2}(x_i-x_j)^2} + \right. \\ & + \frac{1}{L^3} \sum_{i<j<k} \int_0^L dx_i dx_j dx_k e^{-\frac{m}{2\beta\hbar^2}[(x_i-x_j)^2+(x_j-x_k)^2+(x_k-x_i)^2]} \\ & \left. \pm \ldots \right]\end{aligned} \tag{13.4.53}$$

Of course, if all one is interested in is the partition function then, as we have seen in earlier chapters there is a simpler way to going about calculating it: work in the energy basis since the trace is an invariant.

13.5 Path integral for the Density Matrix

The diffusion equation for the density matrix in (13.3.12) can be formally "solved" to yield a position representation for $\widehat{\rho}_U$ with a general Hamiltonian. The solution is only formal in the sense that it is represented as a "path integral", which is ambiguously defined. Nevertheless it is useful because it provides the clearest connection between the classical dynamics of a system and its statistical dynamics. It is also useful because the result is expressed in a compact form in terms of c-numbers (*commuting* numbers) for Bosons or anticommuting (Grassmann) numbers for Fermions, as opposed to operators. This allows for the use of many familiar approximation techniques such as the method of steepest descents or stationary phase.

Consider a set of N non-interacting particles in contact with a heat reservoir of temperature β, and let x be a collective coordinate representing the positions of the N particles, *i.e.,* $x = \{x^{(1)}, \dots x^{(N)}\}$. The density matrix of the system can be expressed as

$$\rho_U(x, x'; \beta) = \langle x'|e^{-\beta\widehat{\mathcal{H}}}|x\rangle \tag{13.5.1}$$

where x and x' are some configurations of the N particles. Write $e^{-\beta\widehat{\mathcal{H}}} = \prod_{j=1}^{n} e^{-\frac{\beta}{n}\widehat{\mathcal{H}}}$ and, calling $\varepsilon_n = \beta/n$, insert the completeness relation $n-1$ times into the expression above as follows ($x' = x_0$ and $x = x_n$):

$$\begin{aligned}
\rho_U(x, x'; \beta) &= \int dx_1 \dots dx_{n-1} \langle x'|e^{-\varepsilon_n\widehat{\mathcal{H}}}|x_1\rangle\langle x_1|e^{-\varepsilon_n\widehat{\mathcal{H}}}|x_2\rangle \dots \langle x_{n-1}|e^{-\varepsilon_n\widehat{\mathcal{H}}}|x\rangle \\
&= \int dx_1 \dots dx_{n-1} \prod_{i=1}^{n} \langle x_{i-1}|e^{-\varepsilon_n\widehat{\mathcal{H}}}|x_i\rangle
\end{aligned} \tag{13.5.2}$$

We now want to take advantage of the fact that ε is small so we can make some approximation to $\langle x_{i-1}|e^{-\varepsilon_n\widehat{\mathcal{H}}}|x_i\rangle$ so that the limit as $n \to \infty$ gives the correct answer. Suppose that the Hamiltonian has the form (p is also a collective coordinate, $p = \{p^{(1)}, \dots p^{(N)}\}$ and $p^2 = \sum_{j=1}^{N} {p^{(j)}}^2$)

$$\mathcal{H} = \frac{p^2}{2m} + V(x) \tag{13.5.3}$$

(we will take a one dimensional situation for illustrative purposes only, but the entire discussion is straightforwardly generalized to an arbitrary number of dimensions) then we insert a complete set of momentum states,

$$\langle x_{i-1}|e^{-\varepsilon_n\widehat{\mathcal{H}}}|x_i\rangle = \frac{L}{2\pi\hbar}\int dp_{i-1} \langle x_{i-1}|p_{i-1}\rangle\langle p_{i-1}|e^{-\varepsilon_n\widehat{\mathcal{H}}}|x_i\rangle \tag{13.5.4}$$

Now

$$\begin{aligned}
\langle p_{i-1}|e^{-\varepsilon_n\widehat{\mathcal{H}}}|x_i\rangle &\approx \langle p_{i-1}|\left(1 - \varepsilon_n\widehat{\mathcal{H}}\right)|x_i\rangle \\
&= \langle p_{i-1}|\left(1 - \varepsilon_n\left[\frac{\widehat{p}^2}{2m} + V(x)\right]\right)|x_i\rangle \\
&= \langle p_{i-1}|x_i\rangle\left(1 - \varepsilon_n\left[\frac{p_{i-1}^2}{2m} + V(x_i)\right]\right) \\
&\approx \langle p_{i-1}|x_i\rangle e^{-\varepsilon_n[p_{i-1}^2/2m + V(x_i)]}
\end{aligned} \tag{13.5.5}$$

and therefore

$$\langle x_{i-1}|e^{-\varepsilon_n\widehat{\mathcal{H}}}|x_i\rangle \approx \frac{L}{2\pi\hbar}\int dp_{i-1}\langle x_{i-1}|p_{i-1}\rangle\langle p_{i-1}|x_i\rangle e^{-\varepsilon_n[p_{i-1}^2/2m + V(x_i)]} \tag{13.5.6}$$

Now, if we use the position representation of the momentum states

$$\langle x|p\rangle = \frac{1}{\sqrt{L}} e^{ipx/\hbar} \tag{13.5.7}$$

we find

$$\langle x_{i-1}|e^{-\varepsilon_n \widehat{\mathcal{H}}}|x_i\rangle = \frac{1}{2\pi\hbar}\int dp_{i-1} e^{-ip_{i-1}(x_i - x_{i-1})/\hbar} e^{-\varepsilon_n [p_{i-1}^2/2m + V(x_i)]} \tag{13.5.8}$$

and the integral expression on the right hand side can be easily evaluated to give

$$\langle x_{i-1}|e^{-\varepsilon_n \widehat{\mathcal{H}}}|x_i\rangle = \sqrt{\frac{m}{2\pi\varepsilon_n \hbar^2}} \exp\left[-\varepsilon_n\left(\frac{m(x_i - x_{i-1})^2}{2\hbar^2\varepsilon_n^2} + V(x_i)\right)\right] \tag{13.5.9}$$

Inserting this into the expression for $\rho(x, x'; \beta)$,

$$\rho_U(x, x'; \beta) = \left(\sqrt{\frac{m}{2\pi\varepsilon_n \hbar^2}}\right)^n \int dx_1 \ldots dx_{n-1} \prod_{i=1}^n \exp\left[-\varepsilon_n\left(\frac{m(x_i - x_{i-1})^2}{2\hbar^2\varepsilon_n^2} + V(x_i)\right)\right] \tag{13.5.10}$$

Now the product on the right hand side above can be rewritten as a sum in the exponent,

$$\exp\left[-\frac{1}{\hbar}\sum_{i=1}^n (\hbar\varepsilon_n)\left(\frac{m}{2}\left[\frac{x_i - x_{i-1}}{\hbar\varepsilon_n}\right]^2 + V(x_i)\right)\right] \tag{13.5.11}$$

Now $\hbar\varepsilon_n$ has the dimension of "time" so let's introduce the variable $\tau \in [0, \hbar\beta]$ and think of the configuration variables as piecewise continuous functions of τ, so that $x = x(\tau)$ together with the boundary conditions $x' = x(0)$, $x = x(\hbar\beta)$. Then

$$\frac{x_i - x_{i-1}}{\hbar\varepsilon_n} = \frac{dx(\tau)}{d\tau} \tag{13.5.12}$$

and the exponent in (13.5.11) becomes a Riemann sum, which, in the limit as $n \to \infty$ turns into a definite integral,

$$\exp\left[-\frac{1}{\hbar}\sum_{i=1}^n (\hbar\varepsilon_n)\left(\frac{m}{2}\left[\frac{x_i - x_{i-1}}{\hbar\varepsilon_n}\right]^2 + V(x_i)\right)\right] \overset{n\to\infty}{\longrightarrow} \exp\left[-\frac{1}{\hbar}\int_0^{\hbar\beta} d\tau \left(\frac{m}{2}\dot{x}^2 + V(x)\right)\right] \tag{13.5.13}$$

We also have to integrate over the intermediate x_i, which we formally gather together in one measure:

$$\left(\sqrt{\frac{m}{2\pi\varepsilon\hbar^2}}\right)^n dx_1 \ldots dx_{n-1} \to \mathcal{D}x \tag{13.5.14}$$

finally getting the following expression for $\rho(x,x';t)$

$$\rho_U(x,x';t) = \int_{x'}^{x} \mathcal{D}x \exp\left[-\frac{1}{\hbar}\int_0^{\hbar\beta} d\tau \left(\frac{m}{2}\dot{x}^2 + V(x)\right)\right] \tag{13.5.15}$$

Some points are worth making:

- The fact that we have to integrate over all possible values of the intermediate points, x_i (except for the initial and final points), indicates that we must account *for all piecewise continuous paths* leading from $x' = x(0)$ to $x = x(\hbar\beta)$. However, note that the exponent in the integration will be small for paths that deviate significantly from the classical path (for which the Lagrangian in minimized) so we can expect that the contribution from the classical path will dominate.

- We have ignored the possible need to symmetrize or antisymmetrize the wave functions in the above discussion. When the particles are distinguishable the the initial and final configurations will depend on the locations of each of the particles but when the particles are indistinguishable the final positions can be occupied by *any* of the particles, so the density matrix must satisfy the additional requirement of symmetry or antisymmetry with respect to the permutation group. The symmetrized or antisymmetrized density matrix can be constructed directly from the unsymmetrized (distinguishable) case. For Bosons the the symmetrized density matrix will be

  $$\rho_B(x_1,\ldots x_N;x'_1,\ldots x'_N) = \frac{1}{N!}\sum_{\{\sigma\}} \rho(x_1,\ldots x_N;x'_{\sigma_1},\ldots x'_{\sigma_N}) \tag{13.5.16}$$

  and for Fermions

  $$\rho_F(x_1,\ldots x_N;x'_1,\ldots x'_N) = \frac{1}{N!}\sum_{\{\sigma\}} (-)^\sigma \rho(x_1,\ldots x_N;x'_{\sigma_1},\ldots x'_{\sigma_N}) \tag{13.5.17}$$

  where, as before $\{\sigma\}$ is the set of all permutations of $\{1,2,\ldots N\}$.

- Finally, one can also obtain an expression in terms of the Hamiltonian if we forgo the integration over the momentum variable that took us from (13.5.8) to (13.5.9) above. Then we will find

  $$\rho_U(x,x';\beta) = \int \mathcal{D}x\mathcal{D}p \exp\left[-\frac{1}{\hbar}\int_0^{\hbar\beta} d\tau\left(ip\dot{x} + \mathcal{H}(x,p)\right)\right]. \tag{13.5.18}$$

  where

  $$\mathcal{D}x\mathcal{D}p = \frac{1}{(2\pi\hbar)^n} dx_1 \ldots dx_{n-1} dp_1 \ldots dp_{n-1}. \tag{13.5.19}$$

This expression is sometimes useful when working with quantum fields for which a convenient path integral may be developed by using coherent states (eigenstates of the annihilation operator). For Bosons the commutation relation

$$[a, a^\dagger] = 1 \tag{13.5.20}$$

plays the same role as the commutation relation between x and p. For Fermions, however, the algebra involves anti-commutators, which means we must develop the path integral using anti-commuting, or Grassmann, numbers. This is presently beyond the scope of these notes.

13.6 Simple Calculations with the Path Integral

One can imagine that performing actual calculations of the density matrix using the path integral formulation is hardly straightforward. Nevertheless, the path integral provides an excellent platform from which approximation methods can be developed. We will examine them in subsequent chapters. Here let's look at some very simple systems, which will indicate how approximation methods may proceed.

13.6.1 Free particle

Let's begin by evaluating the simplest density matrix of all: that describing a single free particle in contact with a heat reservoir at inverse temperature β. We want to compute

$$\rho_U(x, x'; t) = \int_{x'}^{x} \mathcal{D}x \exp\left[-\frac{m}{2\hbar}\int_0^{\hbar\beta} d\tau \dot{x}^2\right] \tag{13.6.1}$$

We know that the integral will be dominated by the classical path, $\overline{x}(\tau)$, for which the velocity is constant,

$$\dot{\overline{x}}(\tau) = v = \frac{(x - x')}{\hbar\beta}. \tag{13.6.2}$$

so consider trajectories that take the form

$$x(\tau) = \overline{x}(\tau) + y(\tau) \tag{13.6.3}$$

where $y(\tau)$ is an arbitrary function constrained only to vanish at the boundaries, *i.e.,* $y(0) = y(\hbar\beta) = 0$. Then

$$\dot{x}^2 = \dot{\overline{x}}^2 + \dot{y}^2 + 2\dot{\overline{x}}\dot{y} \tag{13.6.4}$$

and so

$$\rho_U(x, x'; t) = e^{-\frac{m}{2}\frac{(x-x')^2}{\hbar^2\beta}} \int \mathcal{D}y \exp\left[-\frac{m}{2\hbar}\int_0^{\hbar\beta} d\tau(\dot{y}^2 + 2\dot{\overline{x}}\dot{y})\right] \tag{13.6.5}$$

The second integral in the exponent vanishes, however, for the simple reason that

$$\int_0^{\hbar\beta} \dot{\overline{x}}\dot{y} = (\dot{\overline{x}}y)\big|_0^{\hbar\beta} - \int_0^{\hbar\beta} \ddot{\overline{x}} y d\tau \tag{13.6.6}$$

after integrating by parts. But the first term vanishes because $y(\tau)$ is required to vanish at the boundaries and the second integral vanishes as well because the acceleration of the classical trajectory is identically zero. Therefore we can write

$$\rho_U(x, x'; t) = f(\hbar\beta)\ e^{-\frac{m}{2\hbar^2\beta}(x-x')^2} \tag{13.6.7}$$

where $f(\hbar\beta)$ is given by the path integral remaining,

$$f(\hbar\beta) = \int \mathcal{D}y \exp\left[-\frac{m}{2\hbar}\int_0^{\hbar\beta} d\tau \dot{y}^2\right] \tag{13.6.8}$$

This result agrees with with our earlier answer if

$$f(\hbar\beta) = \sqrt{\frac{m}{2\pi\beta\hbar^2}} \tag{13.6.9}$$

Of course, only the *normalized* density matrix enters into calculations of expectation values and so $f(\hbar\beta)$ is more or less irrelevant. Nevertheless, $f(\hbar\beta) = \mathrm{Tr}(\widehat{\rho}_U) = Z$ is the partition function of the system.

13.6.2 Simple Harmonic Oscillator

For a single harmonic oscillator in contact with a heat bath, the density matrix should read

$$\rho_U(x, x'; t) = \int_{x'}^{x} \mathcal{D}x \exp\left[-\frac{m}{2\hbar}\int_0^{\hbar\beta} d\tau(\dot{x}^2 + \omega^2 x^2)\right] \tag{13.6.10}$$

and, again, let us expand about the classical path

$$x(\tau) = \overline{x}(\tau) + y(\tau) \tag{13.6.11}$$

where the classical equations of motion that govern the evolution of $\overline{x}(\tau)$ are

$$\ddot{\overline{x}} = \omega^2\overline{x} \Rightarrow \overline{x}(\tau) = A\cosh(\omega\tau) + B\sinh(\omega\tau) \tag{13.6.12}$$

and where $y(\tau)$ vanishes on the boundaries. We find

$$\dot{x}^2 + \omega^2 x^2 = (\dot{\overline{x}} + \dot{y})^2 + \omega^2(\overline{x} + y)^2 = \dot{\overline{x}}^2 + \omega^2\overline{x}^2 + \dot{y}^2 + \omega^2 y^2 + 2(\dot{\overline{x}}\dot{y} + \omega^2\overline{x}y) \tag{13.6.13}$$

But

$$\int_0^{\hbar\beta} d\tau(\dot{\overline{x}}\dot{y} + \omega^2\overline{x}y) = \dot{\overline{x}}y\big|_0^{\hbar\beta} - \int_0^{\hbar\beta} d\tau(\ddot{\overline{x}} - \omega^2\overline{x})y \tag{13.6.14}$$

is identically vanishing by the fact that $y(0) = y(\hbar\beta) = 0$ and by the equations of motion. Therefore the integrand in the exponent once again separates nicely into two independent pieces,

$$\int_0^{\hbar\beta} d\tau(\dot{\overline{x}}^2 + \omega^2\overline{x}^2) + \int_0^{\hbar\beta} d\tau(\dot{y}^2 + \omega^2 y^2) \tag{13.6.15}$$

and we can write

$$\begin{aligned}\rho_U(x,x';t) &= e^{-\frac{m}{2\hbar}\int_0^{\hbar\beta} d\tau(\dot{\overline{x}}^2+\omega^2\overline{x}^2)}\int \mathcal{D}y\exp\left[-\frac{m}{2\hbar}\int_0^{\hbar\beta} d\tau(\dot{y}^2+\omega^2y^2)\right]\\ &= f(\hbar\beta)\ \exp\left[-\frac{m}{2\hbar}\int_0^{\hbar\beta} d\tau(\dot{\overline{x}}^2+\omega^2\overline{x}^2)\right]\end{aligned} \tag{13.6.16}$$

where now

$$f(\hbar\beta) = \int \mathcal{D}y\exp\left[-\frac{m}{2\hbar}\int_0^{\hbar\beta} d\tau(\dot{y}^2+\omega^2y^2)\right] \tag{13.6.17}$$

It remains to evaluate the "euclidean" action in the exponent of (13.6.16) along a classical path. The first integral of the motion is

$$\dot{\overline{x}} = \pm\sqrt{v_0^2 + \omega^2\overline{x}^2} \tag{13.6.18}$$

where $v_0 = \dot{\overline{x}}(0)$. Furthermore, the constants A and B in the solution (13.6.12) may be rewritten in terms of the initial and final positions as

$$x' = \overline{x}(0) = A, \quad v_0 = \dot{\overline{x}}(0) = \omega B \tag{13.6.19}$$

and so

$$x = x(\hbar\beta) = x'\cosh(\hbar\beta\omega) + \frac{v_0}{\omega}\sinh(\hbar\beta\omega) \tag{13.6.20}$$

which gives

$$v_0 = \frac{\omega(x - x'\cosh(\hbar\beta\omega))}{\sinh(\hbar\beta\omega)} = \omega B \tag{13.6.21}$$

The integral over τ in the exponent of (13.6.16) may be transformed into an integral over $\overline{x}$ using (13.6.18). Then it can be carried out to yield precisely the result in (13.4.24) modulo the prefactor $f(\hbar\beta)$.[2]

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[2] Problem: Reproduce the result in (13.4.24) for the density matrix describing a single harmonic oscillator.

Chapter 14

Order and Disorder

The term **order** in physics generally refers to the breaking of a symmetry or the presence of correlations in a many particle system. The affected symmetry concerns one or more of the translational, rotational or spin degrees of freedom of the system and the order is represented by an **order parameter** whose value in the perfectly disordered (symmetric and uncorrelated) state is zero and whose value is non-zero in an ordered state. A typical example would be the magnetization in a ferromagnetic system. At very high temperatures, the atomic spins tend to be randomly oriented and the magnetization is zero but, at temperatures below some critical value, say T_c, there is a preferred and spontaneously chosen orientation for the atomic spin resulting in a net magnetization which breaks rotational invariance. When symmetries are broken one needs to employ additional variables, the order parameters, to describe the state of a system. For example, the magnetization, which is the order parameter of a ferromagnetic system, is an additional variable required to describe a ferromagnetic system at low temperatures.

Long range order characterizes systems in which remote regions within it exhibit correlated behavior. Long range order is generally characterized by correlation functions. An example in a spin system would be the function

$$G(x, x') = \langle s(x)s(x') \rangle \tag{14.0.1}$$

where $s(x)$ is the spin quantum number at position x and $\langle \ldots \rangle$ represents an expectation value. The function $G(x, x')$ characterizes the extent to which the spins at x and x' are correlated. If $G(x, x')$ decays exponentially then the spins are taken to be uncorrelated and the system is considered to exhibit no long range order, but if it approaches a constant value as $|x - x'|$ gets large then the system is said to exhibit long range order.

Order arises out of a cooperative behavior between the elementary constituents of the system, via mutual interactions that cannot be transformed away but instead assume macroscopic significance below a **critical temperature**, T_c. Above this critical temperature the thermal energy of the constituents is too large for the cooperative behavior to manifest itself and because it is this cooperative behavior that leads to an ordered phase of the system, ordered and disordered phases of a system are separated by a **phase transition**. During such a transition certain properties of the medium change, sometimes discontinuously, as a result of a change in some external condition, which is often the temperature. Most obvious examples of a phase transition are the condensation of gases and the melting of solids, transitions from normal to superconducting materials, ferromagnetism and anti-ferromagnetism, and the order-disorder transition in alloys. The set of external conditions at which the transformation occurs is called the **phase transition point**.

Near the critical temperature any thermodynamic quantity can usually be expressed as the sum of a regular part and a singular part (if it exists) or have singular derivatives. A basic problem of the theory of phase transitions is to study the behavior of a given system in the neighborhood of a critical point. It is customary to express the singularities by a set of power laws characterized by **critical exponents**. For definiteness, consider a ferromagnetic system and suppose that M is the magnetization corresponding to an ordering field h.

- As $h \to 0$, $M \to M_0$ where $M_0 = 0$ for $T > T_c$ and $M \sim (T_c - T)^\beta$ so long as $T \lesssim T_c$ and β is called the **order parameter exponent**.

- When $T = T_c$ the magnetization vanishes if $h = 0$, but increases rapidly with h. For small h the singular part of M behaves as $M \sim h^{1/\delta}$ where $\delta > 1$. The exponent δ is called the **exponent of the critical isotherm**.

- As T approaches T_c from above or below the magnetic susceptibility behaves as $\chi \sim |T - T_c|^{-\gamma}$ and γ is called the **susceptibility exponent**.

- Likewise the specific heat at constant h behaves as $c_h \sim |T - T_c|^{-\alpha}$ when $h = 0$ and α is called the **specific heat exponent**.

- Finally, the spin-spin correlation function can be parametrized as

$$G(x, x') \sim \frac{1}{|x - x'|^{d-2+\eta}} e^{-\frac{|x-x'|}{\xi}} \tag{14.0.2}$$

  and $\xi \sim |T - T_c|^{-\nu}$ and ν is called the **correlation length exponent** while η is the **correlation function exponent at the critical isotherm**.

Our objective in this chapter is to give an overview of a subset of models in which cooperative behavior exists. Since we are interested only in the cooperative behavior, we will ignore the motion of the constituents, taking them instead to interact with one another while occupying fixed sites on a spatial lattice.

14.1 The Models

14.1.1 Spin Models

The Ising model is the prototype for magnetic phase transitions and and the simplest of the so-called discrete models. It consists of a lattice of spin $\frac{1}{2}$ particles in the presence of a magnetic field, which we take to be oriented in the z direction. Each spin can be either parallel or antiparallel to the magnetic field and will be represented by the symbol "s", which can take on values ± 1. Unless otherwise stated a square lattice is taken and letters $i, j, \ldots$ from the middle of the roman alphabet will label lattice sites, so "s_j" will refer to the spin at site "j". The Hamiltonian of the system can be written as

$$\mathcal{H} = -\sum_{\langle i,j \rangle} J_{ij} s_i s_j - h \sum_i s_i \tag{14.1.1}$$

where $\langle . \rangle$ indicates that the sum is taken over nearest neighbor sites on the lattice. h represents the effect of the external magnetic field (the ordering field) and J_{ij} represents the interaction strength between nearest neighbors, which we will henceforth take to be the same for all nearest neighbor pairs, $J_{ij} = J$, so that

$$\mathcal{H} = -J \sum_{\langle i,j \rangle} s_i s_j - h \sum_i s_i. \tag{14.1.2}$$

If $J > 0$ then the interaction energy is lower when the neighboring spins are aligned and higher if $J < 0$. Thus at low temperature the spins tend to become aligned if $J > 0$ and this gives rise to ferromagnetic systems, in which there is a natural tendency for spontaneous magnetization below a critical temperature. The opposite situation ($J < 0$) gives rise to antiferromagnetism. Although their detailed behavior depends sensitively on the dimensionality of the lattice, all spin models exhibit a phase transition at some non-zero critical temperature in dimension greater than one. In one dimension, the phase transition occurs at $T_c = 0$. The models are named as follows:

- if $d = 1$ the spin model is called the **Ising model** and it is exactly solvable,
- if $d = 2$ then we have the XY **model**,
- the $d = 3$ model is called the **Heisenberg model**,
- the $d = 0$ model is the **polymer model** and the $d = \infty$ model is the **spherical model**.

Only the Ising and XY models have been solved exactly. The one dimensional (Ising) model is relatively easy to solve and we shall do it here. The solution of the two dimensional (XY) model is far from easy and was obtained by Onsager in 1944. It is beyond the scope of this course.

14.1.2 The Lattice Gas

The Lattice Gas is a collection of particles whose momentum contribution to the total Hamiltonian can be neglected. Consider a regular lattice (square, unless otherwise stated) consisting of cells which may be occupied (or not) by the particles. Assume that there cannot be more than one particle per cell and that the sole contributors to the energy of the system are the nearest neighbor interactions among the particles,

$$\mathcal{H} = \sum_{\langle i,j\rangle} u_{ij} p_i p_j - \mu \sum_i p_i \tag{14.1.3}$$

where $u_{ij} = -u$ if $\{i, j\}$ are nearest neighbors and zero otherwise. The p_i are cell occupation numbers, $p_i = 1$ if cell "i" is occupied and zero otherwise and μ is the chemical potential. Although the occupation number is either zero or unity, it is like the spin in the Spin Models, for if we take

$$p_i = \frac{1}{2}(1 + s_i) \tag{14.1.4}$$

then

$$\begin{aligned} \mathcal{H} &= -\frac{u}{4}\sum_{\langle i,j\rangle}(1+s_i)(1+s_j) - \frac{\mu}{2}\sum_i (1+s_i) \\ &= -\frac{u}{4}\sum_{\langle i,j\rangle}[1 + (s_i+s_j) + s_i s_j] - \frac{\mu}{2}\sum_i [1+s_i] \\ &= -\frac{u}{4}[z + 2z\sum_i s_i + \sum_{\langle i,j\rangle} s_i s_j] - \frac{\mu}{2}[N + \sum_i s_i] \end{aligned} \tag{14.1.5}$$

where z is the "coordination number" of the lattice, *i.e.,* the number of nearest neighbors of any site (eg. 2 for a one dimensional lattice, 4 for a square lattice, 6 for a cubic lattice, etc.) and N is the number of lattice sites. Collecting terms we see that

$$\mathcal{H} = -\frac{u}{4}\sum_{\langle i,j\rangle} s_i s_j - \left(\frac{\mu}{2} + \frac{uz}{4}\right)\sum_i s_i - \mathcal{H}_0 \tag{14.1.6}$$

where $\mathcal{H}_0 = (uz + 2\mu N)/4$. Thus the Lattice Gas is identical to the Spin models if we set $J = u/4$ and $h = (uz + 2\mu)/4$, apart from a spin independent constant, $\mathcal{H}_0$. So long as $u > 0$ the atoms will attract and condense at low enough temperatures, whereas when $u < 0$ they will repel.

The Lattice Gas in two dimensions is useful for studies of adsorption on metal surfaces, where the substrate provides discrete lattice sites for the atoms to occupy. Varying the pressure causes a variation in the number of adsorbed atoms ($N_{\text{ad}} = \sum_i p_i$), just as varying the external magnetic field in the Spin Models changes the number of aligned spin pairs.

14.1.3 Binary Alloys

A binary alloy is a collection of two types of atoms, say type A and type B, arranged on a lattice. Let p_i and q_i represent occupation numbers for the two types of atoms,

$$(p_i, q_i) = \begin{cases} (1,0) & \text{site } i \text{ occupied by type } A \\ (0,1) & \text{site } i \text{ occupied by type } B \end{cases} \tag{14.1.7}$$

If we assume that every site is occupied by an atom then $p_i + q_i = 1$. We introduce a 2×2 symmetric matrix, $\widehat{u}$, which encapsulates the three types of nearest neighbor interactions possible:

$$\widehat{u} = \begin{pmatrix} -u_{AA} & -u_{AB} \\ -u_{BA} & -u_{BB} \end{pmatrix} \tag{14.1.8}$$

with $u_{AB} = u_{BA}$ and call

$$\vec{\xi}_i = \begin{pmatrix} p_i \\ q_i \end{pmatrix},$$

then the Hamiltonian for the system is given as

$$\mathcal{H} = \sum_{\langle i,j \rangle} \vec{\xi}_i^T \ \widehat{u} \ \vec{\xi}_j. \tag{14.1.9}$$

This model can be reduced to the Spin Models as well by writing

$$p_i = \frac{1}{2}(1 + S_i), \quad q_i = \frac{1}{2}(1 - S_i), \tag{14.1.10}$$

then $S_i = p_i - q_i$ and therefore

$$S_i = \begin{cases} +1 & \text{if } i \text{ is occupied by type } A \\ -1 & \text{if } i \text{ is occupied by type } B \end{cases} \tag{14.1.11}$$

The Hamiltonian can be reexpressed in terms of S_i as

$$\mathcal{H} = -J \sum_{\langle i,j \rangle} S_i S_j - h \sum_i S_i - \mathcal{H}_0 \tag{14.1.12}$$

with

$$\begin{aligned} J &= \frac{1}{4}(u_{AA} - 2u_{AB} + u_{BB}) \\ h &= \frac{1}{2}(u_{AA} - u_{BB})z \\ \mathcal{H}_0 &= \frac{1}{4}(u_{AA} + 2u_{AB} + u_{BB})Nz, \end{aligned} \tag{14.1.13}$$

where z is the number of nearest neighbors and N is the number of lattice sites as before. Let us now consider an approximate solution, in which the nearest neighbor interaction is replaced by an interaction *with the thermal average value of the spin.*

14.2 The Weiss Mean Field Approximation

The partition function for the Spin Models is

$$Z(\beta,h)=\sum_{\{s\}}e^{\beta(J\sum_{\langle i,j\rangle}s_is_j+h\sum_i s_i)} \tag{14.2.1}$$

where the sum is to be taken over *all* spin configurations, represented by $\{s\}$. In the Mean Field approximation, each spin "sees" only an *effective* average value of s, which is the same for all sites,

$$\langle s_j\rangle=\frac{1}{N}\sum_k\langle s_k\rangle=m. \tag{14.2.2}$$

The quantity m is called the **magnetization density**. If the nearest neighbor interaction is replaced by an interaction with the magnetization density,

$$\sum_{\langle i,j\rangle}s_is_j\approx\sum_{\langle i,j\rangle}s_i\langle s_j\rangle\approx\frac{mz}{2}\sum_i s_i, \tag{14.2.3}$$

where we have divided by a factor of two to avoid duplication in the counting of nearest neighbor pairs, the mean field Hamiltonian of the system becomes

$$\mathcal{H}_{\text{m.f.}}\approx(-mJz/2-h)\sum_i s_i. \tag{14.2.4}$$

We see that the approximation amounts to an interaction of each atom with an additional average magnetic field given by $mJz/2$, which is what gives this approximation its name. The partition function may now be approximated to

$$Z_{\text{m.f.}}=\sum_{\{s\}}e^{\beta(mJz/2+h)\sum_i s_i}, \tag{14.2.5}$$

where there are 2^N terms in the sum over spin configurations. The sum is easily performed if we let r and s be the numbers of atoms with spin "up" and spin "down" respectively, so that $r+s=N$. There are

$${}^NC_r=\frac{N!}{r!(N-r)!} \tag{14.2.6}$$

configurations with r atoms oriented "up", therefore the sum over $\{s\}$ may be replaced by a sum over r, taking into account the degeneracy above

$$Z_{\text{m.f.}}=\sum_r {}^NC_r e^{\beta(mJz/2+h)(2r-N)}=e^{-\beta(mJz/2+h)N}(1+e^{2\beta(mJz/2+h)})^N \tag{14.2.7}$$

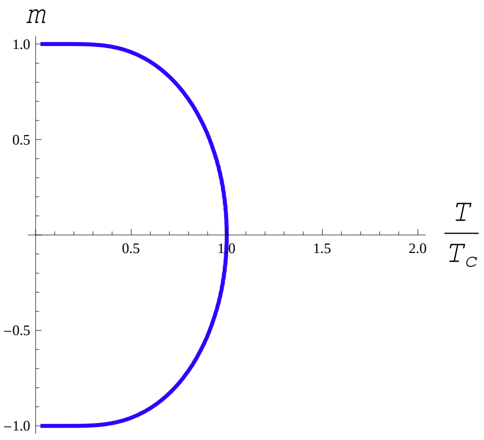

Figure 14.1: $m(T/T_c)T$ with $h = 0$.

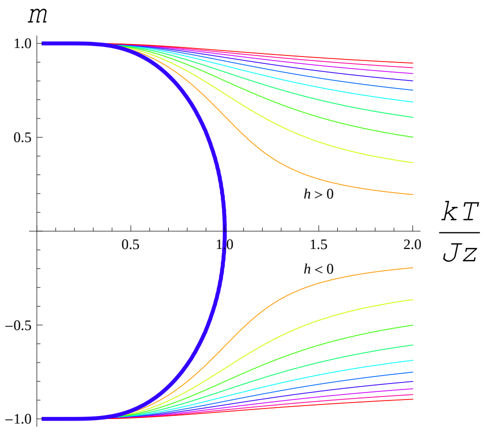

Figure 14.2: $m(kT/Jz)$ with $h \neq 0$.

and one finds

$$Z_{\text{m.f.}} = 2^N \cosh^N \left[\beta \left(mJz/2 + h\right)\right]. \tag{14.2.8}$$

The magnetization per atom is

$$m = \frac{1}{\beta N}\frac{\partial}{\partial h}\ln Z_{\text{m.f.}} = \tanh[\beta(mJz/2 + h)], \tag{14.2.9}$$

which is a self-consistent transcendental equation for m, an equation of state. The solution will depend only on the temperature and the ordering field, h:

- If $h = 0$ there is a non-zero solution for m, but only if $\beta Jz > 1$ *i.e.*, at low temperatures and thus there is a critical temperature, T_c, above which the magnetization is zero. The behavior of m with increasing T is shown in figure 14.1, with $kT_c = zJ$. The ordered state with $m \neq 0$ is a state of spontaneously broken symmetry: in the absence of an external ordering field either the “up” or “down” orientations are permitted but, when it is non-vanishing, h determines which orientation is possible.

- The behavior of m with kT/Jz when $h \neq 0$ is shown in figure 14.2.

The internal energy of the spin system can be written as

$$\langle E\rangle = -\frac{\partial \ln Z}{\partial \beta} = \langle \mathcal{H}_{\text{m.f.}}\rangle = -Nm(Jzm/2 + h) \Rightarrow \varepsilon = -m(Jzm/2 + h) \tag{14.2.10}$$

is the energy per particle in the mean field approximation. The entropy per particle is

$$s = k\left[\frac{1}{N}\ln Z + \beta\varepsilon\right] \quad = \quad k[\ln 2 + \ln\cosh\beta\left(\frac{m}{\beta_c} + h\right) - \beta m\left(\frac{m}{\beta_c} + h\right)]$$

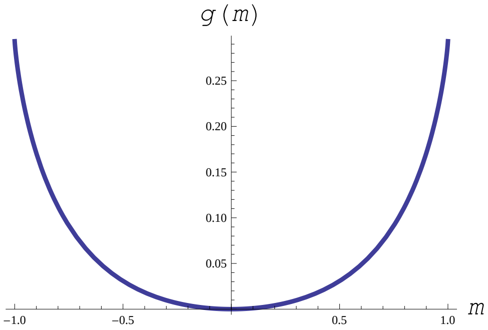

Figure 14.3: The Gibbs potential per particle in the MF approximation, $T > T_c$.

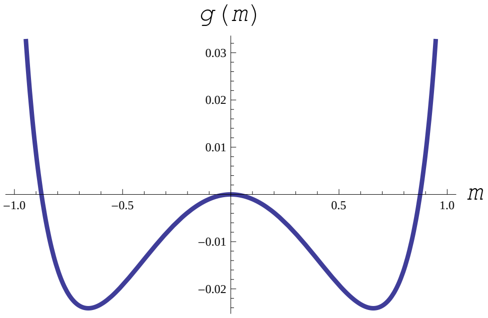

Figure 14.4: The Gibbs potential per particle in the MF approximation, $T < T_c$.

$$= \quad k[\ln 2 + \ln\cosh\tanh^{-1} m - m\tanh^{-1} m] \qquad (14.2.11)$$

where we made use of (14.2.9). With $h = 0$, this can be approximated at high temperatures using the fact that $m \approx 0$ and the asymptotic relations $\tanh^{-1} m \approx m$ and $\cosh m \approx 1 + m^2/2$. We find

$$s \approx k[\ln 2 - \frac{m^2}{2} + \mathcal{O}(m^4)] \qquad (14.2.12)$$

so $s \to k\ln 2$, showing that for each atom both possible orientations are equally probable, *i.e.,* the system is completely disordered. On the other hand, as $m \to 1^-$ $(\beta \to \infty)$

$$s \to k\left[\frac{1}{2}\left(1 - \ln\frac{\delta}{2}\right)\delta + \mathcal{O}(\delta^2)\right] \qquad (14.2.13)$$

where $\delta = 1 - m$. When $h = 0$, the equation of state,

$$m = \tanh\left(\frac{\beta}{\beta_c} m\right), \qquad (14.2.14)$$

can be solved approximately for m if, in addition, $\beta \gg \beta_c$. One finds that

$$m = 1 - 2e^{-2T_c/T}, \qquad (14.2.15)$$

which can be substituted in the expression for s, to give the specific entropy as a function of the temperature, near absolute zero, as

$$s \to k\left(1 + \frac{2T_c}{T}\right)e^{-2T_c/T} + \mathcal{O}(e^{-4T_c/T}). \qquad (14.2.16)$$

It approaches zero as $T \to 0$, but $T = 0$ is seen to be an essential singularity.

Since the partition function depends on β and on h, the first law of thermodynamics for the Spin Models reads

$$T ds = d\varepsilon + m dh \tag{14.2.17}$$

where s, ε are the entropy and average energy per particle, defined respectively by

$$s = \ln Z + \beta\varepsilon \tag{14.2.18}$$

and

$$\varepsilon = -\frac{\partial \ln Z}{\partial \beta} \tag{14.2.19}$$

Equilibrium at fixed T and m is determined by the minimum of the Gibbs potential per particle, which is defined by

$$g = \varepsilon - Ts + mh \tag{14.2.20}$$

and satisfies

$$dg = -s dT + h dm. \tag{14.2.21}$$

Using the mean field expression for h from the equation of state (14.2.9),

$$h = \frac{1}{\beta}\tanh^{-1} m - Jzm/2, \tag{14.2.22}$$

we find

$$\begin{aligned} g(m,T) &= \int_{T\ \text{const.}} h(m,T)dm + \widetilde{g}(T) \\ &= \frac{1}{\beta}\left[-\frac{\beta}{2\beta_c}m^2 + m\tanh^{-1} m + \ln\sqrt{1-m^2}\right] + \widetilde{g}(T), \end{aligned} \tag{14.2.23}$$

where we have set $\beta_c Jz/2 = 1$ and $\widetilde{g}$ is an arbitrary function only of T. At constant T, equilibrium is reached at the minimum of the Gibbs potential,

$$\frac{\partial g}{\partial m} = 0 \Rightarrow m = \frac{T}{T_c}\tanh^{-1} m, \tag{14.2.24}$$

which is the the same as (14.2.14).

When $T > T_c$, the Gibbs potential per particle is minimized only at $m = 0$, as shown in figure 14.3. However, when $T < T_c$ there are two non-vanishing values of m, call them $\pm m_0$, at which g is minimized (see figure 14.4). We can understand this as follows: since the minimization condition, $\partial g/\partial m = 0$, is actually the condition that $h = 0$, two limits are possible, *viz.,* (i) as $h \to 0^+$ the magnetization achieves the value $+m_0$ and (ii) it achieves the value $-m_0$ as $h \to 0^-$. But then the picture in 14.4 for $T < T_c$ cannot be valid for the region between $-m_0$ and $+m_0$ because in this region the magnetic susceptibility turns

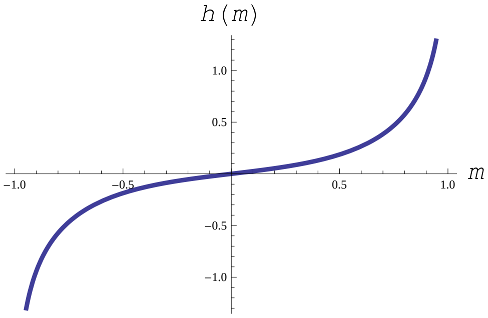

Figure 14.5: $h = h(m)$ when $T > T_c$.

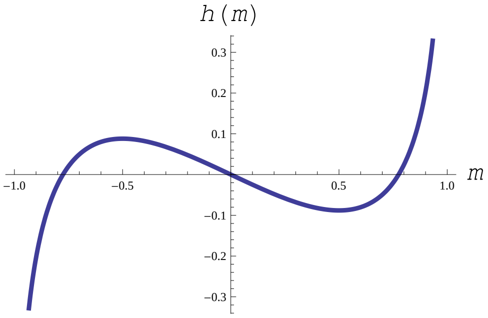

Figure 14.6: $h = h(m)$ when $T < T_c$.

negative as is evident from the behavior of $h(m)$ when $T < T_c$ which is shown in figure 14.6. The function $h(m)$ when $T > T_c$ is shown in figure 14.5 and it is clear in this case that the magnetic susceptibility is always positive. A region of negative magnetic susceptibility is unphysical and must be corrected. This is done by simply *joining* the points between $\mp m_0$ on the $m-$axis as shown by the red line. Recall that a similar correction was originally proposed by Maxwell in connection with the Van der Waals euqation of state and is called **Maxwell's construction**. The resulting picture of the Gibbs potential is shown in 14.8. With this construction one finds that m is discontinuous at $h = 0$. The Helmholz free energy (per atom),

$$f = g - mh, \quad df = -sdT - mdh \Rightarrow \frac{\partial f}{\partial h} = -m(T,h) \tag{14.2.25}$$

has a cusp-like maximum at $h = 0$.

We get a better insight into the reason for the spontaneous breaking of the rotational symmetry if we expand the Gibbs potential per particle around $m = 0$. We find

$$g(T,m) = a(T,T_c)m^2 + b(T,T_c)m^4 + \mathcal{O}(m^6) \tag{14.2.26}$$

where

$$a(T,T_c) = \frac{k}{2}(T - T_c), \quad b(T,T_c) = \frac{kT}{12} \tag{14.2.27}$$

The spontaneous symmetry breaking occurs as T falls below the critical temperature, causing the coefficient $a(T,T_c)$ to become negative.

We are now in a position to calculate the critical exponents of these models in the mean field approximation:

- The order parameter exponent, β can be calculated from the expression for m in the limit as $h \to 0$, expanding the hyperbolic tangent about zero. Retaining up to the

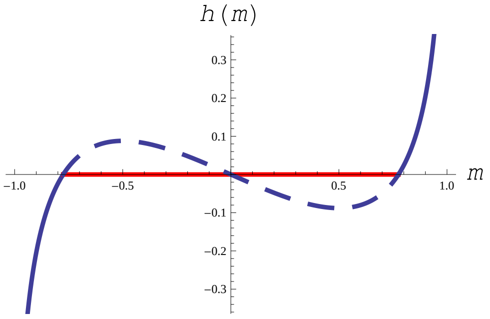

Figure 14.7: Maxwell's correction to the function $h = h(m)$, when $T < T_c$.

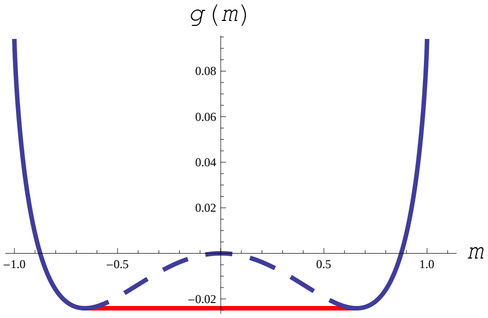

Figure 14.8: The resulting corrected Gibbs function.

cubic term in the expansion, we get the equation

$$m = \tanh \frac{\beta}{\beta_c} m \approx \frac{\beta}{\beta_c} m - \frac{1}{3}\left(\frac{\beta}{\beta_c}\right)^3 m^3 \tag{14.2.28}$$

which has solutions

$$m \approx \sqrt{\frac{3(T_c - T)}{T_c}} \tag{14.2.29}$$

showing that $\beta = \frac{1}{2}$.

- Expanding the equation for h in (14.2.22) about small m, taking $\beta = \beta_c$ we find

  $$h \approx \frac{m^3}{3\beta_c} + \mathcal{O}(m^5) \tag{14.2.30}$$

  so $m \sim (3\beta_c h)^{1/3}$, which shows that the exponent of the critical isotherm is $\delta = 3$.

- To compute the susceptibility exponent, γ, we require an equation for the magnetic susceptibility per particle. This is obtained from the equation of state. Taking a derivative with respect to h and simplifying, we find

  $$\chi = \frac{\partial m}{\partial h} = \frac{\beta(1 - m^2)}{1 - \frac{\beta}{\beta_c}(1 - m^2)}. \tag{14.2.31}$$

  When $T \to T_c^+$ we can set $m = 0$ and then we have the **Curie-Weiss law**

  $$\chi^+ \to \frac{1}{k(T - T_c)} \tag{14.2.32}$$

but when $T \to T_c^-$, then we should use m given by (14.2.29). Then we get

$$\chi^- \to \frac{1}{2k(T_c - T)} \tag{14.2.33}$$

In either case we find that $\gamma = 1$, but we also obtain the amplitude ratio

$$\lim_{T\to T_c} \frac{\chi^+}{\chi^-} = 2. \tag{14.2.34}$$

Furthermore, as $T \to 0$, the susceptibility is seen to behave as

$$\chi \approx \frac{4}{kT} e^{-2T_c/T}, \tag{14.2.35}$$

using the asymptotic form for m. So it vanishes at $T = 0$.

- In the mean field approximation the heat capacity per particle at constant h is obtained from the expression we had earlier for the internal energy,

$$c_h = -k\beta^2 \frac{\partial \varepsilon}{\partial \beta} = k\beta^2 \left(\frac{2m}{\beta_c} + h\right) \frac{\partial m}{\partial \beta}. \tag{14.2.36}$$

To compute $\partial m/\partial \beta$ we must use the expression for m in (14.2.9). After some algebra we get

$$\frac{\partial m}{\partial \beta} = \frac{\frac{1}{\beta} \tanh^{-1} m}{\frac{1}{1-m^2} - \frac{\beta}{\beta_c}} \tag{14.2.37}$$

and therefore

$$c_h = k\beta \left(\frac{2m}{\beta_c} + h\right) \frac{\tanh^{-1} m}{\frac{1}{1-m^2} - \frac{\beta}{\beta_c}}. \tag{14.2.38}$$

With $h = 0$ we take $m = 0$ as $T \to T_c^+$, then

$$c_h^+ \to 0. \tag{14.2.39}$$

On the other hand, as $T \to T_c^-$ when $h = 0$ we find, using (14.2.29), that

$$c_h^- \to 3k \tag{14.2.40}$$

so the specific heat exponent is zero but it has a finite jump discontinuity across $T = T_c$. The asymptotic expression ($T \to 0$) for c_h is

$$c_h \approx 8k \left(\frac{T_c}{T}\right)^2 e^{-2T_c/T} \tag{14.2.41}$$

and so it also vanishes at $T = 0$.

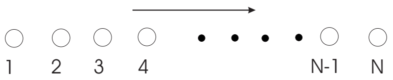

Figure 14.9: Open boundary conditions.

14.3 Exact Solution: Ising Model

We could go beyond the mean field approximation if we had an exact solution for the partition function. This is known only in dimensions one and two, so let's first look at the exact solution of the one dimensional (Ising) models. Since we have a one dimensional chain, the first question to ask is whether or not the chain is closed, *i.e.,* if an additional interaction of the form $-Js_Ns_1$ between the first element of the chain and the last occurs. If not, the boundary conditions are said to be **open** and the Hamiltonian is of the form

$$\mathcal{H} = -J\sum_{i=1}^{N-1} s_i s_{i+1} - h\sum_{i=1}^{N} s_i \tag{14.3.1}$$

If the additional interaction $-Js_Ns_1$ is included then the boundary conditions are said to be **closed**. In this case, the Hamiltonian reads

$$\mathcal{H} = -J\sum_{i=1}^{N} s_i s_{i+1} - h\sum_{i=1}^{N} s_i \tag{14.3.2}$$

where s_{N+1} is identified with s_1. This Hamiltonian has the advantage that both the sums appearing in it run upto N, which simplifies the computation of the partition function considerably as we shall see.

14.3.1 The Partition Function

The partition function, which involves a sum over spin configurations can be written out in long hand as

$$Z = \sum_{\{s\}} e^{\beta(J\sum_{i=1}^{N-1} s_i s_{i+1} + h\sum_{i=1}^{N} s_i)} \tag{14.3.3}$$

We want to rewrite the exponent above so that the sums in both terms run to $N-1$. Using

$$\sum_{i=1}^{N} s_i = \frac{1}{2}\left[s_1 + s_N + \sum_{i=1}^{N-1}(s_i + s_{i+1})\right] \tag{14.3.4}$$

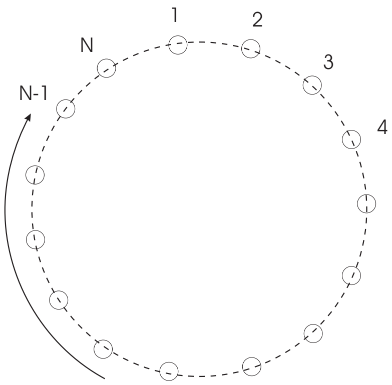

Figure 14.10: Closed boundary conditions.

we have

$$
\begin{aligned}
Z &= \sum_{\{s\}} e^{\frac{\beta h}{2}(s_1+s_N)} e^{\beta \sum_{i=1}^{N-1}[J s_i s_{i+1} + \frac{h}{2}(s_i+s_{i+1})]} \\
&= \sum_{\{s\}} e^{\frac{\beta h}{2}(s_1+s_N)} \prod_{i=1}^{N-1} e^{\beta[J s_i s_{i+1} + \frac{h}{2}(s_i+s_{i+1})]} \qquad (14.3.5)
\end{aligned}
$$

To carry out the spin sum we will now introduce a novel method. Let us define the matrix $\widehat{T}$, called the **transfer matrix**, with matrix elements

$$T_{ij} = \langle s_i|\widehat{T}|s_j\rangle = e^{\beta[J s_i s_j + h(s_i+s_j)/2]}, \qquad (14.3.6)$$

then our spin sum may be written as

$$Z = \sum_{s_1,s_2,\ldots,s_N} e^{\frac{\beta h}{2}(s_1+s_N)} \langle s_1|\widehat{T}|s_2\rangle\langle s_2|\widehat{T}|s_3\rangle \ldots \langle s_{N-1}|\widehat{T}|s_N\rangle \qquad (14.3.7)$$

and we can make use of the completeness of our states, $\{|s_i\rangle\}$, to reduce it to the form

$$Z = \sum_{s_1,s_N} e^{\frac{\beta h}{2}(s_1+s_N)} \langle s_1|\widehat{T}^{N-1}|s_N\rangle. \qquad (14.3.8)$$

Into this we insert a complete set of eigenstates, $\{|e\rangle\}$, of $\widehat{T}$ to get

$$Z = \sum_{s_1,s_N,e,e'} e^{\frac{\beta h}{2}(s_1+s_N)} \langle s_1|e\rangle\langle e|\widehat{T}^{N-1}|e'\rangle\langle e'|s_N\rangle$$

$$= \sum_{s_1,s_N} e^{\frac{\beta h}{2}(s_1+s_N)} \left[\lambda_+^{N-1}\langle s_1|e_+\rangle\langle e_+|s_N\rangle + \lambda_-^{N-1}\langle s_1|e_-\rangle\langle e_-|s_N\rangle\right] \tag{14.3.9}$$

where $\lambda_\pm$ are the eigenvalues of the transfer matrix, $\widehat{T}$, which has the explicit form

$$\widehat{T} = \begin{pmatrix} e^{\beta(J+h)} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta(J-h)} \end{pmatrix}, \tag{14.3.10}$$

Its eigenvalues are easily computed; they are

$$\lambda_\pm = e^{\beta J}\left[\cosh\beta h \pm \sqrt{\sinh^2\beta h + e^{-4\beta J}}\right]. \tag{14.3.11}$$

with normalized eigenvectors

$$|e_\pm\rangle = \frac{1}{\sqrt{1+x_+^2}}\begin{pmatrix} x_\pm \\ 1 \end{pmatrix} \tag{14.3.12}$$

respectively, where

$$x_\pm = e^{2\beta J}(\sinh\beta h \pm \sqrt{e^{-4\beta J} + \sinh^2\beta h}). \tag{14.3.13}$$

A straightforward calculation now reveals that

$$Z = \frac{(x_+e^{\beta h/2} + e^{-\beta h/2})^2}{1+x_+^2}\lambda_+^{N-1} + \frac{(x_-e^{\beta h/2} + e^{-\beta h/2})^2}{1+x_-^2}\lambda_-^{N-1}. \tag{14.3.14}$$

These complicated expressions simplify nicely when $h = 0$, for then

$$\lambda_\pm = e^{\beta J} \pm e^{-\beta J}, \quad x_\pm = \pm 1 \tag{14.3.15}$$

and one easily finds

$$Z_{h=0} = 2\lambda_+^{N-1} = 2(2\cosh\beta J)^{N-1}. \tag{14.3.16}$$

Of course, the case $h = 0$ gives a very simple partition function, which could have been recovered directly, without recourse to the transfer matrix, but when $h \neq 0$ it's best to use the method described above. It has its limitations: for instance if the spin-spin interaction strength were to vary across the chain then J would be depend on the spin label and the method would fail because it relies heavily on the completeness relations.

If one includes an interaction between the first and the last spins in the chain, then one is effectively changing the topology of the chain to that of a circle. In this case,

$$\mathcal{H} = -J\sum_{i=1}^{N} s_i s_{i+1} - h\sum_{i=1}^{N} s_i \tag{14.3.17}$$

and the $N+1$ spin is identified with the first. Then we have the partition function

$$\begin{aligned} Z &= \sum_{\{s\}} \prod_{i=1}^{N} e^{\beta(J s_i s_{i+1} + \frac{h}{2}(s_i + s_{i+1}))} \\ &= \sum_{s_1} \left[\lambda_+^N \langle s_1 | e_+ \rangle \langle e_+ | s_1 \rangle + \lambda_-^N \langle s_1 | e_- \rangle \langle e_- | s_1 \rangle \right] \\ &= \lambda_+^N + \lambda_-^N, \end{aligned} \tag{14.3.18}$$

Again, in the limit $h \to 0$, it reduces to

$$Z_{h=0} = (2\cosh \beta J)^N [1 + (\tanh \beta J)^N]. \tag{14.3.19}$$

The transfer matrix method provides an exceptionally powerful tool in determining Z for these finite dimensional systems. It was introduced for the first time by Kramers and Wannier in 1941. Three years later it was employed by Onsager to treat the free field spin models in two dimensions.

14.3.2 Correlation Functions

Consider the Ising chain, with open boundary conditions. Suppose we want to compute the correlation function $\langle s_i s_j \rangle$. Take the case where there is no external ordering field ($h=0$), then

$$\langle s_i s_j \rangle = \frac{1}{Z} \sum_{\{s\}} s_i s_j \prod_{r=1}^{N-1} e^{\beta J s_r s_{r+1}} \tag{14.3.20}$$

How can we evaluate this sum? To start with, let $j = i + k$ and imagine that J depends on the location on the lattice, *i.e.,* $J \to J_r$. In that case

$$\langle s_i s_{i+k} \rangle = \frac{1}{Z} \sum_{\{s\}} s_i s_{i+k} \prod_{r=1}^{N-1} e^{\beta J_r s_r s_{r+1}} \tag{14.3.21}$$

Now notice that for any index j

$$\sum_{\{s\}} s_j s_{j+1} \prod_{r=1}^{N-1} e^{\beta J_r s_r s_{r+1}} = \frac{1}{\beta} \frac{\partial Z}{\partial J_j}, \tag{14.3.22}$$

but we can always write

$$s_i s_{i+k} = \overbrace{s_i s_{i+1}} \overbrace{s_{i+1} s_{i+2}} \overbrace{s_{i+2} s_{i+3}} \ldots \overbrace{s_{i+k-1} s_{i+k}} \tag{14.3.23}$$

since this amounts to simply inserting unity an appropriate number of times and grouping the spins in a particular way. Therefore

$$\langle s_i s_{i+k}\rangle = \frac{1}{\beta^k Z}\frac{\partial^k Z(J_1, J_2, \ldots, J_{N-1})}{\partial J_i \partial J_{i+1}\ldots \partial J_{i+k-1}}. \tag{14.3.24}$$

and we only need to evaluate the partition function with $N-1$ distinct J's,

$$Z = \sum_{s_1,s_2,\ldots,s_N}\prod_{r=1}^{N-1} e^{\beta J_r s_r s_{r+1}}, \tag{14.3.25}$$

to determine the correlation function. This is easy to do if we recognize that the s_r are random variables, for then calling $\sigma_r = s_r s_{r+1}$ we have

$$Z = 2\sum_{\sigma_1,\ldots\sigma_{N-1}}\prod_{i=1}^{N-1} e^{\beta J_r \sigma_r} = \prod_{r=1}\sum_{\sigma_r} e^{\beta J_r \sigma_r} \tag{14.3.26}$$

and each σ_r can only take the values ± 1, so

$$Z = 2\prod_{r=1}^{N-1}(2\cosh\beta J_r) = 2^N\prod_{r=1}^{N-1}\cosh\beta J_r \tag{14.3.27}$$

When we take the k derivatives required, we simply get

$$\langle s_i s_{i+k}\rangle = \prod_{r=i}^{i+k-1}\tanh\beta J_r \to (\tanh\beta J)^k \tag{14.3.28}$$

where we have reset the J_r to J in the last step. This expression agrees with our definition in (14.0.2), for we could write it as

$$\langle s_i, s_j\rangle = e^{-|j-i|/\xi} \tag{14.3.29}$$

where the correlation length to be

$$\xi = -\frac{1}{\ln\tanh\beta J}. \tag{14.3.30}$$

As $\beta J \to 0^+$, *i.e.,* in the limit of very high temperatures, $\xi \to 0^+$ but as $\beta J \to \infty$, the correlation length diverges as

$$\xi \to e^{2\beta J}. \tag{14.3.31}$$

This tells us that there is no long range order at any finite T and that $T = 0$ is the critical temperature for the one dimensional Ising chain. This behavior is typical for such systems: one finds a critical dimension, d_c such that $T_c = 0$ when $d \le d_c$ and $T_c \neq 0$ when $d > d_c$. In other words, $d_c = 1$ is the critical dimension for the spin models.

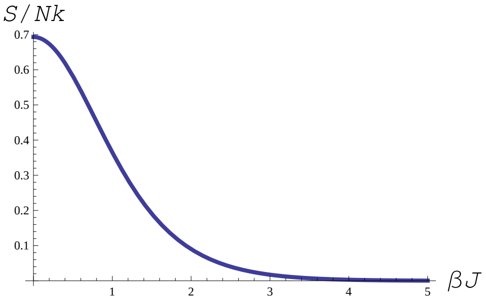

Figure 14.11: Entropy per particle for the Ising chain.

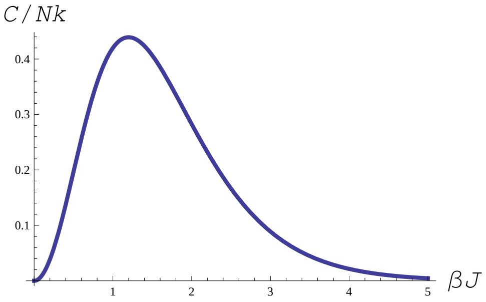

Figure 14.12: Magnetic Heat Capacity per particle for the Ising chain.

14.3.3 Thermodynamics

Continuing with the Ising model with open boundary conditions in the absence of an external ordering field, h, the partition function can be written as

$$Z = 2^N (\cosh \beta J)^{N-1} \tag{14.3.32}$$

In the thermodynamic limit, *i.e.,* as $N \to \infty$, $N-1$ above can be replaced by N. Again, for the Ising chain with closed or circular boundary conditions, because $\lambda_- < \lambda_+$, *i.e.,* $(\lambda_-/\lambda_+)^N \to 0$ in the thermodynamic limit, only the larger eigenvalue determines the major thermodynamic properties of the system. In this limit we can take

$$Z \approx (\lambda_+)^N = (2\cosh \beta J)^N \tag{14.3.33}$$

Not surprisingly, the difference between the boundary conditions is irrelevant in the thermodynamic limit.

The thermodynamic properties follow as usual. The internal energy behaves as

$$\langle E \rangle = -NJ \tanh \beta J \tag{14.3.34}$$

so the magnetic contribution to the internal energy vanishes as $-NJ^2\beta$ in the limit of high temperatures ($\beta J \ll 1$) and approaches its minimum value of $-NJ$ as $T \to 0$. The entropy,

$$S = Nk\left[\ln 2 + \ln\cosh \beta J - \beta J \tanh \beta J\right] \tag{14.3.35}$$

vanishes as $T \to 0$ according to

$$S \to 2Nk\beta J e^{-2\beta J} \tag{14.3.36}$$

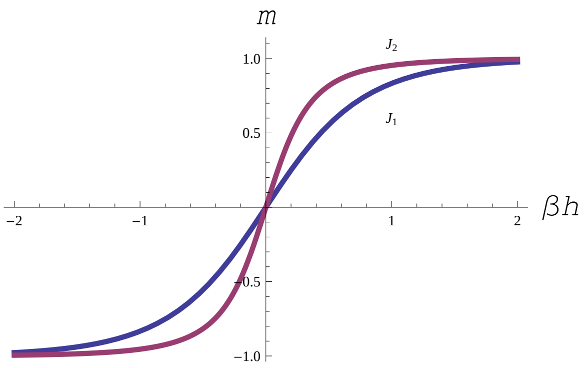

Figure 14.13: The magnetization as a function of βh for two different values of J: $J_1 < J_2$.

therefore the system approaches a perfectly ordered phase as $T \to 0$. On the other hand, as $T \to \infty$,

$$S \to Nk[\ln 2 - \frac{1}{2}(\beta J)^2 + \mathcal{O}((\beta J)^3)] \approx Nk \ln 2 \tag{14.3.37}$$

which says that *all* of the possible 2^N states are occupied and the system is in a completely disordered phase at high temperatures. The magnetic heat capacity of the system (shown in figure 14.12) is

$$C = -k\beta^2 \frac{\partial \langle E \rangle}{\partial \beta} = Nk\beta^2 J^2 \text{sech}^2 \beta J, \tag{14.3.38}$$

which behaves, at high temperatures, as

$$C \approx k \left(\frac{J}{kT}\right)^2 \tag{14.3.39}$$

and at low temperatures as

$$C \approx k \left(\frac{J}{kT}\right)^2 e^{-2J/kT} \tag{14.3.40}$$

again showing the essential singularity at $T = 0$. It achieves its maximum at $T = J/(1.2k)$ and there is no singularity or phase transition at any non-zero value of T.

Consider closed boundary conditions when $h \neq 0$. Now

$$Z \approx 2e^{N\beta J} \left[\cosh \beta h + \sqrt{\sinh^2 \beta h + e^{-4\beta J}}\right]^N \tag{14.3.41}$$

and it follows that

$$m = \frac{1}{N\beta} \frac{\partial \ln Z}{\partial h} = \frac{\sinh \beta h}{\sqrt{\sinh^2 \beta h + e^{-4\beta J}}} \tag{14.3.42}$$

from which the susceptibility (per particle) is found to be

$$\chi = \frac{\partial m}{\partial h} = \frac{\beta \cosh \beta h}{e^{4\beta J}(\sinh^2 \beta h + e^{-4\beta J})^{3/2}} \tag{14.3.43}$$

Clearly, the magnetization vanishes as $h \to 0$, which rules out the possibility of spontaneous magnetization and therefore any phase transition at finite temperatures. However, as $\beta \to \infty$, $m \to 1$ for *any* h, which implies perfect order in the system. This means that there is a phase transition at the critical temperature $T_c = 0$. As $J \to 0$ we find $m = \tanh \beta h$, which is the result we are familiar with for a paramagnetic system. Moreover, a larger positive value of J enhances magnetization and causes a faster approach to saturation, as shown in figure 14.13.

14.4 Mean Field Theory: Landau's Approach

Landau attempted a phenomenological description of all second order phase transitions. A second order phase transition is one in which the second derivatives of the free energy (in the case of the ferromagnetic systems these would be the specific heat and magnetic susceptibility) show either a discontinuity or a divergence while the first derivatives (the entropy and magnetization for ferromagnetic systems) are continuous at the critical point. Landau's description emphasizes the importance of the order parameter and proposes that the basic features of the critical behavior are encapsulated in the Gibbs free energy, expanded about $m = 0$. In the case of the ferromagnetic systems we have been examining the expansion involves only even powers of m when $h = 0$ because the Hamiltonian is invariant under the transformation $s_i \to -s_i$. Thus the zero field Gibbs free energy per particle can be written as

$$g(m, T) = a(T) + b(T)m^2 + c(T)m^4 + \mathcal{O}(m^6). \tag{14.4.1}$$

Ignoring terms of higher than fourth power in the expansion, thermodynamic stability requires that $c(T) > 0$, since $g(m, T)$ must have a global minimum. The equilibrium value of the order parameter is then determined by minimizing $g(m, T)$ with respect to m,

$$b(T)m_0 + 2c(T)m_0^3 = 0 \Rightarrow m_0 = 0 \;\text{ or }\; m_0 = \pm\sqrt{-\frac{b(T)}{2c(T)}} \tag{14.4.2}$$

(Recall that this is the condition for vanishing h.) If $b(T) \geq 0$ in the neighborhood of the critical temperature then the only solution is $m_0 = 0$ and there is no spontaneous magnetization. If, on the contrary, $b(T) < 0$ near the critical point then there are solutions which describe spontaneous magnetization with values $\pm\sqrt{-b(T)/2c(T)}$. Now suppose we expand the coefficients in powers of $t = (T - T_c)$ near the critical temperature,

$$a(T) = \sum_{k=0} a_k t^k, \quad b(T) = \sum_{k=0} b_k t^k, \quad c(T) = \sum_{k=0} c_k t^k, \tag{14.4.3}$$

we find that up to $\mathcal{O}(t)$ the non-zero values of m_0 will be

$$m_0 = \pm\sqrt{-\frac{b_0}{2c_0} + \frac{1}{2c_0^2}\left(b_0 c_1 - b_1 c_0\right) t + \ldots} \tag{14.4.4}$$

so physically sensible results are obtained when $b_0 = 0$ and $b_1 > 0$, in which case

$$m_0 \approx \pm\sqrt{-\frac{b_1}{2c_0}(T - T_c)}, \quad T \lesssim T_c, \tag{14.4.5}$$

straight away showing that $\beta = \frac{1}{2}$. Thus, when $T \lesssim T_c$ there are three extrema of which two are minima at $m = \pm m_0$ and one is maximum at $m = 0$. Now $g(m, T)$ must be a convex function everywhere so that the magnetic susceptibility stays positive, but we have just seen that this is not so between $-m_0$ and $+m_0$ when $T < T_c$. This means that we must employ Maxwell's construction as before and simply join $-m_0$ to m_0 by a straight line along which the susceptibility would be infinite.

When $h \neq 0$, consider instead the Helmholz free energy,

$$f(T, h) = g - mh = a(T) + b(T)m^2 + c(T)m^4 - hm \tag{14.4.6}$$

and recall that $df = -sdT - mdh$, so $m = -(\partial f/\partial h)$ and therefore

$$h = 2b(T)m + 4c(T)m^3. \tag{14.4.7}$$

On the critical isotherm, because $b_0 = 0$, we must have $h = 4cm^3$, showing that the critical exponent of the critical isotherm has the value $\delta = 3$.

The magnetic susceptibility can be given as

$$\chi = \left(\frac{\partial h}{\partial m}\right)_T^{-1} = \frac{1}{2b(T) + 12c(T)m^2}. \tag{14.4.8}$$

But we have seen that when $h = 0$ then $m = 0$ if $T > T_c$, so in that case

$$\chi^+ = \frac{1}{2b(T)} \approx \frac{1}{2b_1(T - T_c)}. \tag{14.4.9}$$

On the other hand, the magnetization is not zero when $T < T_c$ but given instead by (14.4.5), therefore

$$\chi^- \approx \frac{1}{4b_1(T_c - T)} \tag{14.4.10}$$

Both these results show that the susceptibility exponent is unity.

Finally we turn to the heat capacity. Since the specific heat capacity at constant h can be obtained directly from the Helmholz free energy according to

$$c_h = -T \left(\frac{\partial^2 f}{\partial T^2} \right)_h . \tag{14.4.11}$$

Above the critical temperature, because $m = 0$ when $h = 0$, we find

$$c_h^+ \approx -2a_2 T_c + \mathcal{O}(T - T_c) \tag{14.4.12}$$

but below the critical temperature,

$$c_h^- \approx -2a_2 T_c + \frac{b_1^2 T_c}{2c_0} + \mathcal{O}(T - T_c) \tag{14.4.13}$$

and so the specific heat exponent, α, is zero, but there is a jump in c_h at the critical temperature. The heat capacity at constant m exhibits no such jump. It can be directly obtained from

$$c_h - c_m = \frac{T}{\chi} \left(\frac{\partial m}{\partial T} \right)_h^2 , \tag{14.4.14}$$

which follows from the first law and Maxwell's relations.[1] Again, because $m = 0$ above the critical temperature when $h = 0$,

$$c_m = c_h = -2a_2 T_c, \tag{14.4.15}$$

($T \gtrsim T_c$) and when $T \lesssim T_c$ we can use (14.4.5) and (14.4.10) to find

$$c_h - c_m \approx \frac{b_1^2 T_c}{2c_0} \Rightarrow c_m = -2a_2 T_c. \tag{14.4.16}$$

However, although there is no jump at T_c, c_m possesses a cusp-like singularity there, as can be shown by examining the expansion up to first order in $T - T_c$.[2]

It is a remarkable feature of Landau's approach that it gives the same critical exponents as mean field theory. In fact, while it starts with an expression for the free energy of the system containing a set of unspecified, temperature dependent parameters intended to describe the structure and interactions within the system in a phenomenological way, it shows that the critical exponents do *not* depend on these parameters. This suggests that the theory is in fact dealing with an entire class of systems, all members of which, despite

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[1] Problem: Derive this relation following the approach in section 4.2.1.

[2] Problem: Show this.

their structural differences, display the same critical behavior. Such a class is called a **universality class**.

Let us therefore consider any macroscopic system, not necessarily magnetic, for which there exists an order parameter m averaged over some length scale, say a, characteristic of atomic distances. Assume, moreover, that m is a classical field, *i.e.,* a function of the position within the system. Since $m(x)$ is averaged on scales on the order of a there can be no Fourier components of m with wavelength $\lambda \lesssim a$. In terms of m, we take the canonical partition function to be of the form

$$Z = \sum_m \Omega(m) e^{-\beta\mathcal{H}(m,h)} \tag{14.4.17}$$

where h is an external field and the sum is over all possible field configurations, *i.e.,* it takes into account all possible functions $m(x)$. $\Omega(m)$ is an additional degeneracy associated with the fact that $m(x)$ itself is an average over some more fundamental variable (the spins in spin-models) so there may in fact be many, say $\Omega(m)$, configurations of the more fundamental variables that yield the same $m(x)$. Thus we introduce the "entropy" $\mathcal{S} = k \ln \Omega(m)$, in analogy with the Boltzmann formula and write the sum over all configurations of $m(x)$ as

$$Z = \sum_m \Omega(m) e^{-\beta\mathcal{H}(m,h)} = \sum_m \; e^{-\beta(\mathcal{H}-T\mathcal{S})}, \tag{14.4.18}$$

but keep in mind that $\mathcal{S}$ does not represent the true entropy of the system but is related to the number of microscopic states lead to the same $m(x)$ and therefore is a *partial* entropy. The quantity $\mathcal{F} = \mathcal{H} - T\mathcal{S}$ is called the **Landau** free energy.

Now imagine that $\mathcal{F}(m,h)$ is given by the most Taylor general expansion, conforming to the symmetries of the system and up to any desired order in the order parameter and its derivatives. For example, if the system admits an "up-down" symmetry, the Landau free energy would be

$$\mathcal{F} = \int dx \; \left[a + bm^2 + cm^4 + \ldots + \frac{g}{2}(\nabla m)^2 + \ldots - hm\right]. \tag{14.4.19}$$

where we have added a spatial gradient term as well. This term gives a free energy cost for a non-uniform $m(x)$: a positive g would would increase the energy associated with a non-uniform configuration whereas a negative g would do the opposite. The coefficient of the highest order polynomial term must alsways be positive, otherwise the system will be unstable.[3] What we have therefore is,

$$Z = \sum_m e^{-\beta \int dx\ [\frac{g}{2}(\nabla m)^2 + bm^2 + cm^4 + \ldots - hm]}. \tag{14.4.20}$$

and

$$P(m,h) = \frac{1}{Z}\ e^{-\beta \int dx\ [\frac{g}{2}(\nabla m)^2 + bm^2 + cm^4 + \ldots - hm]} \tag{14.4.21}$$

represents the probability for the configuration m. The greatest contribution to the partition function will come from the minimum of the Landau free energy and fluctuations about this minimum value can be systematically computed using the well known tools of path integration that we will study in the forthcoming chapters. The advantage of this approach is that it allows one to recover the macroscopic behavior of the system knowing only its symmetries and without having to contend with its microscopic details.

14.5 Fluctuations

Let us now expand the Landau free energy about the mean magnetization and let $\delta m = m - \langle m \rangle$, then

$$\mathcal{F} = \mathcal{F}(\langle m \rangle) + \int dx\ [b_1 \delta m^2 + \frac{g}{2}(\nabla \delta m)^2 + \ldots] \tag{14.5.1}$$

where we made use of the fact that $\langle m \rangle$ is the minimum of the free energy. Whenever one has gradients in the probability distribution, as occur for example in (14.4.21), it is convenient to perform a Fourier expansion. This is because the gradient terms turn into quadratic terms in the conjugate variable making it easier to take ensemble averages. Accordingly, Fourier transforming $\delta m(x)$,

$$\begin{aligned} \delta m(x) &= \int \frac{dp}{(2\pi)^d}\ \delta\widetilde{m}(p)\ e^{ip\cdot x} \\ \delta\widetilde{m}(p) &= \int dx\ \delta m(x)\ e^{-ip\cdot x} \end{aligned} \tag{14.5.2}$$

we find

$$\int dx (\delta m)^2 = \int \frac{dp}{(2\pi)^d}\ \delta\widetilde{m}(p)\delta\widetilde{m}(-p) = \int \frac{dp}{(2\pi)^d}\ |\delta\widetilde{m}(p)|^2 \tag{14.5.3}$$

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[3] We have neglected to write in a term of the form

$$\int dx\ m(a \cdot \nabla m)$$

because, after an integration by parts over the entire volume, it gives the term proportional to $(\nabla m)^2$ assuming appropriate boundary conditions.

where, because $m(x)$ is real, we set $\delta\widetilde{m}(-p) = \delta\widetilde{m}^*(p)$. This gives

$$\mathcal{F} = \mathcal{F}(\langle m\rangle) + \int \frac{dp}{(2\pi)^d}\ (b_1 + \frac{g}{2}p^2)|\delta\widetilde{m}(p)|^2 \tag{14.5.4}$$

(neglecting the quartic term) and therefore, if the integral over $\vec{p}$ is replaced by the product, the probability distribution in (14.4.21) takes the form

$$P(m,h) \sim e^{-\beta(\mathcal{F}(\langle m\rangle))} \prod_p e^{-\beta(b_1+\frac{g}{2}p^2)|\delta\widetilde{m}(p)|^2}. \tag{14.5.5}$$

It is then straightforward to find the desired ensemble average, $\langle|\delta\widetilde{m}(p)|^2\rangle$, from

$$\begin{aligned}\langle|\delta\widetilde{m}(p)|^2\rangle &= \frac{\int_0^\infty d|\delta\widetilde{m}(p)|\ |\delta\widetilde{m}(p)|^2 e^{-\beta(a_1+\frac{g}{2}p^2)|\delta\widetilde{m}(p)|^2}}{\int_0^\infty d|\delta\widetilde{m}(p)|\ e^{-\beta(a_1+\frac{g}{2}p^2)|\delta\widetilde{m}(p)|^2}} \\ &= \frac{kT}{2(b_1+\frac{g}{2}p^2)}.\end{aligned} \tag{14.5.6}$$

Define the correlation function

$$G(x) = \langle m(x), m(0)\rangle - \langle m\rangle^2 = \langle \delta m(x), \delta m(0)\rangle, \tag{14.5.7}$$

with Fourier transform

$$\int \frac{dp}{(2\pi)^d}\ \frac{dp'}{(2\pi)^d}\ \langle\delta\widetilde{m}(p), \delta\widetilde{m}(p')\rangle e^{ip\cdot x}. \tag{14.5.8}$$

If we now assume that correlations between different modes are independent and uncorrelated, so that $\langle\delta\widetilde{m}(p)\delta\widetilde{m}(-p')\rangle = \delta_{pp'}$, then

$$G(x) = \int \frac{dp}{(2\pi)^d}\ \langle|\delta\widetilde{m}(p)|^2\rangle e^{ip\cdot x}. \tag{14.5.9}$$

This approximation, in which the different Fourier modes are considered to be independent of one another, is called the **random phase** or **Orenstein-Zernicke** approximation. We can now use the expression for $\langle|\delta\widetilde{m}(p)|^2\rangle$ in (14.5.6) and find the expression for $G(x)$ in any dimension. In particular, for $G(x)$ in three dimensions we find

$$\begin{aligned}G(r) &= \frac{kT}{2(2\pi)^2}\int_0^\infty dpp^2 \int_0^\pi d\theta \sin\theta\ \frac{e^{ipr\cos\theta}}{b_1+\frac{g}{2}p^2} \\ &= \frac{kT}{2\pi g}\ \frac{1}{r}\ e^{-\sqrt{2b_1/g}\ r},\end{aligned} \tag{14.5.10}$$

which gives both the correlation length exponent

$$\xi = \sqrt{\frac{g}{2b_1}} \tag{14.5.11}$$

and the correlation function exponent $\eta = 0$.

Chapter 15

Thermal Field Theory