Solution for the Homework 1

Problem 6.5: Imagine a particle that can be in only three states, with energies -0.05eV, 0 and 0.05eV. This particle is in equilibrium with a reservoir at 300K.

(a) Calculate the partition function for this particle.

Solution:

$$Z_1 = \sum_s e^{-E(s)/kT} = e^{+0.05/300k} + 1 + e^{-0.05/300k} \tag{1}$$

(b) Calculate the probability for this particle to be in each of the three states.

Solution:

$$P(s) = e^{-E(s)/kT}/Z_1 = \begin{cases} e^{+0.05/300k}/Z_1 & \text{if the energy of state is -0.05eV} \\ 1/Z_1 & \text{if the energy of state is 0} \\ e^{-0.05/300k}/Z_1 & \text{if the energy of state is +0.05eV} \end{cases} \tag{2}$$

(c) Because the zero point for measuring energies is arbitrary, we could just as well say that the energies of the three states are 0, +0.05eV, and +0.10eV, respectively. Repeat parts (a) and (b) using these numbers. Explain what changes and what doesn't.

Solution:

$$Z_2 = \sum_s e^{-E(s)/kT} = 1 + e^{-0.05/300k} + e^{-0.10/300k} \tag{3}$$

$$= e^{-0.05/300k}\left(e^{+0.05/300k} + 1 + e^{-0.05/300k}\right) = Z_1 e^{-0.05/300k} \tag{4}$$

Similarly to the above,

$$P(s) = e^{-E(s)/kT}/Z_2 = \begin{cases} 1/Z_2 & \text{if the energy of state is 0} \\ e^{-0.05/300k}/Z_2 & \text{if the energy of state is +0.05eV} \\ e^{-0.10/300k}/Z_2 & \text{if the energy of state is +0.10eV} \end{cases} \tag{5}$$

$$= \begin{cases} e^{+0.05/300k}/Z_1 & \text{if the energy of state is 0} \\ 1/Z_1 & \text{if the energy of state is +0.05eV} \\ e^{-0.05/300k}/Z_1 & \text{if the energy of state is +0.10eV} \end{cases} \tag{6}$$

The energies of the three states just moved with same differences of energies. It changes the partition function, but the probability for some particle to be in each of the three states are not changed.

Problem 6.10: A water molecule can vibrate in various ways, but the easiest type of vibration to excite is the "flexing" mode in which the hydrogen atoms move toward and away from each other nut the HO bonds do net stretch. The oscillations of this mode are approximately harmonic, with a frequency of 4.8×10^{13} Hz. As for any quantum harmonic oscillator, the energy levels are $\frac{1}{2}hf$, $\frac{3}{2}hf$, $\frac{5}{2}hf$, and so on. None of these levels are degenerate.

(a) Calculate the probability of a water molecule being in its flexing ground state and in each of the first two exited states, assuming that it is in equilibrium with a reservoir (say the atmosphere) at 300 K. (Hint: Calculate Z by adding up the first few Boltzmann factors, until the rest are negligible.)

Solution:

$$Z = \sum_s e^{-E(s)/kT} = e^{-hf/2kT} + e^{-3hf/2kT} + e^{-5hf/2kT} + \cdots \approx 2.15166 \times 10^{-2} \tag{7}$$

Using this partition function, we can calculate some particle to be in the first three energy states.

$$\begin{aligned} P(s=0) &= e^{-E(s=0)/kT}/Z = e^{-hf/2kT}/Z \approx 9.99537 \times 10^{-1} & (8) \\ P(s=1) &= e^{-E(s=1)/kT}/Z = e^{-3hf/2kT}/Z \approx 4.62323 \times 10^{-4} & (9) \\ P(s=2) &= e^{-E(s=2)/kT}/Z = e^{-5hf/2kT}/Z \approx 2.13842 \times 10^{-7} & (10) \end{aligned}$$

(b) Repeat the calculation for a water molecule in equilibrium with a reservoir at 700 K (perhaps in a steam turbine).

Solution:

$$Z \approx 2.00383 \times 10^{-1} \Rightarrow \begin{cases} P(s=0) \approx 9.6278 \times 10^{-1} \\ P(s=1) \approx 3.58347 \times 10^{-2} \\ P(s=2) \approx 1.33377 \times 10^{-3} \end{cases} \tag{11}$$

Problem 6.12: Cold interstellar molecular clouds often contain the molecule cyanogen (CN), whose first rotational exited states have an energy of 4.7×10^{-4}eV (above the ground state). There are actually three such excited states, all with the same energy. In 1941, studies of the absorption spectrum of starlight that passes through these molecular clouds showed that for every ten CN molecules that are in the ground state, approximately three others are in the three first exited states (that is, an average of one in each of three states). To account for this date, astronomers suggested that the molecules might be in thermal equilibrium with some "reservoir" with a well-defined temperature. What is that temperature?

Solution: From the observation data, we know the ratio of probabilities of ground state and first excited states. There are three first excited states and so we need to divide the ratio by three. Then, using the given energy difference, we can get the result.

$$\frac{P(s=1)}{P(s=0)} = e^{-(E(s=1)-E(s=0))/kT} = e^{-4.7\times10^{-4}eV/kT} \equiv \frac{1}{10} \tag{12}$$

$$\Rightarrow \quad T = \frac{4.7 \times 10^{-4}}{\ln(10) \times k} \approx 2.3687K \tag{13}$$

Problem 6.18: Prove that, for any system in equilibrium with a reservoir at temperature T, the average value of E^2 is

$$\overline{E^2} = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2}. \tag{14}$$

Then use this result and the results of the previous two problems to derive a formula for σ_E in terms of the heat capacity, $C = \partial\overline{E}/\partial T$. You should find

$$\sigma_E = kT\sqrt{C/k} \tag{15}$$

Solution: Consider the partition function $Z = \sum_s e^{-\beta E(s)}$ and let us calculate the right-hand side of given equation.

$$\frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} = \frac{1}{Z}\frac{\partial}{\partial \beta}\left(\sum_s [-E(s)]e^{-\beta E(s)}\right) = \frac{1}{Z}\left(\sum_s E(s)^2 e^{-\beta E(s)}\right) \equiv \overline{E^2} \tag{16}$$

Similarly, we can get the average value of arbitrary power of E by differentiating the partition function several times. Use this result and the average value of E, we can find the expressions of standard deviation of E in terms of heat capacity.

$$\sigma_E^2 = \overline{E^2} - \overline{E}^2 = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} - \frac{1}{Z^2}\left(\frac{\partial Z}{\partial \beta}\right)^2 = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} + \frac{\partial}{\partial \beta}\left(\frac{1}{Z}\right)\frac{\partial Z}{\partial \beta} \tag{17}$$

$$= \frac{\partial}{\partial \beta}\left(\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right) = -\frac{\partial \overline{E}}{\partial \beta} = -\frac{\partial T}{\partial \beta}\frac{\partial \overline{E}}{\partial T} = kT^2 C \tag{18}$$

So, take square root to get the given result.

$$\sigma_E = kT\sqrt{\frac{C}{k}} \tag{19}$$

Problem 6.20: This problem concerns a collection of N identical harmonic oscillators (perhaps an Einstein solid or the internal vibrations of gas molecules) at temperature T. As in Section 2.2, the allowed energies of each oscillator are 0, hf, $2hf$, and so on.

(a) Prove by long division that

$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + \cdots. \tag{20}$$

For what values of x does this series have a finite sum?

Solution: Divide 1 by $(1-x)$, then you can easily get the result. But the result is infinite series. We want to make this series converge, so the magnitude of x should less than 1, i.e. $|x| < 1$.

(b) Evaluate the partition function for a single harmonic oscillator. Use the result of part (a) to simplify your answer as much as possible.

Solution:

$$Z = \sum_s e^{-\beta E(s)} = 1 + e^{-\beta hf} + e^{-2\beta hf} + \cdots = \frac{1}{1-e^{-\beta hf}} \tag{21}$$

(c) Use formula 6.25 to find an expression for the average energy of a single oscillator at temperature T. Simplify your answer as much as possible.

Solution:

$$\overline{E} \;=\; -\frac{1}{Z}\frac{\partial Z}{\partial \beta} \;=\; -\frac{1}{Z}\frac{\partial}{\partial \beta}\left(\frac{1}{1-e^{-\beta hf}}\right) \;=\; hf\frac{e^{-\beta hf}}{1-e^{-\beta hf}} \;=\; \frac{hf}{e^{\beta hf}-1} \tag{22}$$

(d) What is the total energy of the system of N oscillators at temperature T? Your result should agree with what you found in Problem 3.25.

Solution: Let the total energy is U. Then,

$$U \;=\; N\overline{E} \;=\; \frac{Nhf}{e^{\beta hf}-1} \tag{23}$$

(e) If you haven't already done so in Problem 3.25, compute the heat capacity of this system and check that it has the expected limits as T $\rightarrow$ 0 and T $\rightarrow \infty$.

Solution: Take the derivative of temperature to the total energy.

$$C \;=\; \frac{\partial U}{\partial T} \;=\; \frac{\partial \beta}{\partial T}\frac{\partial}{\partial \beta}\left(\frac{hf}{e^{\beta hf}-1}\right) \;=\; \frac{-1}{kT^2}\frac{-Nh^2f^2e^{\beta hf}}{(e^{\beta hf}-1)^2} \;=\; \frac{Nh^2f^2}{kT^2}\frac{e^{\beta hf}}{(e^{\beta hf}-1)^2} \tag{24}$$

Now, take a limit for the temperature.

$$T \;\rightarrow\; 0\;, \qquad \frac{Nh^2f^2}{kT^2}\frac{e^{\beta hf}}{(e^{\beta hf}-1)^2} \;\approx\; \frac{Nh^2f^2}{kT^2}\frac{1}{e^{hf/kT}} \;\rightarrow\; 0 \tag{25}$$

$$T \;\rightarrow\; \infty\;, \qquad \frac{Nh^2f^2}{kT^2}\frac{e^{\beta hf}}{(e^{\beta hf}-1)^2} \;\approx\; \frac{Nh^2f^2}{kT^2}\frac{1+hf/kT}{(1+hf/kT-1)^2} \;\rightarrow\; Nk \tag{26}$$

Problem 6.22: In most paramagnetic materials, the individual magnetic particles have more than two independent states (orientations). The number of independent states depends on the particle's angular momentum "quantum number" j, which must be a multiple of 1/2. For $j = 1/2$ there are just two independent states, as discussed in the text above and in Section 3.3. More generally, the allowed values of the z component of a particle's magnetic moment are

$$\mu_z \;=\; -j\delta_\mu, (-j+1)\delta_\mu, \cdots, (j-1)\delta_\mu, j\delta_\mu, \tag{27}$$

where δ_μ is a constant, equal to the difference in μ_z between one state and the next. (When the particle's angular momentum comes entirely from electron spins, δ_μ equals twice the Bohr magneton. When orbital angular momentum also contributes, δ_μ is somewhat different but comparable in magnitude. For an atomic nucleus, δ_μ is roughly a thousand times smaller.) Thus the number of states is $2j+1$. In the presence of a magnetic field B pointing in the z direction, the particle's magnetic energy (neglecting interactions between dipoles) is $-\mu_z B$.

(a) Prove the following identity for the sum of a finite geometric series:

$$1 + x + x^2 + \cdots + x^n \;=\; \frac{1-x^{n+1}}{1-x}. \tag{28}$$

(Hint: Either prove this formula by induction on n, or write the series as a difference between two infinite series and use the result of Problem 6.20(a).)

Solution: For $n = 1$, given identity is simply true.

$$1 + x = \frac{1 - x^2}{1 - x} \tag{29}$$

Let us suppose that the identity is satisfied for $n = k - 1$ case. Then,

$$1 + x + \cdots + x^{k-1} + x^k = \frac{1 - x^k}{1 - x} + x^k = \frac{1 - \cancel{x^k}}{1 - x} + \frac{\cancel{x^k} - x^{k+1}}{1 - x} = \frac{1 - x^{k+1}}{1 - x} \tag{30}$$

By the mathematical induction, the relation is true.

(b) Show that the partition function of a single magnetic particle is

$$Z = \frac{\sinh\left[b\left(j + 1/2\right)\right]}{\sinh b/2}, \tag{31}$$

where $b = \beta\delta_\mu B$.

Solution: The energy states are discrete because of the magnetic moments of particles are discrete.

$$Z = \sum_s e^{\beta\mu_z B} = \sum_{i=-j}^{j} e^{i\beta\delta_\mu B} \tag{32}$$

$$= e^{-jb} + e^{(-j+1)b} + \cdots + e^{jb} = e^{-jb}\left(1 + e^b + \cdots + e^{2jb}\right) \tag{33}$$

$$= \frac{e^{-jb} - e^{(j+1)b}}{1 - e^b} = \frac{e^{-(j+1/2)} - e^{(j+1/2)b}}{e^{-b/2} - e^{b/2}} = \frac{\sinh\left[b\left(j + 1/2\right)\right]}{\sinh b/2} \tag{34}$$

(c) Show that the total magnetization of a system of N such particles is

$$M = N\delta_\mu\left[\left(j + \frac{1}{2}\right)\coth\left[b\left(j + \frac{1}{2}\right)\right] - \frac{1}{2}\coth\frac{b}{2}\right], \tag{35}$$

where $\coth x$ is the hyperbolic cotangent, equal to $\cosh x/\sinh x$. Plot the quantity $M/N\delta_\mu$ vs. b, for a few different values of j.

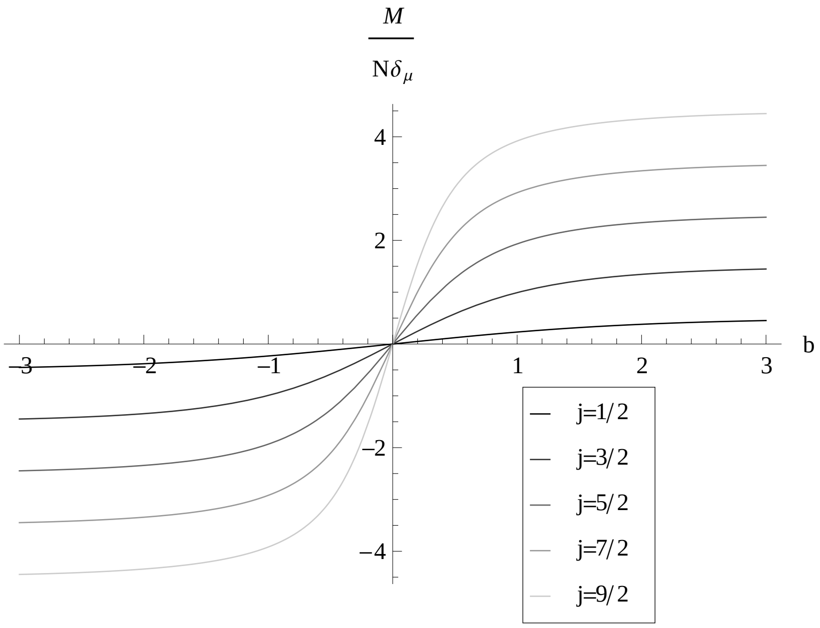
Solution: Using the similar trick with the average of energy,

$$M = N\overline{\mu_z} = \frac{N}{BZ}\frac{\partial Z}{\partial\beta} = \frac{N}{BZ}\frac{\partial}{\partial\beta}\left(\frac{\sinh\left[b\left(j + 1/2\right)\right]}{\sinh b/2}\right) \tag{36}$$

$$= \frac{N}{BZ}\frac{\partial b}{\partial\beta}\frac{\partial}{\partial b}\left(\frac{\sinh\left[b\left(j + 1/2\right)\right]}{\sinh b/2}\right) \tag{37}$$

$$= \frac{N}{\cancel{B}Z}\delta_\mu\cancel{B}\left[\left(j + \frac{1}{2}\right)\frac{\cosh\left[b\left(j + 1/2\right)\right]}{\sinh b/2} - \left(\frac{1}{2}\coth\frac{b}{2}\right)\frac{\sinh\left[b\left(j + 1/2\right)\right]}{\sinh b/2}\right] \tag{38}$$

$$= N\delta_\mu\left[\left(j + \frac{1}{2}\right)\coth\left[b\left(j + \frac{1}{2}\right)\right] - \frac{1}{2}\coth\frac{b}{2}\right] \tag{39}$$



(d) Show that the magnetization has the expected behavior as T→ 0.

Solution: If T→ 0, then $b \to \infty$ and so $\coth b \to 1$.

$$T \to 0, \qquad M = N\delta_\mu \left[\left(j + \frac{1}{2} \right) \coth \left[b \left(j + \frac{1}{2} \right) \right] - \frac{1}{2} \coth \frac{b}{2} \right] \tag{40}$$

$$\approx N\delta_\mu \left[j + \frac{1}{2} - \frac{1}{2} \right] = jN\delta_\mu \tag{41}$$

(e) Show that the magnetization is proportional to 1/T (Curie's law) in the limit T→ ∞. (Hint: First show that $\coth x \approx 1/x + x/3$ when $x \ll 1$.)

Solution: Show the hint first.

$$x \ll 1, \qquad \coth x = \frac{e^x + e^{-x}}{e^x - e^{-x}} \tag{42}$$

$$= \frac{(1 + x + x^2/2) + (1 + x + x^2/2)}{(1 + x + x^2/2 + x^3/6) - (1 + x + x^2/2 + x^3/6)} \tag{43}$$

$$= \frac{2 + x^2}{2x + x^3/3} = \frac{2 + x^2}{2x} \left(1 + \frac{x^2}{6} \right)^{-1} \tag{44}$$

$$\approx \left(\frac{1}{x} + \frac{x}{2} \right) \left(1 - \frac{x^2}{6} \right) \tag{45}$$

$$\approx \frac{1}{x} + \frac{x}{2} - \frac{x}{6} = \frac{1}{x} + \frac{x}{3} \tag{46}$$

Since T$\to\infty$, $b\to 0$ and so $\coth b$ follows the hint. So,

$$T\to\infty, \qquad M = N\delta_\mu\left[\left(j+\frac{1}{2}\right)\coth\left[b\left(j+\frac{1}{2}\right)\right]-\frac{1}{2}\coth\frac{b}{2}\right] \tag{47}$$

$$\approx N\delta_\mu\left[\left(j+\frac{1}{2}\right)\left(\frac{1}{b(j+1/2)}+\frac{b}{3}\left(j+\frac{1}{2}\right)\right)-\frac{1}{2}\left(\frac{2}{b}+\frac{b}{6}\right)\right] \tag{48}$$

$$= N\delta_\mu b\left[\frac{1}{3}\left(j+\frac{1}{2}\right)^2-\frac{1}{12}\right] \tag{49}$$

Result is proportional to b and so the magnetization is proportional to 1/T in the limit T$\to\infty$.

(f) Show that for $j=1/2$, the result of part (c) reduces to the formula derived in the text for a two-state paramagnet.

Solution: Let $j=1/2$. Then,

$$M = N\delta_\mu\left[\coth b-\frac{1}{2}\coth\frac{b}{2}\right] \tag{50}$$

$$= N\delta_\mu\left[\frac{e^b+e^{-b}}{e^b-e^{-b}}-\frac{e^{b/2}+e^{-b/2}}{2(e^{b/2}-e^{-b/2})}\right] \tag{51}$$

$$= N\delta_\mu\left[\frac{2(e^b+e^{-b})-(e^{b/2}+e^{-b/2})^2}{2(e^{b/2}+e^{-b/2})(e^{b/2}-e^{-b/2})}\right] \tag{52}$$

$$= N\delta_\mu\left[\frac{(e^{b/2}-e^{-b/2})^2}{2(e^{b/2}+e^{-b/2})(e^{b/2}-e^{-b/2})}\right] = N\delta_\mu\left(\frac{1}{2}\tanh\frac{b}{2}\right) \tag{53}$$

This result exactly follows the formula derived in the text for a two-state paramagnet.