11. (Statistical Mechanics)

The only degrees of freedom we retain in an approximate description of an assembly of N weakly interacting particles are their internal energy levels, which we assume to be non-degenerate and taking the three possible values $-\varepsilon$, 0, ε with $\varepsilon > 0$. The system is in equilibrium contact with a heat bath at temperature T. Assume Boltzmann statistics. Evaluate the following quantities for the system,

(a) the entropy at zero temperature;

(b) the maximal possible entropy;

(c) the minimal possible energy;

(d) the partition function;

(e) the average energy

(f) the value of $\int_0^\infty dT \frac{C(T)}{T}$ where $C(T)$ is the specific heat function.

Solution: *Solution by Jonah Hyman (jthyman@g.ucla.edu)*

We assume that the N particles are distinguishable.

(a) At zero temperature, the system is in the ground state. This system has only one ground state (the state in which all particles have internal energy $-\varepsilon$). A system that can only be in one state has zero entropy. That's because the entropy S is given by $S = k \ln \Omega$, where Ω is the number of accessible states. Therefore, the entropy at zero temperature is zero.

This is a statement of one form of the third law of thermodynamics. We can also derive the entropy at zero temperature from the partition function, which we will do at the end of the problem.

(b) As the temperature of the heat bath T increases, the thermal energy exchanged between the heat bath and the system becomes much larger than the differences between the internal energy levels. Therefore, as $T \to \infty$, each particle becomes equally likely to be in any of its three internal energy levels. This is the maximum number of equally likely states available to each particle, so it also corresponds to the maximum possible entropy. The entropy per particle is then given by

$$S_1 = k \ln \Omega = k \ln 3 \tag{357}$$

Since there are N independent and distinguishable particles, and since the entropy is an extensive quantity, the total entropy of the system is equal to the entropy per particle times N:

$$S = NS_1 = Nk \ln 3 \tag{358}$$

We can also derive the maximum entropy from the partition function, which we will do at the end of this problem.

(c) This may seem like a trick question, but it isn't. The minimum internal energy of each particle is $-\varepsilon$. There are N particles, so the minimum energy of the system is $-N\varepsilon$.

(d) The definition of the partition function is

$$Z \equiv \sum_{\text{microstates } r} e^{-\beta E_r} \quad \text{where } E_r \text{ is the energy of the } r\text{th microstate and } \beta \equiv \frac{1}{kT} \tag{359}$$

For this problem, the partition function for a single particle is

$$Z_1 = e^{-\beta(-\varepsilon)} + e^{-\beta(0)} + e^{-\beta(\varepsilon)} = 1 + e^{\beta\varepsilon} + e^{-\beta\varepsilon} \tag{360}$$

For N distinguishable and independent particles, each with identical partition function Z_1, the partition function of the entire system is $(Z_1)^N$. Therefore, for this problem, the partition function for the system is

$$Z = (Z_1)^N = \left(1 + e^{\beta\varepsilon} + e^{-\beta\varepsilon}\right)^N \tag{361}$$

(e) Given the partition function, we can find the average energy using the formula

$$E = \frac{1}{Z} \sum_{\text{microstates } r} E_r e^{-\beta E_r} \tag{362}$$

In this problem, we can use the formula to calculate the energy per particle:

$$\begin{aligned} E_1 &= \frac{1}{Z_1} \left((-\varepsilon)e^{-\beta(-\varepsilon)} + (0)e^{-\beta(0)} + (\varepsilon)e^{-\beta\varepsilon}\right) \\ &= \frac{1}{Z_1} \left(\varepsilon e^{-\beta\varepsilon} - \varepsilon e^{\beta\varepsilon}\right) \\ &= \frac{\varepsilon \left(e^{-\beta\varepsilon} - e^{\beta\varepsilon}\right)}{1 + e^{\beta\varepsilon} + e^{-\beta\varepsilon}} \end{aligned} \tag{363}$$

Since there are N independent and distinguishable particles, and since the energy is an extensive quantity, the total energy of the system is equal to the energy per particle times N:

$$E = NE_1 = N\varepsilon \frac{e^{-\beta\varepsilon} - e^{\beta\varepsilon}}{1 + e^{\beta\varepsilon} + e^{-\beta\varepsilon}} \quad \text{where } \beta = \frac{1}{kT} \tag{364}$$

Alternatively, we can calculate the energy using the formula

$$E = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial(\ln Z)}{\partial \beta} \tag{365}$$

Applying this formula to the partition function (361), we get

$$\begin{aligned} E &= -\frac{1}{Z}\frac{\partial Z}{\partial \beta} \\ &= -\frac{1}{\left(1 + e^{\beta\varepsilon} + e^{-\beta\varepsilon}\right)^N} \frac{\partial}{\partial \beta}\left(1 + e^{\beta\varepsilon} + e^{-\beta\varepsilon}\right)^N \\ &= -\frac{1}{\left(1 + e^{\beta\varepsilon} + e^{-\beta\varepsilon}\right)^N} \left[N\left(1 + e^{\beta\varepsilon} + e^{-\beta\varepsilon}\right)^{N-1}\left(\varepsilon e^{\beta\varepsilon} - \varepsilon e^{-\beta\varepsilon}\right)\right] \\ &= -\frac{N\left(\varepsilon e^{\beta\varepsilon} - \varepsilon e^{-\beta\varepsilon}\right)}{1 + e^{\beta\varepsilon} + e^{-\beta\varepsilon}} \\ E &= N\varepsilon \frac{e^{-\beta\varepsilon} - e^{\beta\varepsilon}}{1 + e^{\beta\varepsilon} + e^{-\beta\varepsilon}} \quad \text{where } \beta = \frac{1}{kT} \end{aligned} \tag{366}$$

(f) The specific heat is defined as

$$C(T) = T\frac{dS}{dT} \tag{367}$$

(Sometimes, we define the specific heat holding some quantity, like volume or pressure, constant. In this case, we are assuming the system cannot expand in volume, since the only degrees of freedom we are interested in is the internal energy levels. Therefore, we don't need to worry about holding anything else constant here.) Therefore,

$$dT\frac{C(T)}{T} = dT\frac{dS}{dT} = dS \tag{368}$$

and so

$$\int_0^\infty dT\frac{C(T)}{T} = \int_0^\infty dS = S(T=\infty) - S(T=0) \tag{369}$$

From part (a), we know that $S(T=0) = 0$. From part (b), we know that $S(T=\infty) = Nk\ln 3$. Therefore,

$$\int_0^\infty dT\frac{C(T)}{T} = Nk\ln 3 - 0 = Nk\ln 3 \tag{370}$$

To check parts (a) and (b), we can use the partition function to find the entropy, via the energy and the free energy. The free energy is given by

$$F = -kT\ln Z = -\frac{1}{\beta}\ln Z \tag{371}$$

Using the partition function (361), we can calculate that

$$F = -kT\ln\left(1 + e^{\beta\varepsilon} + e^{-\beta\varepsilon}\right)^N = -NkT\ln\left(1 + e^{\beta\varepsilon} + e^{-\beta\varepsilon}\right) \tag{372}$$

The free energy is defined as $F = E - ST$, so the entropy is defined by

$$S = \frac{1}{T}(E - F) \tag{373}$$

Plugging in our part (e) expression for E (366), as well as our new expression for F (372), we get an expression for the entropy

$$\begin{aligned} S &= \frac{1}{T}\left(N\varepsilon\frac{e^{-\beta\varepsilon} - e^{\beta\varepsilon}}{1 + e^{\beta\varepsilon} + e^{-\beta\varepsilon}} + NkT\ln\left(1 + e^{\beta\varepsilon} + e^{-\beta\varepsilon}\right)\right) \\ &= \frac{N\varepsilon}{T}\frac{e^{-\beta\varepsilon} - e^{\beta\varepsilon}}{1 + e^{\beta\varepsilon} + e^{-\beta\varepsilon}} + Nk\ln\left(1 + e^{\beta\varepsilon} + e^{-\beta\varepsilon}\right) \end{aligned} \tag{374}$$

The entropy at $T = 0$, i.e, $\beta = \infty$, can be calculated from this equation. First, drop all terms of order 1 or $e^{-\beta\varepsilon}$, since they are subleading compared to $e^{\beta\varepsilon}$:

$$S(T = 0) = \frac{N\varepsilon}{T}\frac{-e^{\beta\varepsilon}}{e^{\beta\varepsilon}} + Nk\ln\left(e^{\beta\varepsilon}\right)\Big|_{T\to 0}$$

Then, simplify to get

$$\begin{aligned} S(T = 0) &= -\frac{N\varepsilon}{T} + Nk\beta\varepsilon\Big|_{T=0} \\ &= -\frac{N\varepsilon}{T} + \frac{N\varepsilon}{T} \\ &= 0 \end{aligned} \tag{375}$$

which matches part (a).

We can also calculate the entropy as $T \to \infty$, i.e., $\beta \to 0$, using this general formula:

$$\begin{aligned} S(T \to \infty) &= S(\beta \to 0) \\ &= \frac{N\varepsilon}{T}\frac{e^{-\beta\varepsilon} - e^{\beta\varepsilon}}{1 + e^{\beta\varepsilon} + e^{-\beta\varepsilon}} + Nk\ln\left(1 + e^{\beta\varepsilon} + e^{-\beta\varepsilon}\right)\Big|_{T\to\infty,\beta\to 0} \\ &= \frac{N\varepsilon}{T}\frac{e^{-\beta\varepsilon} - e^{\beta\varepsilon}}{1 + e^{\beta\varepsilon} + e^{-\beta\varepsilon}}\Big|_{T\to\infty,\beta\to 0} + Nk\ln 3 \\ &= Nk\ln 3 \end{aligned} \tag{376}$$

This matches part (b) (although it doesn't establish that this is the maximum entropy).