2012 Classical – 9 (SM)

9. Assume that a solid can be modelled as a collection of identical oscillators with quantized energy. Let ϵ be the unit of energy in the Einstein solid.

(a) Derive an expression for the number of microstates, $\Omega(N, q)$, in the macrostate with total energy $q\epsilon$ for an Einstein solid with N particles.

(b) Assume N and q are both large to show that

$$\Omega(N, q) \approx \left(\frac{q+N}{q}\right)^{q} \left(\frac{q+N}{N}\right)^{N}. \tag{4}$$

(c) Prove that the total energy is given by

$$U = q\epsilon = \frac{N\epsilon}{e^{\frac{\epsilon}{kT}} - 1}. \tag{5}$$

(d) Derive an expression for the heat capacity, $C = \frac{dU}{dT}$, and show that

$$\lim_{T \to \infty} C = Nk. \tag{6}$$

First lines of first chapter of "States of Matter", by D.L. Goodstein:

ONE

THERMODYNAMICS AND STATISTICAL MECHANICS

1.1 INTRODUCTION: THERMODYNAMICS AND STATISTICAL MECHANICS OF THE PERFECT GAS

Ludwig Boltzmann, who spent much of his life studying statistical mechanics, died in 1906, by his own hand. Paul Ehrenfest, carrying on the work, died similarly in 1933. Now it is our turn to study statistical mechanics.

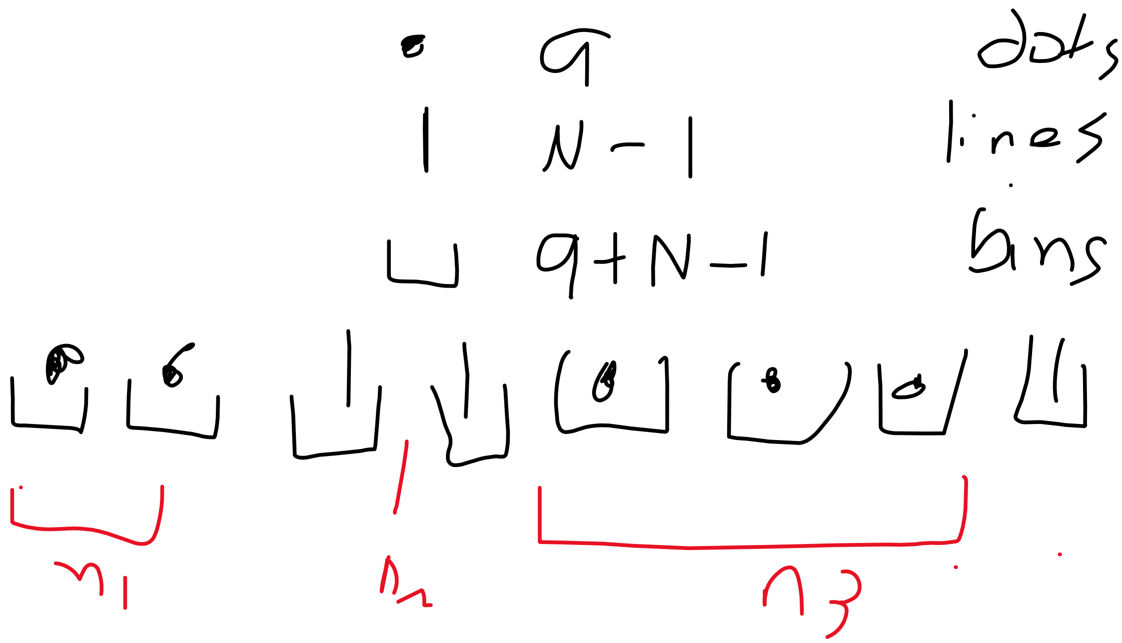
Perhaps it will be wise to approach the subject cautiously. We will begin by considering the simplest meaningful example, the perfect gas, in order

a) For N particles we need:

$$n_1 + n_2 + \cdots n_N = q$$

where each n_i is a non-negative integer.

Let's take q dots, $N - 1$ vertical lines and place them into $q + N - 1$ slots



We can view the n_i's as represented by the number of dots between vertical dividers. Two back-to-back dividers represents $n_i = 0$. Thus, the number of ways to sum up the $N - 1$ non-negative integers to q is equivalent the number of ways to place the dots into $q + N - 1$ bins. That is, choosing q bins from $q + N - 1$. From combinatorics we know:

$$\boxed{\Omega(N, q) = \binom{q + N - 1}{q} = \frac{(q + N - 1)!}{(N - 1)!\ q!}} \tag{1}$$

See: Schroeder *Thermal Physics* Section 2.2.

b) Taking the ln of Eq. (1)

$$\ln(\Omega(N, q)) = \ln(q + N - 1)! - \ln(N - 1)! - \ln q!$$

Now use Stirling's approximation, $\ln n! \approx n \ln n - n$:

$$\ln\big(\Omega(N,q)\big) \approx (q+N-1)\ln(q+N-1) - (q+N-1) - (N-1)\ln(N-1) + (N-1) - q\ln q + q$$

$$\ln\big(\Omega(N,q)\big) \approx (q+N-1)\ln(q+N-1) - (N-1)\ln(N-1) - q\ln q$$

Since N is large we'll use $N-1 \approx N$

$$\begin{aligned}\ln\big(\Omega(N,q)\big) &\approx (q+N)\ln(q+N) - N\ln N - q\ln q \quad \textit{(Group q and N terms)}\\ &= q(\ln(q+N) - \ln q) + N(\ln(q+N) - \ln N)\\ &= q\ln\left(\frac{q+N}{q}\right) + N\ln\left(\frac{q+N}{N}\right)\\ &= \ln\left(\frac{q+N}{q}\right)^q + \ln\left(\frac{q+N}{N}\right)^N\end{aligned}$$

Therefore,

$$\ln\big(\Omega(N,q)\big) \approx \ln\left(\frac{q+N}{q}\right)^q + \ln\left(\frac{q+N}{N}\right)^N$$

$$\rightarrow \boxed{\Omega(N,q) \approx \left(\frac{q+N}{q}\right)^q\left(\frac{q+N}{N}\right)^N}$$

c) The partition function for a single particle is

$$\begin{aligned}z &= \sum_{n=0}^{\infty} e^{-\frac{E_n}{k_BT}}\\ &= \sum_{n=0}^{\infty} e^{-\frac{\epsilon n}{k_BT}}\\ &= \frac{1}{1-e^{-\frac{\epsilon}{k_BT}}}\end{aligned}$$

Let $\beta = \frac{1}{k_BT}$. For the N independent particles the partition function is then:

$$Z = \prod_{n=1}^{N} z_i$$

$$Z = \left[\frac{1}{1-e^{-\epsilon\beta}}\right]^N$$

Now,

$$\begin{aligned}U &= -\frac{\partial \ln Z}{\partial \beta}\\ &= -\frac{\partial}{\partial\beta}\ln\big(1-e^{-\epsilon\beta}\big)^{-N}\\ &= N\frac{\partial}{\partial\beta}\ln\big(1-e^{-\epsilon\beta}\big)\\ &= N\left(\frac{-(-\epsilon)e^{-\epsilon\beta}}{1-e^{-\epsilon\beta}}\right)\end{aligned}$$

$$= N\epsilon \frac{e^{-\epsilon\beta}}{1 - e^{-\epsilon\beta}} \qquad \frac{e^{\epsilon\beta}}{e^{\epsilon\beta}}$$

Thus,

$$\boxed{U = \frac{N\epsilon}{e^{\epsilon\beta} - 1}}$$

d)

$$\begin{aligned} C &= \frac{dU}{dT} \\ &= \frac{d\beta}{dT}\frac{dU}{d\beta} \\ &= N\epsilon\left(\frac{-1}{k_B T^2}\right)\left[-\frac{\epsilon\, e^{\epsilon\beta}}{(e^{\epsilon\beta} - 1)^2}\right] \end{aligned}$$

$$\boxed{C = \frac{N\epsilon^2}{k_B T^2}\frac{1}{(e^{\epsilon\beta} - 1)^2}} \qquad (2)$$

Rewriting Eq. (2) in terms of β

$$C = k_B N\epsilon^2 \frac{\beta^2}{(e^{\epsilon\beta} - 1)^2}$$

Therefore,

$$\begin{aligned} \lim_{T\to\infty} C &= \lim_{\beta\to 0} C \\ &= k_B N\epsilon^2 \lim_{\beta\to 0}\frac{\beta^2}{(1 - e^{-\epsilon\beta})^2} \end{aligned}$$

$$\begin{aligned} 1 - e^{-\epsilon\beta} &= 1 - (1 - \epsilon\beta) + \mathcal{O}((\epsilon\beta)^2) \\ &= \epsilon\beta + \mathcal{O}((\epsilon\beta)^2) \end{aligned}$$

Therefore:

$$\lim_{T\to\infty} C = k_B N\epsilon^2 \lim_{\beta\to 0}\frac{\beta^2}{(\epsilon\beta)^2}$$

$$\rightarrow \boxed{\lim_{T\to\infty} C = k_B N}$$