Statistical Thermodynamics 3rd Homework Assignment

Elijan Mastnak

January 20, 2020

The lattice oscillation in a two dimensional solid is described by the Debye model. Determine the Debye frequency if the speed of sound in the solid is $2800\,\mathrm{m/s}$*, the number density of the constituent atoms is* $2 \times 10^{20}\,\mathrm{m}^{-2}$*, and the sound has two degrees of polarization. What is the contribution of the lattice oscillations to the specific heat of the two-dimensional solid at a temperature of* $3\,\mathrm{K}$*? What is the deviation of the specific heat from the high temperature limit at* $1800\,\mathrm{K}$*?*

Problem Set-Up

We view the solid as a two-dimensional crystal lattice composed of a large number of quantum harmonic oscillators, where the energy of the ith oscillator is given by $E_i = \hbar\omega_i$. Since we are studying sound, the relevant particles are phonons; since phonons are virtual particles, their chemical potential is zero. In two dimensions, sound has $\mathcal{P} = 2$ degrees of polarization and is described by the dispersion relation $\omega = ck$.

Deriving Density of States

The phase space Γ consists of position and momentum components; the integral over the position components evaluates to the area A of the solid.

$$\sum_i \to \mathcal{P}\int \frac{\mathrm{d}\Gamma}{h^2} = 2\int \frac{\mathrm{d}^2p\,\mathrm{d}^2r}{h^2} = \mathcal{P}A\int \frac{\mathrm{d}^2p}{h^2} = \mathcal{P}A\int \frac{\hbar^2\,\mathrm{d}^2k}{h^2}$$
$$= \mathcal{P}A\int \frac{2\pi k\,\mathrm{d}k}{(2\pi)^2} = \frac{\mathcal{P}A}{2\pi}\int k\,\mathrm{d}k = \frac{\mathcal{P}A}{2\pi}\int \frac{w}{c^2}\,\mathrm{d}\omega$$

The resulting density of states function is

$$g(\omega) = \frac{\mathcal{P}A}{2\pi}\frac{w}{c^2} = \frac{A\omega}{\pi c^2}$$

when evaluated for $\mathcal{P} = 2$.

Deriving 2D Debye Frequency

The Debye frequency ω_D is the upper limit to the frequency of vibration in the solid. Assuming are N particles in the two-dimensional solid, there are $2N$ quantum harmonic oscillators over the frequency range 0 to ω_D. This gives the relationship:

$$
\begin{aligned}
2N &= \int_0^{\omega_D} g(\omega)\,\mathrm{d}\omega = \int_0^{\omega_D} \frac{\mathcal{P}A}{2\pi}\frac{w}{c^2}\,\mathrm{d}\omega = \frac{\mathcal{P}A}{4\pi}\frac{w_D^2}{c^2} \\
\omega_D &= \sqrt{\frac{8\pi}{\mathcal{P}}\frac{N}{A}}c = 2c\sqrt{\pi\frac{N}{A}} = 2\,(2800\,\mathrm{m/s})\,\sqrt{\pi\left(2\times 10^{20}\,\mathrm{m}^{-2}\right)} \\
&= \boxed{1.40\times 10^{14}\,\mathrm{Hz}} \iff \nu_D = \frac{\omega_D}{2\pi} = \boxed{2.23\times 10^{13}\,\mathrm{Hz}}
\end{aligned}
$$

The corresponding Debye temperature is

$$
T_D = \frac{\hbar\omega_D}{k_B} = \frac{(1.051\times 10^{-35}\,\mathrm{J\cdot s})(1.40\times 10^{14}\,\mathrm{Hz})}{(1.38\times 10^{-23}\,\mathrm{J\cdot K^{-1}})} \approx \boxed{107\,\mathrm{K}}
$$

Average Energy and Heat Capacity

Phonons are described by a Bose-Einstein distribution with chemical potential μ equal to zero. The expected number $\langle n_i\rangle$ of particles occupying an energy state E_i is thus given by

$$
\langle n_i\rangle(E_i) = \frac{1}{e^{\beta E_i}-1} \qquad \text{or} \qquad \langle n_i\rangle(\omega_i) = \frac{1}{e^{\beta\hbar\omega_i}-1}
$$

where $\beta = \frac{1}{k_BT}$. In terms of the Bose-Einstein distribution and density of states, the average energy $\langle E\rangle$ of the system is:

$$
\begin{aligned}
\langle E\rangle &= \int_0^{\omega_D} [g(\omega)][\langle n\rangle(\omega)][E(\omega)]\,\mathrm{d}\omega = \int_0^{\omega_D}\left[\frac{A\omega}{\pi c^2}\right]\left[\frac{1}{e^{\beta\hbar\omega}-1}\right]\hbar\omega\,\mathrm{d}\omega \\
&= \frac{A\hbar}{\pi c^2}\int_0^{\omega_D}\frac{\omega^2}{e^{\beta\hbar\omega}-1}\,\mathrm{d}\omega = \frac{A\hbar}{\pi c^2}\frac{1}{\beta^3\hbar^3}\int_0^{u_D}\frac{u^2}{e^u-1}\,\mathrm{d}u \\
&= \frac{A}{\pi}\frac{k_B^3T^3}{c^2\hbar^2}\int_0^{u_D}\frac{u^2}{e^u-1}\,\mathrm{d}u \qquad (1)
\end{aligned}
$$

where $u = \beta\hbar\omega$.

Low Temperature Heat Capacity

Because $T = 3\,\mathrm{K}$ is significantly less than the Debye temperature $T_D = 107\,\mathrm{K}$, we can safely operate in the low-temperature limit with $u_D \to \infty$

as the upper limit of integration. In this case, we can directly evaluate the integral in Equation 1 using the tabulated value

$$\int_0^{u_D} \frac{u^2}{e^u - 1}\, \mathrm{d}u \approx 2.404$$

The resulting expressions for $\langle E \rangle$ and C, respectively, are:

$$\langle E \rangle = 2.404 \left(\frac{A}{\pi} \frac{k_B^3 T^3}{c^2 \hbar^2} \right)$$

$$C = \frac{\mathrm{d} \langle E \rangle}{\mathrm{d}T} = 7.212 \left(\frac{A}{\pi} \frac{k_B^3 T^2}{c^2 \hbar^2} \right)$$

Note that the low-temperature heat capacity is proportional to T^2, not T^3 as in the three-dimensional Debye model. Although we do not know the area A of the solid explicitly, we can calculate the specific heat capacity $c = \frac{C}{N}$ with the given number density. The resulting value is

$$\begin{aligned} c = \frac{C}{N} &= 7.212 \left(\frac{A}{N} \right) \left(\frac{k_B^3 T^2}{\pi c^2 \hbar^2} \right) \\ &= 7.212 \left(\frac{1}{2 \times 10^{20}\,\mathrm{m}^{-2}} \right) \left(\frac{\left(1.38 \times 10^{-23}\,\mathrm{J \cdot K^{-1}}\right)^3 (3\,\mathrm{K})^2}{\pi\, (2800\,\mathrm{m/s})^2 \left(1.051 \times 10^{-35}\,\mathrm{J \cdot s}\right)^2} \right) \\ &= \boxed{2.28 \times 10^{-2}\,\mathrm{J/K}} \end{aligned}$$

Deviation from High-Temperature Heat Capacity

First, we find the upper-temperature limit, then calculate the deviation from the limit with an appropriate Taylor series expansion. As $T \to \infty$, the upper limit of integration u_D in Equation 1 approaches zero. If we define

$$f(x) \coloneqq \frac{x^2}{e^x - 1}$$

we get (using a mathematics engine such as Wolfram Mathematica) the Taylor series coefficients

$$\begin{aligned} a_0 &= \lim_{x \to 0} f(x) = 0 & \qquad a_1 &= \lim_{x \to 0} f'(x) = 1 \\ a_2 &= \lim_{x \to 0} f''(x) = 1 & \qquad a_3 &= \lim_{x \to 0} f'''(x) = \frac{1}{2} \end{aligned}$$

These coefficients give the third-order Taylor series expansion about $x = 0$

$$f(x) \approx a_0 + a_1 x + a_2 \frac{x^2}{2} + a_3 \frac{x^3}{6} = x - \frac{x^2}{2} + \frac{x^3}{12}$$

Applying this expansion to our to our expression for $\langle E\rangle$ in Equation 1, we get:

$$
\begin{aligned}
\langle E\rangle &\approx \frac{A}{\pi}\frac{k_B^3T^3}{c^2\hbar^2}\int_0^{u_D}\left(u-\frac{u^2}{2}+\frac{u^3}{12}\right)\mathrm{d}u = \frac{A}{\pi}\frac{k_B^3T^3}{c^2\hbar^2}\left(\frac{u_D^2}{2}-\frac{u_D^3}{6}+\frac{u_D^4}{48}\right)\\
&= \frac{A}{\pi}\frac{k_B^3T^3}{c^2\hbar^2}\frac{u_D^2}{2}\left(1-\frac{u_D}{3}+\frac{u_D^2}{24}\right)
\end{aligned}
$$

Plugging in the definitions $u_D = \beta\hbar\omega_D$ and $\omega_D = 2c\sqrt{\pi\frac{N}{A}}$ results in

$$
\begin{aligned}
\langle E\rangle &\approx 2k_BTN\left(1-\frac{\hbar\omega_D}{3k_BT}+\frac{1}{24}\left(\frac{\hbar\omega_D}{k_BT}\right)^2\right)\\
C &= 2k_BN\left(1-\frac{1}{24}\left(\frac{\hbar\omega_D}{k_BT}\right)^2\right)\\
c &= \frac{C}{N} = 2k_B\left(1-\frac{1}{24}\left(\frac{\hbar\omega_D}{k_BT}\right)^2\right)
\end{aligned}
$$

The high temperature limits are $C = 2k_BN$ and $c = 2k_B$, which can be interpreted as two-dimensional analogs of the law of Dulong and Petit, while the second-order term is the deviation Δc from the limit. Plugging in values with $T = 1800\,\mathrm{K}$ gives a deviation of

$$
\begin{aligned}
\Delta c &= \frac{k_B}{12}\left(\frac{\hbar\omega_D}{k_BT}\right)^2 = \frac{k_B}{12}\left(\frac{(1.051\times10^{-35}\,\mathrm{J\cdot s})(1.40\times10^{14}\,\mathrm{s^{-1}})}{(1.38\times10^{-23}\,\mathrm{J\cdot K^{-1}})\,(1800\,\mathrm{K})}\right)^2\\
&= \left(2.92\times10^{-4}\right)k_B\\
&= \boxed{4.035\times10^{-27}\,\mathrm{J/K}}
\end{aligned}
$$