PHSX 671: Homework #7

December 1, 2024

Grant Saggars

Problem 1

Determine the expression for the entropy of an Einstein solid.

Solution:

$$S = \ln Z + \beta \bar{E}; \quad \bar{E} = -\frac{\partial \ln Z}{\partial \beta}$$
$$S = -\left(\frac{\partial F}{\partial T}\right)_V = \frac{\beta^2}{k_B}\left(\frac{\partial F}{\partial \beta}\right)_V$$

Using

$$\ln Z = -3N\left[\frac{1}{2}\beta h\omega_0 + \ln\left(1 - e^{-\beta h\omega_0}\right)\right]$$
$$\bar{E} = 3Nh\omega_0\left[\frac{1}{2} - \frac{e^{-\beta h\omega_0}}{1 - e^{-\beta h\omega_0}}\right]$$

So entropy is:

$$S = -3N\left[\frac{1}{2}\beta h\omega_0 + \ln\left(1 - e^{-\beta h\omega_0}\right)\right] + 3N\beta h\omega_0\left[\frac{1}{2} - \frac{e^{-\beta h\omega_0}}{1 - e^{-\beta h\omega_0}}\right]$$

Problem 2

Derive an expression for the pressure of an Einstein solid in terms of $\frac{\partial \omega_0}{\partial V}$. Then use the proportion $\omega_0 \propto V^{-\frac{1}{3}}$ to determine an approximate expression for the pressure of an Einstein solid at $T = 0$.

Solution:
Again I will use Helmholtz Free energy, since it is fewer computations

$$\ln Z = -3N \left[\frac{1}{2}\beta h\omega_0 + \ln\left(1 - e^{-\beta h\omega_0}\right)\right] = -3N \left[\frac{1}{2}\beta h\lambda V^{-1/3} + \ln\left(1 - e^{-\beta h\lambda V^{-1/3}}\right)\right]$$

$$P = \left(\frac{\partial F}{\partial V}\right)_T; \quad F = -\frac{1}{\beta}\ln Z$$

I choose to substitute $\omega \to V^{-1/3}$ times some proportionality constant λ. Differentiating, we get

$$P = \frac{3N}{\beta}\left[\frac{1}{2}\beta h\lambda V^{-4/3} - \frac{\beta\lambda h}{3V^{\frac{4}{3}}}\frac{e^{-\beta\lambda h V^{-1/3}}}{(1 - e^{-\beta\lambda h V^{-1/3}})}\right]$$

Without rigorously proving it, I'll say that the fraction of exponentials converges to zero when $\beta \to \infty$. This leaves us with a constant pressure at low temperature proportional to

$$P \propto \frac{3NhV^{-4/3}}{2}$$

Problem 3

Use the Debye approximation to find the expressions for the entropy of a 3-dimensional solid as a function of the temperature T. For simplicity, express your answer in terms of the "Debye Function" $D(y) = \frac{3}{y^3}\int_0^y \frac{x^3}{e^x-1}dx$ and the "Debye Temperature" $\Theta_D = \frac{h\omega_D}{k_B} = Tx_D$. Assume that each oscillation is independent of the others.

Solution:

$$S = \ln Z - \beta\left(\frac{\partial \ln Z}{\partial \beta}\right) = -\left(\frac{\partial F}{\partial T}\right)$$

$$F = -\frac{1}{\beta}\ln Z$$

I'll choose to do this from the Helmholtz Free energy since it can be done a bit easier. We found:

$$\begin{aligned}\ln Z &= -\frac{9N\beta h\omega}{8} - 3N\ln(1-e^{-x_D}) - \frac{N}{x_D^3}\int_0^{x_D}\frac{x^3}{e^x-1}\,dx \\ &= -\frac{9Nx_D}{8} - 3N\ln(1-e^{-x_D}) - ND_3(x_D); \quad x_D = \beta h\omega\end{aligned}$$

I'll just keep things in terms of beta, so

$$-\left(\frac{\partial F}{\partial T}\right) = -\left(\frac{\partial F}{\partial \beta}\right)\left(\frac{\partial \beta}{\partial T}\right) = -\left(\frac{\partial F}{\partial \beta}\right)\frac{\partial}{\partial T}\left(\frac{1}{k_BT}\right) = \frac{\beta^2}{k_B}\left(\frac{\partial F}{\partial \beta}\right)$$

Now we can just compute entropy

$$\begin{aligned}S &= -\frac{\partial}{\partial \beta}\left[\frac{1}{\beta}\frac{\beta^2}{k_B}\left(-\frac{9N\beta h\omega}{8} - 3N\ln(1-e^{-\beta h\omega}) - ND_3(x_D)\right)\right] \\ &= \frac{\partial}{\partial \beta}\left[\frac{\beta}{k_B}\left(\frac{9N\beta h\omega}{8} + 3N\ln(1-e^{-\beta h\omega}) + ND_3(x_D)\right)\right]\end{aligned}$$

I will assume the form of $\frac{1}{k_B}(U) + \frac{\beta}{k_B}(U')$ (product rule), where U is the contents of the parenthesis. Focusing on the U' term for cleanliness:

$$\begin{aligned}U' &= \frac{\partial}{\partial \beta}\left(\frac{9N\beta h\omega}{8} + 3N\ln(1-e^{-\beta h\omega}) + ND_3(x_D)\right) \\ &= \left(\frac{9Nh\omega}{8} - 3Nh\omega\frac{e^{-\beta h\omega}}{1-e^{-\beta h\omega}} + N\frac{\partial D_3(x_D)}{\partial \beta}\right)\end{aligned}$$

Which gives this beefy eqaution

$$S = \frac{1}{k_B}\left(\frac{9N\beta h\omega}{8} + 3N\ln(1-e^{-\beta h\omega}) + ND_3(x_D)\right) + \frac{\beta}{k_B}\left(\frac{9Nh\omega}{8} - 3Nh\omega\frac{e^{-\beta h\omega}}{1-e^{-\beta h\omega}} + N\frac{\partial D_3(x_D)}{\partial \beta}\right)$$

And we can tidy it up with the Debye temperature instead of $h\omega$ terms

$$S = \left(\frac{9N\beta\Theta_D}{8} + \frac{3N}{k_B}\ln(1-e^{-\beta k_B\Theta_D}) + \frac{N}{k_B}D_3(x_D)\right) + \left(\frac{9N\beta\Theta_D}{8} - 3N\beta\Theta_D\frac{e^{-\beta k_B\Theta_D}}{1-e^{-\beta k_B\Theta_D}} + \frac{N\beta}{k_B}\frac{\partial D_3(x_D)}{\partial \beta}\right)$$

Problem 4

What is the equation of state for a Debye solid? That is, find an expression for the pressure P in terms of the volume V and the temperature T. Express your answer in terms of the "Debye function", $D(y)$, the "Debye temperature", Θ_D, and the Grüneisen parameter, $\gamma = -\frac{V}{\Theta_D}\frac{\partial \Theta_D}{\partial V}$.

Solution:

$$P = \left(\frac{\partial F}{\partial V}\right)_T, \quad F = -\frac{1}{\beta}\ln Z, \quad \Theta_D = \frac{\hbar\omega_D}{k_B}$$

We have already determined F:

$$\begin{aligned} F &= \frac{1}{\beta}\left[\frac{9N\beta\hbar\omega_D}{8} - 3N\ln(1-e^{-\beta\hbar\omega_D}) + ND_3(\beta\hbar\omega_D)\right] \\ &= k_BT\left[\frac{9N}{8}\frac{\Theta_D}{T} + 3N\ln(1-e^{-\Theta_D/T}) + ND_3(\Theta_D/T)\right] \end{aligned}$$

Using $\gamma = -\frac{V}{\Theta_D}\frac{\partial\Theta_D}{\partial V}$, so equivalently $\frac{\partial \Theta_D}{\partial V} = -\gamma\frac{\Theta_D}{V}$

$$\begin{aligned} P &= -k_BT\left[\frac{9N}{8}\frac{1}{T}\frac{\partial\Theta_D}{\partial V} + \frac{3N}{1-e^{-\Theta_D/T}}e^{-\Theta_D/T}\left(-\frac{1}{T}\right)\frac{\partial\Theta_D}{\partial V} + N\frac{\partial D_3(\Theta_D/T)}{\partial V}\right] \\ &= \frac{k_BT\gamma}{V}\left[\frac{9N}{8}\frac{\Theta_D}{T} + \frac{\Theta_D}{T}\frac{3N}{e^{\Theta_D/T}-1} - N\frac{\partial D_3(y)}{\partial y}\bigg|_{y=\Theta_D/T}\right] \end{aligned}$$

Problem 5

A rigid 1-D rod can excite longitudinal normal modes of oscillation down its length, denoted as L. Determine the heat capacity of the rod, C_V, as a function of temperature resulting from these oscillations using a Debye approximation model. Express your answer in terms of an integral and, for the sake of simplicity, consider using the dimensionless variable $x = \beta h\omega$.

Solution:
For this I really just need to derive the Debye model in 1-D. We have N normal modes of oscillation, and the density of phase space is given by

$$k^2 = k_x^2$$
$$\Gamma(k) = \left(\frac{1}{2}\frac{k}{\pi/L}\right) = \frac{kL}{2\pi} = \frac{L\omega}{2\pi v}$$
$$D(k)\,dk = \frac{d}{dk}\Gamma(k) = \frac{L}{2\pi v}d\omega, \quad \omega \leq \omega_D$$

We drop the 3, since now only 1 longitudinal oscillation is possible. The 1/2 reflects the portion of phase space which is positive.

$$\begin{aligned} N &= \int_0^{\omega_D} D(\omega)\,d\omega \\ &= \int_0^{\omega_D} \frac{L}{2\pi v}\,d\omega \end{aligned}$$
$$\omega_D = 2\pi v\frac{N}{L} \implies D(\omega) = \begin{cases} \frac{N}{\omega_D} & \omega \leq \omega_D \\ 0 & \omega > \omega_D \end{cases}$$

Now I can write the partition function

$$\begin{aligned} \ln Z &= -\beta\int_0^{\omega_D}\frac{1}{2}h\omega D(\omega)\,d\omega - \int_0^{\omega_D}\ln(1-e^{-\beta h\omega})D(\omega)\,d\omega \\ &= -\frac{N\beta h\omega_D}{4} - \frac{N}{\omega_D}\int_0^{\omega_D}\ln(1-e^{-\beta h\omega})\,d\omega \\ &= -\frac{N\beta h\omega_D}{4} - \frac{N}{\omega_D}\int_0^{\beta h\omega_D}\ln\left(1-e^{-x}\right)\,dx, && (x=\beta h\omega) \\ &= -\frac{N\beta h\omega_D}{4} - \left[\frac{N}{\omega_D}\frac{x}{e^x-1}\right]\Bigg|_{x=0}^{x=\beta h\omega_D} + \frac{N}{\omega_D}\int_0^{\beta h\omega_D}\frac{x}{e^x-1}\,dx && \text{(integration by parts)} \\ &= -\frac{N\beta h\omega_D}{4} - \frac{N\beta h}{e^{\beta h\omega_D}-1} + D_1(\beta h\omega_D) \end{aligned}$$

Doing integration by parts, taking 1 to be the integrating part and the logarithm to be the differentiating part, we arrive at something very similar to what we got in class for 3-D.

$$C_V = \left(\frac{\partial S}{\partial T}\right)_V = k_B\beta^2\left(\frac{\partial S}{\partial \beta}\right)_V$$

So, two derivatives have to be taken to get to the final result. The first to get entropy ($S = \ln Z + \beta\frac{\partial \ln Z}{\partial \beta}$):

$$\begin{aligned} \bar{E} = -\frac{\partial \ln Z}{\partial \beta} &= -\frac{\partial}{\partial\beta}\left[-\frac{N\beta h\omega_D}{4} - \frac{N}{\omega_D}\int_0^{\omega_D}\ln(1-e^{-\beta h\omega})\,d\omega\right] \\ &= \frac{Nh\omega_D}{4} - \frac{N}{\beta}D_1(\beta h\omega_D) \end{aligned}$$

Problem 5 continued on next page...

So then,

$$S = \frac{Nh\omega_D}{4}(1-\beta) - \frac{N\beta h}{e^{\beta h\omega_D}-1} + \left(1-\frac{N}{\beta}\right)D_1(\beta h\omega_D)$$

and,

$$\begin{aligned}
C_V &= k_B\beta^2\left(\frac{\partial S}{\partial \beta}\right)_V \\
&= k_B\beta^2\left[-\frac{Nh\omega_D}{4} - \frac{Nh(e^{\beta h\omega_D} - \beta h\omega_D e^{\beta h\omega_D} - 1)}{(e^{\beta h\omega_D}-1)^2} + \frac{1}{\beta^2}D_1(\beta h\omega_D) + \left(1-\frac{N}{\beta}\right)\frac{\partial D_1(\beta h\omega_D)}{\partial \beta}\right] \\
&= -\frac{Nk_B\beta^2 hk_B\beta^2\omega_D}{4} - \frac{Nh(e^{\beta h\omega_D} - \beta h\omega_D e^{\beta h\omega_D} - 1)}{(e^{\beta h\omega_D}-1)^2} + k_B D_1(\beta h\omega_D) + k_B\beta^2\left(1-\frac{N}{\beta}\right)\frac{\partial D_1(\beta h\omega_D)}{\partial \beta}
\end{aligned}$$