

Chapter 7

Solids

7.1 Lattice Vibrations

Back in 1819, Pierre Dulong and Alexis Petit found that the mass-specific heat capacity (*i.e.*, the heat capacity per weight of substance) was close to a constant value for many solid elements. As expected, this observation is now called the Law of Dulong and Petit. In 1877, our friend Boltzmann showed that this could be a result of classical vibrations of the atoms constituting these solids. Specifically, he argued that the solid could be modeled as a lattice of atoms and, as we have learned in many previous courses, that small amplitude oscillations of these atoms around their equilibrium positions can be modeled as simple harmonic motion. We can then use the equipartition theorem to determine the average energy associated with these vibrations. For a single oscillator we have

$$E = K + U \rightarrow E = \frac{p^2}{2m} + \frac{1}{2}k(\Delta x)^2$$

$$\overline{E} = \overline{\frac{p^2}{2m}} + \overline{\frac{1}{2}k(\Delta x)^2} \rightarrow \overline{E} = \frac{1}{2}k_B T + \frac{1}{2}k_B T \rightarrow \overline{E} = k_B T$$

For a 3-dimension solid consisting of N atoms, this would approximately be

$$\overline{E} = 3Nk_B T$$

The heat capacity at constant volume can then be calculated using Equation 1.4¹

$$C_V = \frac{d}{dT}(3Nk_B T) \rightarrow C_V = 3Nk_B$$

This value for C_V agrees with the Law of Dulong and Petit. While it worked well in this limit, Boltzmann's model was unfortunately able to predict the

¹We are again assuming that if the system is large enough, \overline{E} is the same as E

temperature dependence of the heat capacity of these substances, especially at low temperature. People also didn't like Boltzmann's model since they didn't believe in atoms.

Fast forward several years and folks decided to build off Boltzmann's work by modeling the $3N$ normal modes of the motion of the atoms in the solid as $3N$ quantum mechanical harmonic oscillators. When we write the partition function we need to sum over all $3N$ oscillators and all possible associated quantum numbers. Since for one oscillator

$$E_n = \left(n + \frac{1}{2} \right) \hbar\omega$$

the total energy of the whole system of oscillators is

$$\begin{aligned} E_{total} &= \sum_{r=1}^{3N} \left(n_r + \frac{1}{2} \right) \hbar\omega_r \quad \rightarrow \quad E_{total} = \sum_{r=1}^{3N} n_r \hbar\omega_r + \sum_{r=1}^{3N} \frac{1}{2} \hbar\omega_r \\ E_{total} &= \alpha + \sum_{r=1}^{3N} n_r \hbar\omega_r \end{aligned}$$

Where we have defined $\alpha = \sum_{r=1}^{3N} \frac{1}{2} \hbar\omega_r$. In these summations, each oscillator is in a well-defined energy state, with a corresponding quantum number. To calculate the partition function we need to sum up all the possible quantum numbers for each oscillator.

$$Z = \sum_{n_1, n_2, \dots, n_{3N}} e^{-\beta(\alpha + n_1 \hbar\omega_1 + n_2 \hbar\omega_2 + \dots + n_{3N} \hbar\omega_{3N})}$$

If the oscillators are acting independently of each other then we can simplify the partition function

$$Z = e^{-\beta\alpha} \left(\sum_{n_1=0}^{\infty} e^{-\beta n_1 \hbar\omega_1} \right) \left(\sum_{n_2=0}^{\infty} e^{-\beta n_2 \hbar\omega_2} \right) \dots \left(\sum_{n_{3N}=0}^{\infty} e^{-\beta n_{3N} \hbar\omega_{3N}} \right)$$

$$Z = e^{-\beta\alpha} \left(\frac{1}{1 - e^{-\beta n_1 \hbar\omega_1}} \right) \left(\frac{1}{1 - e^{-\beta n_2 \hbar\omega_2}} \right) \dots \left(\frac{1}{1 - e^{-\beta n_{3N} \hbar\omega_{3N}}} \right)$$

So

$$\ln Z = -\beta\alpha - \sum_{r=1}^{3N} \ln(1 - e^{-\beta \hbar\omega_r})$$

$$\ln Z = -\beta \sum_{r=1}^{3N} \frac{1}{2} \hbar\omega_r - \sum_{r=1}^{3N} \ln(1 - e^{-\beta \hbar\omega_r})$$

We can now replace the summations with an integral if we use the density of states.

$$\ln Z = -\beta \int_0^\infty \frac{1}{2} \hbar \omega D(\omega) d\omega - \int_0^\infty \ln(1 - e^{-\beta \hbar \omega}) D(\omega) d\omega \quad (7.1)$$

7.2 Einstein's Model

Einstein assumed that all the oscillators constituting the solid had the exact same frequency of oscillation, denoted as ω_0 , and could thus express the density of states using a delta function.

$$D(\omega) d\omega = C \delta(\omega - \omega_0) d\omega$$

The constant C in this equation is determined through normalization. Specifically, since a system of $3N$ oscillators can have a total of $3N$ normal modes of oscillation, we know that

$$\int_0^\infty D(\omega) d\omega = 3N$$

Thus,

$$\int_0^\infty C \delta(\omega - \omega_0) d\omega = 3N \rightarrow C = 3N$$

$$D(\omega) d\omega = 3N \delta(\omega - \omega_0) d\omega$$

7.2.1 Partition Function

Substituting this density of states into Equation 7.1 yields

$$\begin{aligned} \ln Z &= -\beta \int_0^\infty \frac{1}{2} \hbar \omega 3N \delta(\omega - \omega_0) d\omega - \int_0^\infty \ln(1 - e^{-\beta \hbar \omega}) 3N \delta(\omega - \omega_0) d\omega \\ \ln Z &= -\frac{3}{2} N \beta \hbar \omega_0 - 3N \ln(1 - e^{-\beta \hbar \omega_0}) \\ \ln Z &= -3N \left[\frac{1}{2} \beta \hbar \omega_0 + \ln(1 - e^{-\beta \hbar \omega_0}) \right] \end{aligned}$$

7.2.2 Mean Energy

The mean energy can be calculated using Equation 4.1.

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

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

7.2.3 Heat Capacity

We can calculate the heat capacity from the mean energy using Equation 1.4.

$$C_V = -k_B \beta^2 \left(\frac{\partial}{\partial \beta} \right)_V \left[3N \hbar \omega_0 \left[\frac{1}{e^{\beta \hbar \omega_0} - 1} + \frac{1}{2} \right] \right]$$

$$C_V = 3N k_B \left((\beta \hbar \omega_0)^2 \frac{e^{\beta \hbar \omega_0}}{(e^{\beta \hbar \omega_0} - 1)^2} \right)$$

In the limit of high temperature (*i.e.*, low β), we can approximate the exponential functions in this expression.

$$e^{\beta \hbar \omega_0} \approx 1 + \beta \hbar \omega_0$$

$$C_V \approx 3N k_B \left((\beta \hbar \omega_0)^2 \frac{1 + \beta \hbar \omega_0}{(1 + \beta \hbar \omega_0 - 1)^2} \right)$$

$$C_V \approx 3N k_B (1 + \beta \hbar \omega_0) \approx 3N k_B$$

This limit agrees with the Law of Dulong and Petit. In the limit of low temperature (*i.e.*, high β), we have

$$C_V \approx 3N k_B \left((\beta \hbar \omega_0)^2 \frac{e^{\beta \hbar \omega_0}}{(e^{\beta \hbar \omega_0})^2} \right)$$

$$C_V \approx 3N k_B \frac{(\beta \hbar \omega_0)^2}{e^{\beta \hbar \omega_0}}$$

The heat capacity decreases as the temperature decreases and approaches zero as the temperature approaches zero. This is as expected from the Third Law of Thermodynamics.

By the way, it is common for people to write the expression for the heat capacity of an Einstein solid in terms of a characteristic temperature, $\theta_E = \frac{\hbar \omega_0}{k_B}$, that is referred to as the Einstein temperature.

$$C_V = 3Nk_B \left(\left(\frac{\Theta_E}{T} \right)^2 \frac{e^{\frac{\Theta_E}{T}}}{\left(e^{\frac{\Theta_E}{T}} - 1 \right)^2} \right)$$

You know you're cool when you have a temperature named after you.

7.3 Debye's Model

The problem with Einstein's model is that the temperature dependence it predicts for the heat capacity at low temperatures does not agree with experimental results. In 1912, Debye modified Einstein's model to include a different approximation for the density of states. In contrast with Einstein's model, which reflected oscillations of individual atoms in the solid, Debye's model focused on the normal modes of oscillation of the entire system of atoms.

7.3.1 Density of States

Debye assumed that the normal modes of vibration are isotropic and continuous and calculated the density of states using the approach we discussed in Section 4.2. For a 3-dimensional wave we have

$$k^2 = k_x^2 + k_y^2 + k_z^2$$

$$\Gamma(k) = 3 \left[\frac{1}{8} \frac{\frac{4}{3}\pi k^3}{\left(\frac{\pi}{L}\right)^3} \right] \rightarrow \Gamma(k) = \frac{L^3 k^3}{2\pi^2}$$

The factor of $\frac{1}{8}$ reflects the requirement that the values of k_x , k_y , and k_z are positive and the factor of 3 accounts for the fact that there are three possible directors of polarization for each oscillation (two transverse and one longitudinal).

$$D(k)dk = \frac{d}{dk} \Gamma(k) \rightarrow D(k)dk = \frac{3L^3 k^2}{2\pi^2}$$

If we substitute $L^3 = V$, where V is the volume of the system, and $k = \frac{\omega}{v}$, where v is the speed of the wave, we have

$$D(\omega)d\omega = \frac{3V\omega^2}{2\pi^2 v^3}$$

Of course, by doing this we are assuming that all polarizations have the same speed. That is not strictly true, but this is an approximation.

Debye next assumed that each solid would have a characteristic frequency, denoted as ω_D , above which the density of states is zero.

$$D(\omega) = \begin{cases} \frac{3V\omega^2}{2\pi^2 v^3} & \omega \leq \omega_D \\ 0 & elsewhere \end{cases}$$

Thus, the normalization condition becomes

$$\int_0^{\omega_D} \frac{3V\omega^2}{2\pi^2v^3} = 3N \rightarrow \frac{V\omega_D^3}{2\pi^2v^3} = 3N$$

$$\omega_D = v \left(6\pi^2 \frac{N}{V} \right)^{\frac{1}{3}}$$

This normalization also allows us to express the density of states in terms of ω_D .

$$D(\omega) = \begin{cases} \frac{9N\omega^2}{\omega_D^3} & \omega \leq \omega_D \\ 0 & elsewhere \end{cases}$$

7.3.2 Partition Function

Substituting this density of states into Equation 7.1 yields

$$\ln Z = -\beta \int_0^{\omega_D} \frac{1}{2} \hbar \omega \frac{9N\omega^2}{\omega_D^3} d\omega - \int_0^{\omega_D} \ln(1 - e^{-\beta\hbar\omega}) \frac{9N\omega^2}{\omega_D^3} d\omega$$

$$\ln Z = -\frac{9N\beta\hbar}{2\omega_D^3} \int_0^{\omega_D} \omega^3 d\omega - \frac{9N}{\omega_D^3} \int_0^{\omega_D} \ln(1 - e^{-\beta\hbar\omega}) \omega^2 d\omega$$

$$\ln Z = -\frac{9N\beta\hbar\omega_D}{8} - \frac{9N}{\omega_D^3} \int_0^{\omega_D} \ln(1 - e^{-\beta\hbar\omega}) \omega^2 d\omega$$

This is a perfectly fine place to stop. However, there are some simplifications and modifications that you will encounter in other textbooks and references so it would be good to go through them too.

First off, people frequently write this expression using the dimensionless parameter $x = \beta\hbar\omega$.

$$\ln Z = -\frac{9Nx_D}{8} - \frac{9N}{x_D^3} \int_0^{x_D} \ln(1 - e^{-x}) x^2 dx$$

In this expression, $x_D = \beta\hbar\omega_D$. We can simplify this expression further through integration by parts².

$$\ln Z = -\frac{9Nx_D}{8} - \frac{9N}{x_D^3} \left[\frac{x_D^3}{3} \ln(1 - e^{-x_D}) - \int_0^{x_D} \frac{1}{3} \frac{x^3}{e^x - 1} dx \right]$$

²Kinda cool that good ole integration by parts is making an appearance this late in your matriculation.

$$\ln Z = -\frac{9N x_D}{8} - 3N \ln(1 - e^{-x_D}) - \frac{3N}{x_D^3} \int_0^{x_D} \frac{x^3}{e^x - 1} dx$$

Now it's time to introduce the Debye Function³, $D_n(y)$.

$$D_n(y) = \frac{n}{y^n} \int_0^y \frac{x^n}{e^x - 1} dx$$

This allows us to write the expression for $\ln Z$ as

$$\ln Z = -\frac{9N x_D}{8} - 3N \ln(1 - e^{-x_D}) - ND_3(x_D)$$

And finally, since people are obsessed with temperature, we can introduce a Debye Temperature, $\Theta_D = T x_D = \frac{\hbar \omega_D}{k_B}$.

$$\ln Z = -\frac{9N}{8} \frac{\Theta_D}{T} - 3N \ln\left(1 - e^{-\frac{\Theta_D}{T}}\right) - ND_3\left(\frac{\Theta_D}{T}\right)$$

7.3.3 Mean Energy

We can calculate the mean energy from the partition function using Equation 4.1.

$$\begin{aligned} \bar{E} &= -\frac{\partial}{\partial \beta} \left[-\frac{9N\beta\hbar\omega_D}{8} - \frac{9N}{\omega_D^3} \int_0^{\omega_D} \ln(1 - e^{-\beta\hbar\omega}) \omega^2 d\omega \right] \\ \bar{E} &= \frac{9N\hbar\omega_D}{8} + \frac{9N}{\omega_D^3} \int_0^{\omega_D} \frac{-e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} (-\hbar\omega) \omega^2 d\omega \\ \bar{E} &= \frac{9N\hbar\omega_D}{8} + \frac{9N\hbar}{\omega_D^3} \int_0^{\omega_D} \frac{\omega^3}{e^{\beta\hbar\omega} - 1} d\omega \end{aligned}$$

We can stop here but, as before, there are some other representations of this equation that you may encounter. Let's begin by substituting $x = \beta\hbar\omega$.

$$\bar{E} = \frac{9N\hbar\omega_D}{8} + \frac{9N}{\beta x_D^3} \int_0^{x_D} \frac{x^3}{e^x - 1} dx$$

The final integral we can express in terms of the Debye function

$$\bar{E} = \frac{9N\hbar\omega_D}{8} + \frac{3N}{\beta} D_3(x_D)$$

³It is left as an exercise to the reader to determine if it's better to have a function or a temperature named after you.

And, finally, let's substitute the Debye temperature.

$$\overline{E} = \frac{9Nk_B\Theta_D}{8} + \frac{3N}{\beta}D_3\left(\frac{\Theta_D}{T}\right)$$

$$\overline{E} = 3Nk_B\left[\frac{3}{8}\Theta_D + TD_3\left(\frac{\Theta_D}{T}\right)\right]$$

7.3.4 Heat Capacity

We can calculate the heat capacity from the mean energy using Equation 1.4.

$$\begin{aligned} C_V &= -k_B\beta^2 \left(\frac{\partial}{\partial\beta} \right)_V \left[\frac{9N\hbar\omega_D}{8} + \frac{9N\hbar}{\omega_D^3} \int_0^{\omega_D} \frac{\omega^3}{e^{\beta\hbar\omega} - 1} d\omega \right] \\ C_V &= -k_B\beta^2 \left(\frac{9N\hbar}{\omega_D^3} \right) \int_0^{\omega_D} \frac{-e^{\beta\hbar\omega}\hbar\omega}{(e^{\beta\hbar\omega} - 1)^2} \omega^3 d\omega \\ C_V &= \left(\frac{9Nk_B\beta^2\hbar^2}{\omega_D^3} \right) \int_0^{\omega_D} \frac{\omega^4 e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2} d\omega \end{aligned}$$

In the limit of high temperature (*i.e.*, low β), we can approximate the exponential functions in this expression.

$$\lim e^{\beta\hbar\omega} \approx 1 + \beta\hbar\omega$$

$$\begin{aligned} C_V &\approx \left(\frac{9Nk_B\beta^2\hbar^2}{\omega_D^3} \right) \int_0^{\omega_D} \frac{\omega^4 (1 + \beta\hbar\omega)}{(1 + \beta\hbar\omega - 1)^2} d\omega \\ C_V &\approx \left(\frac{9Nk_B\beta^2\hbar^2}{\omega_D^3} \right) \int_0^{\omega_D} \frac{\omega^2}{\beta^2\hbar^2} + \frac{\omega^3}{\beta\hbar} d\omega \end{aligned}$$

If β is small, we can ignore the second term in the integration.

$$C_V \approx \left(\frac{9Nk_B\beta^2\hbar^2}{\omega_D^3} \right) \int_0^{\omega_D} \frac{\omega^2}{\beta^2\hbar^2} d\omega \rightarrow C_V \approx \left(\frac{9Nk_B\beta^2\hbar^2}{\omega_D^3} \right) \left(\frac{\omega_D^3}{3\beta^2\hbar^2} \right)$$

$$C_V \approx 3Nk_B$$

This limit agrees with the Law of Dulong and Petit. In order to examine what happens in the limit of low temperature (*i.e.*, high β), let's rewrite the expression for the heat capacity in terms of the dimensionless variable $x = \beta\hbar\omega$.

$$C_V = \left(\frac{9Nk_B}{\omega_D^3 (\beta\hbar)^3} \right) \int_0^{\beta\hbar\omega_D} \frac{x^4 e^x}{(e^x - 1)^2} dx$$

In the limit of large values of β , we can approximate the upper limit of the integration with ∞ .

$$\begin{aligned} C_V &\approx \left(\frac{9Nk_B}{\omega_D^3 (\beta\hbar)^3} \right) \int_0^{\infty} \frac{x^4 e^x}{(e^x - 1)^2} dx \\ C_V &\approx \left(\frac{9Nk_B}{\omega_D^3 (\beta\hbar)^3} \right) \left(\frac{4\pi^4}{15} \right) \rightarrow C_V \approx T^3 \end{aligned}$$

This predicted dependence on temperature is consistent with experimental results. Therefore, this model is probably capturing a lot of the physics taking place.

7.4 Summary

- The partition function for the oscillations within a solid

$$\ln Z = -\beta \int_0^{\infty} \frac{1}{2} \hbar\omega D(\omega) d\omega - \int_0^{\infty} \ln(1 - e^{-\beta\hbar\omega}) D(\omega) d\omega$$

- Density of states for lattice vibrations within a solid

– Einstein: $D(\omega) = 3N\delta(\omega - \omega_0)$

– Debye: $D(\omega) = \begin{cases} \frac{9N\omega^2}{\omega_D^3} & \omega \leq \omega_D \\ 0 & elsewhere \end{cases}$