9. Consider a system with two non-degenerate energy levels with energies ε_0 and ε_1, where $\varepsilon_1 > \varepsilon_0 > 0$. Suppose that the system contains N distinguishable particles at temperature T, so that the system is described by classical Boltzmann statistics.

a) Show that the average energy per particle in the system is given by the expression
$\langle u \rangle = {}^{U}/_{N} = (\varepsilon_0 + \varepsilon_1 e^{-\alpha})/(1 + e^{-\alpha})$,
where $\alpha = (\varepsilon_0 - \varepsilon_1)/k_B T$ with k_B denoting Boltzmann's constant.

b) show that the constant volume heat capacity per particle is given by
$\frac{C_V}{N} = k_B \alpha^2 e^{-\alpha}/(1 + e^{-\alpha})^2$.

c) Show that C_V/N goes to zero as T goes to zero, and that as the temperature becomes very large, $C_V/N \cong \frac{1}{4} k_B \alpha^2$.

CL: Sign error in the expressions for $\langle u \rangle$ *and* $\frac{C_V}{N}$. It's correct if you make the change $\alpha \to -\alpha$

BONUS: Show why the expression for $\langle u \rangle$ as given gives the wrong answer when $T \to 0$.

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a) The partition function for a single particle:

$$z_j = \sum_i e^{-\epsilon_i \beta} = e^{-\epsilon_0 \beta} + e^{-\epsilon_1 \beta}$$

where $\beta = \frac{1}{kT}$. Now the partition function is:

$$Z = \prod_{j=1}^{N} z_j$$

$$Z = \left(e^{-\epsilon_0 \beta} + e^{-\epsilon_1 \beta}\right)^N \qquad (1)$$

Now,

$$U = -\frac{\partial \log Z}{\partial \beta} \qquad (2)$$

This follows from the fact that the average energy is:

$$U = \sum_i \epsilon_i p_i$$

Since $p_i = \frac{e^{-\epsilon_i \beta}}{Z}$ (from your statistical mechanics class) then:

$$U = \sum_i \epsilon_i \frac{e^{-\epsilon_i \beta}}{Z}$$

$$= \frac{1}{Z} \sum_i \epsilon_i e^{-\epsilon_i \beta} \qquad \left(use \ \frac{\partial e^{-\epsilon_i \beta}}{\partial \beta} = -\epsilon_i e^{-\epsilon_i \beta} \right)$$

$$= -\frac{1}{Z} \sum_i \frac{\partial e^{-\epsilon_i \beta}}{\partial \beta}$$

$$= -\frac{1}{Z}\frac{\partial}{\partial\beta}\sum_i e^{-\epsilon_i\beta}$$
$$= -\frac{1}{Z}\frac{\partial}{\partial\beta}Z$$
$$= -\frac{\partial \log Z}{\partial\beta}$$

So, by Eq. (1) and (2):

$$U = -\frac{\partial \log Z}{\partial\beta}$$
$$= -\frac{\partial \log\left(e^{-\epsilon_0\beta} + e^{-\epsilon_1\beta}\right)^N}{\partial\beta}$$
$$= -N\frac{\partial \log\left(e^{-\epsilon_0\beta} + e^{-\epsilon_1\beta}\right)}{\partial\beta}$$
$$= -\frac{N}{e^{-\epsilon_0\beta} + e^{-\epsilon_1\beta}}\frac{\partial}{\partial\beta}\left(e^{-\epsilon_0\beta} + e^{-\epsilon_1\beta}\right)$$
$$= -\frac{N}{e^{-\epsilon_0\beta} + e^{-\epsilon_1\beta}}\left(-\epsilon_0 e^{-\epsilon_0\beta} - \epsilon_1 e^{-\epsilon_1\beta}\right)$$

$$U = N\frac{\epsilon_0 e^{-\epsilon_0\beta} + \epsilon_1 e^{-\epsilon_1\beta}}{e^{-\epsilon_0\beta} + e^{-\epsilon_1\beta}} \tag{3}$$

Now, divide both sides of (3) by N:

$$\frac{U}{N} = \frac{\epsilon_0 e^{-\epsilon_0\beta} + \epsilon_1 e^{-\epsilon_1\beta}}{e^{-\epsilon_0\beta} + e^{-\epsilon_1\beta}} \quad \left(multiply\ by\ \frac{e^{\epsilon_0\beta}}{e^{\epsilon_0\beta}}\right)$$
$$u = \frac{\epsilon_0 e^{-\epsilon_0\beta} + \epsilon_1 e^{-\epsilon_1\beta}}{e^{-\epsilon_0\beta} + e^{-\epsilon_1\beta}}\frac{e^{\epsilon_0\beta}}{e^{\epsilon_0\beta}}$$
$$u = \frac{\epsilon_0 + \epsilon_1 e^{\epsilon_0\beta-\epsilon_1\beta}}{1 + e^{\epsilon_0\beta-\epsilon_1\beta}} \quad \left(use\ def.of\ \alpha = \frac{\epsilon_0 - \epsilon_1}{kT} = (\epsilon_0 - \epsilon_1)\beta\ \right)$$

$$\rightarrow\ u = \frac{\epsilon_0 + \epsilon_1 e^{\alpha}}{1 + e^{\alpha}}$$

b) Heat capacity per particle is defined as:

$$\frac{C_V}{N} = \frac{1}{N}\frac{\partial U}{\partial T}$$
$$= \frac{\partial u}{\partial T}$$
$$= \frac{\partial\alpha}{\partial T}\frac{\partial u}{\partial\alpha}$$

$$\frac{C_V}{N} = \frac{\partial}{\partial T}\left(\frac{(\epsilon_0 - \epsilon_1)}{k_B T}\right)\frac{\partial}{\partial\alpha}\left(\frac{\epsilon_0 + \epsilon_1 e^{\alpha}}{1 + e^{\alpha}}\right) \tag{4}$$

Let's do them separately:

$$\frac{\partial}{\partial T}\left(\frac{(\epsilon_0-\epsilon_1)}{k_B T}\right)=\frac{(\epsilon_0-\epsilon_1)}{k_B}\frac{\partial}{\partial T}\frac{1}{T}$$
$$=-\frac{(\epsilon_0-\epsilon_1)}{k_B}\frac{1}{T^2}$$

$$\frac{\partial}{\partial T}\left(\frac{(\epsilon_0-\epsilon_1)}{k_B T}\right)=-\frac{\alpha}{T} \qquad (5)$$

As for the other partial derivative in Eq. (4):

$$\frac{\partial}{\partial \alpha}\left(\frac{\epsilon_0+\epsilon_1 e^{\alpha}}{1+e^{\alpha}}\right)=\frac{(1+e^{\alpha})\frac{\partial}{\partial \alpha}(\epsilon_0+\epsilon_1 e^{\alpha})-(\epsilon_0+\epsilon_1 e^{\alpha})\frac{\partial}{\partial \alpha}(1+e^{\alpha})}{(1+e^{\alpha})^2}$$
$$=\frac{(1+e^{\alpha})\epsilon_1 e^{\alpha}-(\epsilon_0+\epsilon_1 e^{\alpha})e^{\alpha}}{(1+e^{\alpha})^2}$$
$$=\frac{\epsilon_1 e^{\alpha}+\ \epsilon_1 e^{2\alpha}-\epsilon_0 e^{\alpha}-\ \epsilon_1 e^{2\alpha}}{(1+e^{\alpha})^2}$$
$$=\frac{\epsilon_1 e^{\alpha}-\epsilon_0 e^{\alpha}}{(1+e^{\alpha})^2}$$

$$\frac{\partial}{\partial \alpha}\left(\frac{\epsilon_0+\epsilon_1 e^{\alpha}}{1+e^{\alpha}}\right)=\frac{(\epsilon_1-\epsilon_0)e^{\alpha}}{(1+e^{\alpha})^2} \qquad (6)$$

$$\frac{C_V}{N}=-\frac{\alpha}{T}\frac{(\epsilon_1-\epsilon_0)e^{\alpha}}{(1+e^{\alpha})^2}$$
$$=\frac{\alpha}{T}\frac{(\epsilon_0-\epsilon_1)e^{\alpha}}{(1+e^{\alpha})^2}$$

$$\rightarrow\ \frac{C_V}{N}=k_B\frac{\alpha^2 e^{\alpha}}{(1+e^{\alpha})^2} \qquad (7)$$

c) As $T \rightarrow 0$ we have $\alpha \rightarrow -\infty$. Looking at the numerator and denominator in the RHS of Eq. (7),

$$\alpha^2 e^{\alpha} \rightarrow 0$$
$$(1+e^{\alpha})^2 \rightarrow 1$$

The first asymptotic follows from the fact that an exponential dominates over the polynomial term α^2 (you can use l'Hopital's rule, formally). Thus,

$$\frac{C_V}{N} \to 0 \quad as \;\; T \to 0$$

As $T \to \infty$ we have $\alpha \to 0$. Since:

$$\frac{e^{\alpha}}{(1+e^{\alpha})^2} \to \frac{1}{4} \quad as \; \alpha \to 0$$

Then,

$$\frac{C_V}{N} \to \frac{k_B \alpha^2}{4}$$