Discussion 6

Name and section: ______________________________

1. The partition function, q, can generally be written as

$$q = \sum_i \mathrm{e}^{-\beta\epsilon_i} \tag{1}$$

where ϵ_i is the energy of the state i and $\beta = 1/(k_B T)$.

(a) Derive the average energy in terms of the partition function. Starting from the expression

$$\langle\epsilon\rangle = \sum_i \epsilon_i p(\epsilon_i) = \sum_i \frac{\epsilon_i \mathrm{e}^{-\beta\epsilon_i}}{q} \tag{2}$$

where $p(\epsilon_i)$ is the probability of occupying state i. Derive

$$\langle\epsilon\rangle = -\frac{1}{q}\frac{\partial q}{\partial\beta} = -\frac{\partial \ln q}{\partial\beta} \tag{3}$$

using eqs. (1) and (2).

Solution: First, using the chain rule:

$$\frac{\partial \ln q}{\partial\beta} = \frac{1}{q}\frac{\partial q}{\partial\beta}$$

which shows part.
Next,

$$\begin{aligned}
-\frac{1}{q}\frac{\partial q}{\partial\beta} &= -\frac{1}{q}\frac{\partial}{\partial\beta}\sum_i \mathrm{e}^{-\beta\epsilon_i} \\
&= -\frac{1}{q}\sum_i -\epsilon_i \mathrm{e}^{-\beta\epsilon_i} \\
&= \sum_i \frac{\epsilon_i \mathrm{e}^{-\beta\epsilon_i}}{q}
\end{aligned}$$

(b) Now let's study the temperature dependence of the average vibrational energy of a diatomic molecule. We learned from CH351 that the vibrational motion of a diatomic molecule can be described as a one-dimensional harmonic oscillator problem. If the molecule vibrates with frequency ω, what are the quantized vibrational energy levels?

Solution:

$$\epsilon_i = \hbar\omega\left(i + \frac{1}{2}\right)$$

(c) Let's derive the vibrational partition function for this diatomic molecule. Starting with the definition of the partition function given in eq. (1), show that

$$q = \frac{\mathrm{e}^{-\beta\hbar\omega/2}}{1 - \mathrm{e}^{-\beta\hbar\omega}}. \tag{4}$$

Solution:

$$\begin{aligned}
q &= \sum_{i=0}^{\infty} \mathrm{e}^{-\beta\hbar\omega\left(i+\frac{1}{2}\right)} \\
&= \mathrm{e}^{-\beta\hbar\omega/2} \sum_{i=0}^{\infty} \mathrm{e}^{-\beta\hbar\omega i} \\
&= \mathrm{e}^{-\beta\hbar\omega/2} \frac{1}{1 - \mathrm{e}^{-\beta\hbar\omega}} \\
q &= \frac{\mathrm{e}^{-\beta\hbar\omega/2}}{1 - \mathrm{e}^{-\beta\hbar\omega}}
\end{aligned}$$

(d) Show that the average vibrational energy for the diatomic molecule is

$$\langle \epsilon \rangle = \frac{1}{2}\hbar\omega \left(\frac{1 + \mathrm{e}^{-\beta\hbar\omega}}{1 - \mathrm{e}^{-\beta\hbar\omega}} \right). \tag{5}$$

Solution:

$$\begin{aligned}
\langle \epsilon \rangle &= -\frac{\partial}{\partial \beta} \left(-\beta\hbar\omega/2 - \ln\left(1 - \mathrm{e}^{-\beta\hbar\omega}\right) \right) \\
&= \frac{\hbar\omega}{2} + \frac{\hbar\omega \mathrm{e}^{-\beta\hbar\omega}}{1 - \mathrm{e}^{-\beta\hbar\omega}} \\
&= \frac{1}{2}\hbar\omega \left(\frac{1 - \mathrm{e}^{-\beta\hbar\omega} + 2\mathrm{e}^{-\beta\hbar\omega}}{1 - \mathrm{e}^{-\beta\hbar\omega}} \right) \\
\langle \epsilon \rangle &= \frac{1}{2}\hbar\omega \left(\frac{1 + \mathrm{e}^{-\beta\hbar\omega}}{1 - \mathrm{e}^{-\beta\hbar\omega}} \right)
\end{aligned}$$

(e) In the limit as $T \to 0$, to what value does $\langle \epsilon \rangle$ converge?

Solution: As $T \to 0$, $\beta \to \infty$:

$$\lim_{\beta \to \infty} \langle \epsilon \rangle = \frac{1}{2}\hbar\omega \left(\frac{1}{1}\right)$$

as is expected because of the zero point energy for quantum harmonic oscillators.

(f) What about the limit of $T \to \infty$? Taylor series expand the exponential terms to first order in $\beta\hbar\omega$ to estimate the *classical* limit of $\langle \epsilon \rangle$.

Solution: As $T \to \infty$, $\beta \to 0$:
Taking the Maclaurin Series of $\mathrm{e}^{-\beta\hbar\omega}$,

$$\begin{aligned}
\mathrm{e}^{-\beta\hbar\omega} &\approx 1 - \beta\hbar\omega \\
\langle \epsilon \rangle &\approx \frac{1}{2}\hbar\omega \left(\frac{2 + \beta\hbar\omega}{\beta\hbar\omega}\right) \\
&= \frac{1}{\beta} + \frac{1}{2}\hbar\omega \\
\lim_{T \to \infty} \langle \epsilon \rangle &\approx k_B T
\end{aligned}$$

(g) Graphically show how $\langle \epsilon \rangle$ varies with T.

Solution:

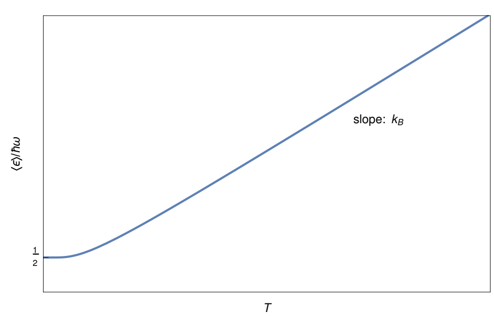

Figure 1: $\langle \epsilon \rangle$ vs. temperature for a quantum harmonic oscillator: At the low temperature limit, the expected energy approaches the zero point energy of the oscillator, but as the temperature rises, the expected energy grows linearly with slope k_B.