Problem 2.63

The Boltzmann equation[68]

$$P(n) = \frac{1}{Z}e^{-\beta E_n}, \quad Z \equiv \sum_n e^{-\beta E_n}, \quad \beta \equiv \frac{1}{k_B T}, \tag{2.202}$$

gives the probability of finding a system in the state n (with energy E_n), at temperature T (k_B is Boltzmann's constant). *Note:* The probability here refers to the random thermal distribution, and has nothing to do with quantum indeterminacy. Quantum mechanics will only enter this problem through quantization of the energies E_n.

(a) Show that the thermal average of the system's energy can be written as

$$\overline{E} = \sum_n E_n P(n) = -\frac{\partial}{\partial \beta}\ln(Z). \tag{2.203}$$

(b) For a quantum simple harmonic oscillator the index n is the familiar quantum number, and $E_n = (n + 1/2)\hbar\omega$. Show that in this case the **partition function** Z is

$$Z = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}}. \tag{2.204}$$

You will need to sum a geometric series. Incidentally, for a *classical* simple harmonic oscillator it can be shown that $Z_{\text{classical}} = 2\pi/(\omega\beta)$.

(c) Use your results from parts (a) and (b) to show that for the quantum oscillator

$$\overline{E} = \left(\frac{\hbar\omega}{2}\right)\frac{1 + e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}. \tag{2.205}$$

For a *classical* oscillator the same reasoning would give $\overline{E}_{\text{classical}} = 1/\beta = k_B T$.

(d) A crystal consisting of N atoms can be thought of as a collection of $3N$ oscillators (each atom is attached by springs to its 6 nearest neighbors, along the x, y, and z directions, but those springs are shared by the atoms at the two ends). The **heat capacity** of the crystal (per atom) will therefore be

$$C = 3\frac{\partial \overline{E}}{\partial T}. \tag{2.206}$$

Show that (in this model)

$$C = 3k_B\left(\frac{\theta_E}{T}\right)^2 \frac{e^{\theta_E/T}}{\left(e^{\theta_E/T} - 1\right)^2}, \tag{2.207}$$

where $\theta_E \equiv \hbar\omega/k_B$ is the so-called **Einstein temperature**. The same reasoning using the *classical* expression for $\overline{E}$ yields $C_{\text{classical}} = 3k_B$, independent of temperature.

(e) Sketch the graph of C/k_B versus T/θ_E. Your result should look something like the data for diamond in Figure 2.24, and nothing like the classical prediction.

[68]See, for instance, Daniel V. Schroeder, *An Introduction to Thermal Physics*, Pearson, Boston (2000), Section 6.1.

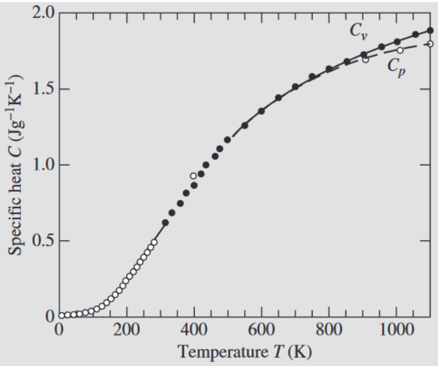


Figure 2.24: Specific heat of diamond (for Problem 2.63). From *Semiconductors on NSM* (http://www.ioffe.rssi.ru/SVA/NSM/Semicond/).

Solution

Part (a)

The average energy of the system can be written as

$$\begin{aligned}\overline{E} = \sum_n E_n P(E_n) = \sum_n E_n \left(\frac{1}{Z}e^{-\beta E_n}\right) = \frac{1}{Z}\sum_n E_n e^{-\beta E_n} &= \frac{1}{Z}\sum_n \left(-\frac{\partial}{\partial \beta}e^{-\beta E_n}\right) \\ &= -\frac{1}{Z}\frac{\partial}{\partial \beta}\left(\sum_n e^{-\beta E_n}\right) \\ &= -\frac{1}{Z}\frac{\partial Z}{\partial \beta} \\ &= -\frac{\partial}{\partial \beta}\ln Z.\end{aligned}$$

Part (b)

For a quantum harmonic oscillator, the energy is $E_n = (n+1/2)\hbar\omega$ $(n = 0, 1, \ldots)$, which means the partition function is

$$\begin{aligned}Z = \sum_n e^{-\beta E_n} = \sum_{n=0}^{\infty} e^{-\beta(n+1/2)\hbar\omega} = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega n}e^{-\beta\hbar\omega/2} &= e^{-\beta\hbar\omega/2}\sum_{n=0}^{\infty} e^{-\beta\hbar\omega n} \\ &= e^{-\beta\hbar\omega/2}\sum_{n=0}^{\infty}(e^{-\beta\hbar\omega})^n \\ &= e^{-\beta\hbar\omega/2}\left(\frac{1}{1-e^{-\beta\hbar\omega}}\right) \\ &= \frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}}.\end{aligned}$$

Part (c)

Substitute this formula for Z into the one for $\overline{E}$.

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

Part (d)

Calculate the heat capacity of the crystal.

$$\begin{aligned}
C &= 3\frac{\partial\overline{E}}{\partial T} \\
&= 3\frac{\partial}{\partial T}\left[\left(\frac{\hbar\omega}{2}\right)\frac{1+e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}\right] \\
&= \frac{3\hbar\omega}{2}\frac{\partial}{\partial T}\left[\frac{1+\exp\left(-\frac{\hbar\omega}{k_BT}\right)}{1-\exp\left(-\frac{\hbar\omega}{k_BT}\right)}\right] \\
&= \frac{3\hbar\omega}{2}\frac{\frac{\partial}{\partial T}\left[1+\exp\left(-\frac{\hbar\omega}{k_BT}\right)\right]\left[1-\exp\left(-\frac{\hbar\omega}{k_BT}\right)\right] - \frac{\partial}{\partial T}\left[1-\exp\left(-\frac{\hbar\omega}{k_BT}\right)\right]\left[1+\exp\left(-\frac{\hbar\omega}{k_BT}\right)\right]}{\left[1-\exp\left(-\frac{\hbar\omega}{k_BT}\right)\right]^2} \\
&= \frac{3\hbar\omega}{2}\frac{\left[\exp\left(-\frac{\hbar\omega}{k_BT}\right)\left(\frac{\hbar\omega}{k_BT^2}\right)\right]\left[1-\exp\left(-\frac{\hbar\omega}{k_BT}\right)\right] - \left[-\exp\left(-\frac{\hbar\omega}{k_BT}\right)\left(\frac{\hbar\omega}{k_BT^2}\right)\right]\left[1+\exp\left(-\frac{\hbar\omega}{k_BT}\right)\right]}{\left[1-\exp\left(-\frac{\hbar\omega}{k_BT}\right)\right]^2} \\
&= \frac{3\hbar\omega}{2}\left(\frac{\hbar\omega}{k_BT^2}\right)\frac{\left[1-\exp\left(-\frac{\hbar\omega}{k_BT}\right)\right]+\left[1+\exp\left(-\frac{\hbar\omega}{k_BT}\right)\right]}{\left[1-\exp\left(-\frac{\hbar\omega}{k_BT}\right)\right]^2}\exp\left(-\frac{\hbar\omega}{k_BT}\right) \\
&= \frac{3k_B}{2}\left(\frac{\hbar^2\omega^2}{k_B^2T^2}\right)\frac{2}{\left[1-\exp\left(-\frac{\hbar\omega}{k_BT}\right)\right]^2}\exp\left(-\frac{\hbar\omega}{k_BT}\right)
\end{aligned}$$

Continue the simplification.

$$C = 3k_B \left(\frac{\hbar^2\omega^2}{k_B^2T^2}\right) \frac{\exp\left(-\frac{\hbar\omega}{k_BT}\right)}{\left[1-\exp\left(-\frac{\hbar\omega}{k_BT}\right)\right]^2} \cdot \frac{\exp\left(2\frac{\hbar\omega}{k_BT}\right)}{\exp\left(2\frac{\hbar\omega}{k_BT}\right)}$$

$$= 3k_B \left(\frac{\hbar\omega}{k_BT}\right)^2 \frac{\exp\left(\frac{\hbar\omega}{k_BT}\right)}{\left[1-\exp\left(-\frac{\hbar\omega}{k_BT}\right)\right]^2 \left[\exp\left(\frac{\hbar\omega}{k_BT}\right)\right]^2}$$

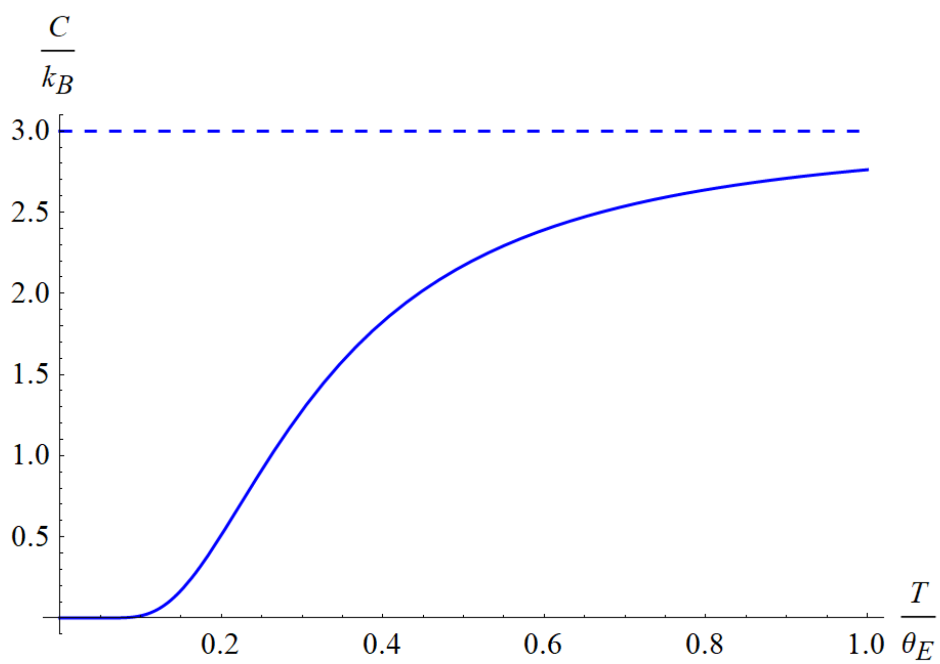
$$= 3k_B \left(\frac{\hbar\omega}{k_BT}\right)^2 \frac{\exp\left(\frac{\hbar\omega}{k_BT}\right)}{\left[\exp\left(\frac{\hbar\omega}{k_BT}\right)-1\right]^2}$$

Therefore, setting $\theta_E = \hbar\omega/k_B$,

$$C = 3k_B \left(\frac{\theta_E}{T}\right)^2 \frac{e^{\theta_E/T}}{\left(e^{\theta_E/T}-1\right)^2}.$$

Part (e)

In order to illustrate the function's behavior, plot C/k_B versus T/θ_E.



As long as the temperature is at least as high as the Einstein temperature ($T \geq \theta_E$), the classical result is a useful approximation.

$$\lim_{T\to\infty} C = 3k_B$$