Chapter 7

Failure of Classical Equipartition

Consider a classical solid, consisting of “atoms” located at regular lattice sites. Each atom is subject to harmonic restoring forces in three directions, so there are 3 kinetic and 3 potential-energy degrees of freedom per atom:

$$H_{\text{atom}} = \frac{\mathbf{p}^2}{2m} + \frac{1}{2}m\omega^2\mathbf{r}^2. \tag{7.1}$$

Therefore by the equipartition theorem, for a solid consisting of N atoms, the energy is

$$U = 3NkT, \tag{7.2}$$

and so the specific heat at constant volume is

$$c_V = 3Nk = 3R \text{ per mole}, \tag{7.3}$$

where $R = N_A k$ is the gas constant, in terms of Avogadro’s number $N_A = 6.02 \times 10^{23}$. This is the “Law of Dulong and Petit.” It is well-satisfied at high temperatures, but not at low. Experimentally, the specific heat vanishes at low termperature. The characteristic temperature T_0, above which the Dulong and Petit law holds, may be above or below room temperature, depending on the solid.

The explanation for the “freezing-out” of degrees of freedom is provided by quantum mechanics. As we have just seen, for a harmonic oscillator,

$$U = \frac{h\nu}{2}\coth\frac{\beta h\nu}{2} = \frac{h\nu}{2} + \frac{h\nu}{e^{\beta h\nu} - 1}, \tag{7.4}$$

and then for one oscillator

$$c = \frac{\partial U}{\partial T} = \frac{\partial \beta}{\partial T}\frac{\partial U}{\partial \beta} = -\frac{1}{kT^2}\left[-\frac{(h\nu)^2 e^{\beta h\nu}}{(e^{\beta h\nu} - 1)^2}\right]$$

$$
\begin{aligned}
&= k\left(\frac{h\nu}{kT}\right)^2 \frac{1}{\left(e^{\beta h\nu/2}-e^{-\beta h\nu/2}\right)^2} \\
&= k\left(\frac{h\nu\beta}{2}\right)^2 \frac{1}{(\sinh\beta h\nu/2)^2}. \qquad (7.5)
\end{aligned}
$$

The limits are

- $T\to\infty$ ($\beta\to 0$), $c\to k$,
- $T\to 0$ ($\beta\to\infty$), $c\to 0$, exponentially fast.

The *Einstein* theory of specific heats consisted in multiplying this by $3N$, but while this agrees with the Dulong and Petit law at high temperature, this does not agree with the data at low temperature. Instead, *Debye* proposed that the oscillators had a range of frequencies between 0 and $\nu_{\max}$, and that, in fact, they were elastic waves of momentum $p = h\nu/v_s$, where v_s is the speed of sound. The density of modes is

$$dN = 3\frac{V4\pi dp\, p^2}{h^3} = \frac{12\pi V\nu^2\, d\nu}{v_s^3}. \qquad (7.6)$$

(Another derivation of this is given in Sec. 7.1.) Here the factor of 3 comes from the three polarization of the elastic waves, and it is assumed, for simplicity, that the sound velocity v_s is the same for both longitudinal and transverse polarizations. Then, from Eq. (7.5),

$$c = \frac{12\pi V}{v_s^3}k\int_0^{\nu_{\max}} \frac{\nu^2(h\nu/2kT)^2}{(\sinh h\nu/2kT)^2}d\nu. \qquad (7.7)$$

We determine $\nu_{\max}$ by requiring that we have the correct number of degrees of freedom:

$$3N = \int dN = \frac{12\pi V}{v_s^3}\int_0^{\nu_{\max}} \nu^2 d\nu = \frac{4\pi V}{v_s^3}\nu_{\max}^3, \qquad (7.8)$$

or

$$\nu_{\max} = \left(\frac{3N}{4\pi V}\right)^{1/3} v_s. \qquad (7.9)$$

The density of states, $dN/d\nu$ is proportional to ν^2 between $\nu = 0$ and $\nu_{\max}$. The result for the specific heat is usually written in terms of the Debye temperature, defined by

$$k\Theta = h\nu_{\max}. \qquad (7.10)$$

Then the specific heat is

$$
\begin{aligned}
c &= \frac{12\pi kV}{v_s^3}\left(\frac{2kT}{h}\right)^3 \int_0^{h\nu_{\max}/2kT} dx\frac{x^4}{\sinh^2 x} \\
&= 72Nk\left(\frac{T}{\Theta}\right)^3 \int_0^{\Theta/2T} dx\frac{x^4}{\sinh^2 x}, \\
&= 9Nk\left(\frac{T}{\Theta}\right)^3 \int_0^{\Theta/T} dy\frac{y^4\, e^y}{(e^y-1)^2}, \qquad (7.11)
\end{aligned}
$$

where in the last step we substituted $y = 2x$. Thus the specific heat is

$$c = 3Nkf\left(\frac{\Theta}{T}\right), \tag{7.12}$$

where the Debye function is

$$f(z) = \frac{3}{z^3}\int_0^z dy \frac{y^4\, e^y}{(e^y-1)^2}. \tag{7.13}$$

Here, the limiting values of the Debye function are

$$f(z) \to \begin{cases} 1, & z \to 0\,(T\to\infty), \\ \frac{4}{5}\pi^4\frac{1}{z^3}, & z\to\infty\,(T\to 0). \end{cases} \tag{7.14}$$

The latter is true because

$$I = \int_0^\infty dy\, \frac{y^4\, e^y}{(e^y-1)^2} = -\frac{d}{d\lambda}\int_0^\infty dy \frac{y^3}{e^{\lambda y}-1}\bigg|_{\lambda=1}, \tag{7.15}$$

where generally

$$\begin{aligned}\int_0^\infty dt \frac{t^n}{e^t-1} &= \int_0^\infty dt\, t^n \frac{e^{-t}}{1-e^{-t}} \\ &= \int_0^\infty dt\, t^n \sum_{k=1}^\infty e^{-kt} = \sum_{k=1}^\infty \int_0^\infty dt\, t^n e^{-kt} \\ &= \sum_{k=1}^\infty \frac{1}{k^{n+1}}\Gamma(n+1) = \zeta(n+1)\Gamma(n+1), \end{aligned} \tag{7.16}$$

where $\zeta(s)$ is the Riemann zeta function. Thus

$$I = -\frac{d}{d\lambda}\frac{1}{\lambda^4}\Gamma(4)\zeta(4)\bigg|_{\lambda=1} = \frac{4\pi^4}{15}, \tag{7.17}$$

because $\zeta(4) = \pi^4/90$. Thus, in the Debye model, at low temperatures,

$$c \sim 3Nk\frac{4}{5}\pi^4\left(\frac{T}{\Theta}\right)^3, \quad T \ll \Theta. \tag{7.18}$$

The Debye function is shown in Fig. 7.1. In reality, this is not particularly realistic, because the ν spectrum is much more complicated in solids.

7.1 Alternative Derivation of the Number of Modes

We conclude this chapter by rederiving the number of modes, Eq. (7.6). Consider a periodic lattice in one dimension, that is, equally spaced points (spacing a) from 1 to M, and consider periodic waves $\psi(x)$ such that

$$\psi(0) = \psi(M). \tag{7.19}$$

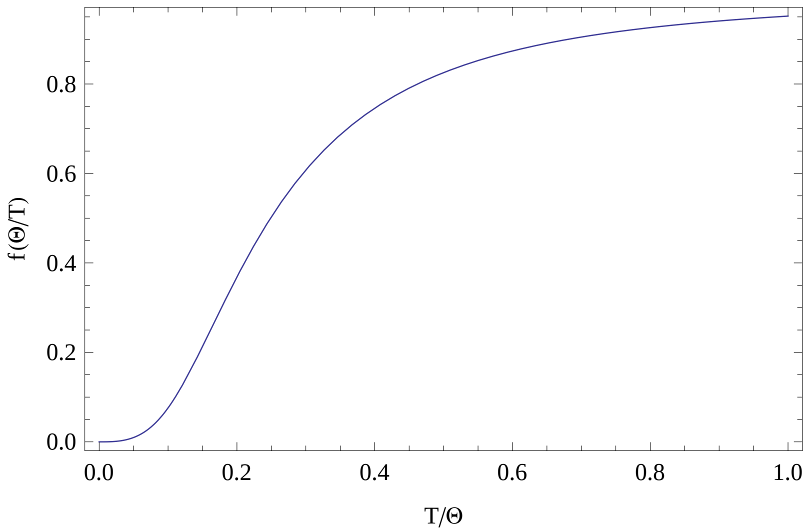

Figure 7.1: Plot of the Debye function $f(1/t)$, Eq. (7.13), as a function of $t = T/\Theta$.

Because a plane wave has the form

$$\psi(x) = e^{ipx}, \tag{7.20}$$

the periodicity condition implies

$$e^{ipMa} = 1, \tag{7.21}$$

so the possible wavenumbers are

$$p_k = \frac{2\pi}{Ma}k, \quad k = 1, 2, \ldots, M. \tag{7.22}$$

In three dimensions, the number of modes, for a given polarization, is

$$dN = d^3\mathbf{k} = \left(\frac{Ma}{2\pi}\right)^3 d^3\mathbf{p} = \frac{V}{(2\pi)^3} d^3\mathbf{p}. \tag{7.23}$$

But the relation between $p = |\mathbf{p}|$ and the wavelength is given by

$$e^{ip\lambda} = e^{i2\pi}, \Rightarrow p = \frac{2\pi}{\lambda} = 2\pi\frac{\nu}{v_s}, \tag{7.24}$$

which implies

$$dN = \frac{V}{v_s^3} 4\pi\nu^2 d\nu, \tag{7.25}$$

which is Eq. (7.6), apart from the factor of three reflecting the three polarizations of sound waves.