Solutions

Chapter 6

Problem 6.5

Part a

Let $x = .05/kT$. Then,

$$Z = e^x + e^0 + e^{-x} = 1 + 2\cosh x = 1 + 2\cosh\left(\frac{.05\text{eV}}{8.617\times 10^{-5}\times 300}\right) = 8.063. \tag{1}$$

Part b

For the state of energy -0.05 eV, the probability is,

$$P_- = \frac{e^x}{Z} = \frac{6.918}{8.063} = 0.858. \tag{2}$$

For the state of energy 0 eV, the probability is,

$$P_0 = \frac{e^0}{Z} = \frac{1}{8.063} = 0.124. \tag{3}$$

For the state of energy 0.05 eV, the probability is,

$$P_+ = \frac{e^{-x}}{Z} = \frac{0.1445}{8.063} = 0.0179. \tag{4}$$

Part c

$$Z = e^0 + e^{-x} + e^{-2x} = e^{-x}(e^x + 1 + e^{-x}) = e^{-x}(1 + 2\cosh x) = 1.165. \tag{5}$$

For the state of energy 0 eV, the probability is,

$$P_0 = \frac{e^0}{Z} = \frac{1}{1.165} = 0.858. \tag{6}$$

For the state of energy .05 eV, the probability is,

$$P_+ = \frac{e^{-x}}{Z} = 0.124. \tag{7}$$

For the state of energy 0.10 eV, the probability is,

$$P_{++} = \frac{e^{-2x}}{Z} = 0.0179. \tag{8}$$

Problem 6.11

Let

$$a = \mu B/2 = 3.24 \times 10^{-8} \text{ eV}. \tag{9}$$

Then the four possible energies are,

$$E_{-3} = 3a, \quad E_{-1} = a, \quad E_1 = -a, \quad E_3 = -3a. \tag{10}$$

The corresponding exponents ($x = E/kT$) are,

$$x_{-3} = 3b, \quad x_{-1} = b, \quad x_1 = -b, \quad x_3 = -3b. \tag{11}$$

where,

$$b = \frac{a}{kT} = 1.25 \times 10^{-6}. \tag{12}$$

b being very small, the exponents are all going to be close to 1. So, the partition function is,

$$Z = e^{-3b} + e^{-b} + e^{b} + e^{3b} = 4. \tag{13}$$

The resulting probabilities will be very close to 1/4 each[1]. Nonetheless, the lowest energy will have the highest probability. However, quickly reversing the magnetic field direction will switch the signs of the energies without changing the probabilities. Then, of course, the highest energy will have the highest probabilities. This is mathematically equivalent to switching the sign of the temperature.

Problem 6.13

Let the fraction that are neutrons be f_n and that are protons be f_p. Then, using the Boltzmann factor,

$$\frac{f_n}{f_p} = \frac{e^{-m_n c^2/kT}}{e^{-m_p c^2/kT}} = e^{-(m_n - m_p)c^2/kT} = 0.861, \quad \text{and} \quad f_n + f_p = 1, \tag{14}$$

where m_n is the neutron mass and m_p is the proton mass. Hence,

$$f_p = \frac{1}{1 + f_n/f_p} = 0.537, \quad \text{and} \quad f_n = 1 - f_p = 0.463. \tag{15}$$

Problem 6.16

$$Z = \sum_s e^{-\beta E(s)}. \tag{16}$$

[1]For a more precise estimate one may use the first order expansion: $e^x = 1 + x$.

Hence,

$$\frac{\partial Z}{\partial \beta} = -\sum_s E(s) e^{-\beta E(s)}. \tag{17}$$

Then, from equation 6.17 of the textbook,

$$\overline{E} = \frac{1}{Z} \sum_s E(s) e^{-\beta E(s)} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta}. \tag{18}$$

Problem 6.18

$$Z = \sum_s e^{-\beta E(s)}. \tag{19}$$

Hence,

$$\frac{\partial^2 Z}{\partial \beta^2} = \sum_s E^2(s) e^{-\beta E(s)}. \tag{20}$$

Then, from the definition of an average,

$$\overline{E^2} = \frac{1}{Z} \sum_s E^2(s) e^{-\beta E(s)} = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2}. \tag{21}$$

Problem 6.20

Part a

$$\frac{1}{1-x} = \frac{1-x}{1-x} + \frac{x}{1-x} = 1 + \frac{x}{1-x} = 1 + x\frac{1}{1-x} = 1 + x\left(1 + \frac{x}{1-x}\right) = \cdots. \tag{22}$$

Repeating this process will give,

$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + \cdots. \tag{23}$$

This series will converge iff $|x| < 1$.

Part b

The possible energies of a harmonic oscillator can be written as,

$$E(s) = (s + 1/2)h\nu, \quad s = 0, 1, 2, \ldots \tag{24}$$

where h is Planck's constant and ν is the classical natural frequency of the oscillator. We can use this form of the energy as is to compute the partition function Z. However, it is mathematically convenient to notice that the $h\nu/2$ part is never accessed and hence, the zero point of energy can be shifted to get the following form of the energy.

$$E(s) = sh\nu, \quad s = 0, 1, 2, \ldots. \tag{25}$$

Then,

$$Z = \sum_{s=0}^{\infty} e^{-\beta E(s)} = \sum_{s=0}^{\infty} e^{-s\beta h\nu} = \sum_{s=0}^{\infty} x^s. \tag{26}$$

where,

$$x = e^{-\beta h\nu}. \tag{27}$$

Hence, using the result of the last part,

$$Z = \frac{1}{1-x} = \frac{1}{1-e^{-\beta h\nu}}. \tag{28}$$

Part c

$$\overline{E} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -(1-e^{-\beta h\nu})\left(\frac{-h\nu e^{-\beta h\nu}}{(1-e^{-\beta h\nu})^2}\right) = \left(\frac{h\nu e^{-\beta h\nu}}{1-e^{-\beta h\nu}}\right) = \left(\frac{h\nu}{e^{\beta h\nu}-1}\right). \tag{29}$$

Part d

The average energy of N oscillators would be,

$$\overline{E}_N = N\overline{E} = \left(\frac{Nh\nu}{e^{\beta h\nu}-1}\right). \tag{30}$$

Part e

The heat capacity is,

$$C_V = \frac{\partial \overline{E}_N}{\partial T} = \frac{\partial \overline{E}_N}{\partial \beta}\frac{\partial \beta}{\partial T} = \left(\frac{-N(h\nu)^2 e^{\beta h\nu}}{(e^{\beta h\nu}-1)^2}\right)\frac{-1}{kT^2} = \left(\frac{Nk(\beta h\nu)^2 e^{\beta h\nu}}{(e^{\beta h\nu}-1)^2}\right). \tag{31}$$

as $\beta = 1/kT$.

As $T \to 0$, $\beta \to \infty$. Hence, the exponential becomes much larger than 1. That gives,

$$\lim_{T\to 0} C_V = \lim_{\beta\to\infty}\left(\frac{Nk(h\nu)^2\beta^2}{e^{\beta h\nu}}\right) = 0. \tag{32}$$

The last step requires a couple of applications of L'Hospital's rule.

As $T \to \infty$, $\beta \to 0$. Then the exponential can be expanded in a power series keeping up to fourth power terms to give,

$$e^{\beta h\nu} = 1 + \beta h\nu + \frac{(\beta h\nu)^2}{2} + \frac{(\beta h\nu)^3}{6} + \frac{(\beta h\nu)^4}{24} + \ldots. \quad (33)$$

Then,

$$(e^{\beta h\nu} - 1)^2 = (\beta h\nu)^2 + (\beta h\nu)^3 + \frac{7(\beta h\nu)^4}{12} + \ldots. \quad (34)$$

And,

$$\begin{aligned}
\frac{(\beta h\nu)^2 e^{\beta h\nu}}{(e^{\beta h\nu} - 1)^2} &\approx \frac{(\beta h\nu)^2 + (\beta h\nu)^3 + \frac{(\beta h\nu)^4}{2}}{(\beta h\nu)^2 + (\beta h\nu)^3 + \frac{7(\beta h\nu)^4}{12}} \\
&= \left(1 + \beta h\nu + \frac{(\beta h\nu)^2}{2}\right)\left(1 + \beta h\nu + \frac{7(\beta h\nu)^2}{12}\right)^{-1} \\
&\approx \left(1 + \beta h\nu + \frac{(\beta h\nu)^2}{2}\right)\left(1 - \beta h\nu - \frac{7(\beta h\nu)^2}{12} + (\beta h\nu)^2\right) \\
&\approx 1 - \frac{(\beta h\nu)^2}{12}. \quad (35)
\end{aligned}$$

In the above a power series expansion is used (as in part a) and then, in the final result, powers up to 2 of $\beta h\nu$ are maintained.

Now going back to C_V in this high temperature limit we get (from equation 31),

$$C_V = Nk\left(1 - \frac{(\beta h\nu)^2}{12}\right) \quad (36)$$

Problem 6.31

Using the format of equation 6.37 of the textbook for this case gives,

$$\begin{aligned}
Z &= \frac{1}{\Delta q}\int_{-\infty}^{\infty} e^{-\beta c|q|} dq \\
&= \frac{1}{\Delta q}\left(\int_{-\infty}^{0} e^{\beta cq} dq + \int_{0}^{\infty} e^{-\beta cq} dq\right) \\
&= \frac{2}{\beta c\Delta q}. \quad (37)
\end{aligned}$$

Then,

$$\overline{E} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = \frac{\beta c\Delta q}{2}\frac{2}{\beta^2 c\Delta q} = \frac{1}{\beta} = kT. \quad (38)$$

Problem 6.35

The most likely speed is at the maximum point of the function $\mathcal{D}(v)$. Hence, at that point,

$$\frac{d}{dv}(v^2 e^{-mv^2/2kT}) = 0. \tag{39}$$

This gives,

$$2v - \frac{mv^3}{kT} = 0. \tag{40}$$

This has two roots for v. As there is a minimum at $v = 0$, the maximum must be at the other root:

$$v = \sqrt{\frac{2kT}{m}}. \tag{41}$$

Problem 6.37

Using the substitution,

$$x = \sqrt{\frac{m}{2kT}}\, v, \tag{42}$$

we get,

$$\begin{aligned}
\overline{v^2} &= \int_0^\infty v^2 \mathcal{D}\, dv \\
&= \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi \int_0^\infty v^4 e^{-mv^2/2kT} dv \\
&= \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi \left(\frac{2kT}{m}\right)^{5/2} \int_0^\infty x^4 e^{-x^2} dx \\
&= \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi \left(\frac{2kT}{m}\right)^{5/2} \left(\frac{3\sqrt{\pi}}{8}\right) \\
&= \frac{3kT}{m}.
\end{aligned} \tag{43}$$