PHY 293F – WAVES AND PARTICLES
DEPARTMENT OF PHYSICS, UNIVERSITY OF TORONTO

PROBLEM SET #7

Marked Q1 out of a total of 10.

1. The standard deviation, σ_E, is the most common measure of the fluctuation of system away from its average value.
   a. Consider a system in equilibrium with a reservoir at a given temperature, T. Prove that the average value of E^2 is: $\overline{E^2} = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2}$.
   Calculate the second derivative of Z:

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

$$\begin{aligned}
\frac{\partial^2 Z}{\partial \beta^2} &= \frac{\partial^2}{\partial \beta^2}\left[\sum_s e^{-\beta E(s)}\right] \\
&= \sum_s \frac{\partial}{\partial \beta}\left[-E(s)e^{-\beta E(s)}\right] \\
&= \sum_s \left[E(s)\right]^2 e^{-\beta E(s)} \\
&= Z\sum_s \left[E(s)\right]^2 \frac{e^{-\beta E(s)}}{Z} \\
&= Z \cdot \overline{E^2}
\end{aligned}$$

   So,

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

   b. Using ${\sigma_E}^2 = \overline{E^2} - \left(\overline{E}\right)^2$ and the result from part (a), show that the standard deviation of this system is $\sigma_E = kT\sqrt{C/k}$, where C is the heat capacity $\partial\overline{E}/\partial T$.
   Using the result from part (a), we can calculate:

$$\begin{aligned}
\overline{E^2} &= \frac{1}{Z}\frac{\partial}{\partial \beta}\left(\frac{\partial Z}{\partial \beta}\right) \\
&= \frac{1}{Z}\frac{\partial}{\partial \beta}\left[-Z\overline{E}\right] \\
&= -\frac{1}{Z}\left[\frac{\partial \overline{E}}{\partial \beta}Z + \overline{E}\frac{\partial Z}{\partial \beta}\right] \\
&= -\frac{1}{Z}\left[\frac{\partial \overline{E}}{\partial \beta}Z + \overline{E}\left[Z\overline{E}\right]\right] \\
&= \frac{\partial \overline{E}}{\partial \beta} + \left(\overline{E}\right)^2
\end{aligned}$$

Therefore, the right hand side of the equation above is:

$$\overline{E^2} - \left(\overline{E}\right)^2 = -\frac{\partial \overline{E}}{\partial \beta}$$
$$= -\frac{\partial T}{\partial \beta}\frac{\partial \overline{E}}{\partial T}.$$

Then we can substitute in with $\frac{\partial T}{\partial \beta} = \left(\frac{\partial \beta}{\partial T}\right)^{-1} = \left(-\frac{1}{kT^2}\right)^{-1} = -kT^2$ *and* $C = \frac{\partial \overline{E}}{\partial T}$.

$$\overline{E^2} - \left(\overline{E}\right)^2 = kT^2 C$$
$$\sigma_E^2 = kT^2 C$$
$$\sigma_E = kT\sqrt{C/k} \quad \textit{as required}.$$

c. Using your results from part (b), apply the general expression to calculate the standard deviation of the energy of a system of N identical harmonic oscillators (as we have in an Einstein solid). Assume that your system is in the high temperature limit.

For a system of N harmonic oscillators in the high temperature limit, we know that

$$\overline{E} = nkT \quad \textit{and} \quad C = Nk.$$

and, therefore,

$$\sigma_E = kT\sqrt{Nk/k}$$
$$= kT\sqrt{N}.$$

d. Calculate the fractional fluctuation in energy ($\sigma_E / \overline{E}$) for $N = 1$, 10^6 and 10^{24}. Comment on your results and the implication for the average energy of the system in each case.

The fractional fluctuation in the energy is:

$$\left(\frac{\sigma_E}{\overline{E}}\right) = \frac{kT\sqrt{N}}{NkT} = \frac{1}{\sqrt{N}}.$$

For N = 1, $(\sigma_E/\overline{E})$ *= 100%*
For N = 10^6*,* $(\sigma_E/\overline{E})$ *= 1 in 1000*
For N = 10^{24}*,* $(\sigma_E/\overline{E})$ *= 1 in* 10^{12}*.*

The fluctuations decrease as the size of the system increases from N=1 to N=10^{24}*. For smallest system, fluctuations are 100% and these decrease to immeasurable when N is a large number (N=*10^{24}*). Therefore, for large N, we can consider E or U rather than the average value of E or U.*

2. Problem 6.20 on page 233 of Schroeder (only parts (b) – (d)).

   (b) We take the ground state energy for the harmonic oscillator to be zero and thus the partition function for a single harmonic oscillator is:

$$\begin{aligned} Z &= e^{0} + e^{-\beta\varepsilon} + e^{-\beta 2\varepsilon} + e^{-\beta 3\varepsilon} + \ldots \qquad \textit{where} \qquad \varepsilon = hf \\ &= 1 + e^{-\beta\varepsilon} + \left(e^{-\beta\varepsilon}\right)^{2} + \left(e^{-\beta\varepsilon}\right)^{3} + \ldots \\ &= \frac{1}{1-e^{-\beta\varepsilon}} \qquad (\textit{using result from part}(a)). \end{aligned}$$

   (c) For our harmonic oscillator, the average energy is:

$$\begin{aligned} \overline{E} &= -\frac{1}{Z}\frac{\partial Z}{\partial\beta} \\ &= -\frac{1}{1-e^{-\beta\varepsilon}}\frac{\partial}{\partial\beta}\left(1-e^{-\beta\varepsilon}\right)^{-1} \\ &= -\left(1-e^{-\beta\varepsilon}\right)(-1)\left(1-e^{-\beta\varepsilon}\right)^{-2}\left(\varepsilon e^{-\beta\varepsilon}\right) \\ &= \frac{\varepsilon e^{-\beta\varepsilon}}{1-e^{-\beta\varepsilon}} \\ &= \frac{\varepsilon}{e^{\beta\varepsilon}-1} \qquad (\textit{as we did in class}). \end{aligned}$$

   (d) The total energy of N identical, independent harmonic oscillators is N times the average energy of a single harmonic oscillator:

$$\begin{aligned} U &= N\overline{E} \\ &= \frac{N\varepsilon}{e^{\beta\varepsilon}-1}. \end{aligned}$$

3. Problem 6.42 on page 249 of Schroeder.

   (a) The Helmholtz Free Energy for a single harmonic oscillator is

$$\begin{aligned} F_1 &= -kT\ln Z_1 \\ &= -kT\ln\left(1-e^{-\beta\varepsilon}\right)^{-1} \\ &= kT\ln\left(1-e^{-\beta\varepsilon}\right). \end{aligned}$$

   Since it is an extensive property, the Helmholtz Free Energy for N identical oscillators is

$$F = NkT\ln\left(1-e^{-\beta\varepsilon}\right).$$

   (b) The entropy of a system of N identical harmonic oscillators is

$$\begin{aligned} S = -\left(\frac{\partial F}{\partial T}\right)_N &= -Nk\ln\left(1-e^{-\beta\varepsilon}\right) - NkT\left(1-e^{-\beta\varepsilon}\right)^{-1}\varepsilon e^{-\beta\varepsilon}\left(\frac{\partial\beta}{\partial\varepsilon}\right) \\ &= -Nk\ln\left(1-e^{-\beta\varepsilon}\right) + Nk\frac{\varepsilon/kT}{e^{\beta\varepsilon}-1}. \end{aligned}$$

   It is not typical for an exam question to get this ugly without any hints on what to do.