

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:

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

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

$$U = 3NkT, \quad (7.2)$$

and so the specific heat at constant volume is

$$c_V = 3Nk = 3R \text{ per mole}, \quad (7.3)$$

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 temperature. 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,

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

and then for one oscillator

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

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

The limits are

- $T \rightarrow \infty$ ($\beta \rightarrow 0$), $c \rightarrow k$,
- $T \rightarrow 0$ ($\beta \rightarrow \infty$), $c \rightarrow 0$, 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 ν_{\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

$$dN = 3 \frac{V 4\pi dp p^2}{h^3} = \frac{12\pi V \nu^2 d\nu}{v_s^3}. \tag{7.6}$$

(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),

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

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

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

or

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

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

$$k\Theta = h\nu_{\max}. \tag{7.10}$$

Then the specific heat is

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

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

$$c = 3Nk f\left(\frac{\Theta}{T}\right), \quad (7.12)$$

where the Debye function is

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

Here, the limiting values of the Debye function are

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

The latter is true because

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

where generally

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

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

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

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

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

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

$$\psi(0) = \psi(M). \quad (7.19)$$

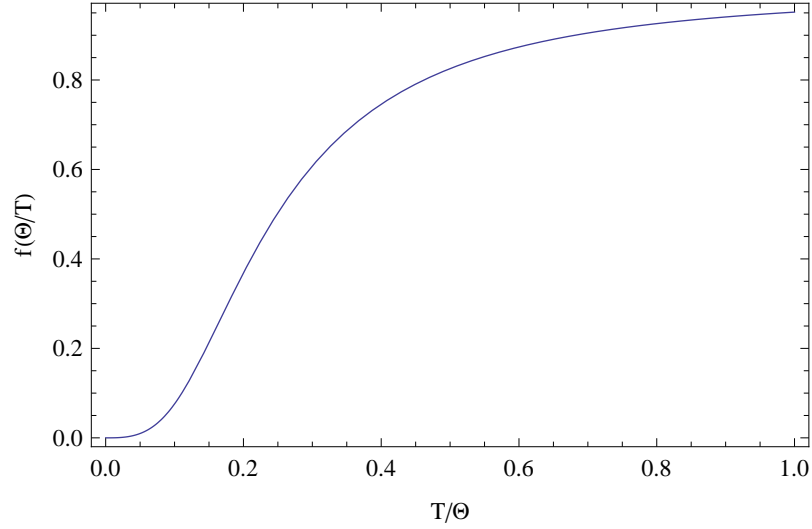


Figure 7.1: Plot of the Debye function $f(1/t)$, Eq. (7.13), as a function of $t = T/\Theta$.

Because a plane wave has the form

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

the periodicity condition implies

$$e^{ipMa} = 1, \quad (7.21)$$

so the possible wavenumbers are

$$p_k = \frac{2\pi}{Ma}k, \quad k = 1, 2, \dots, M. \quad (7.22)$$

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

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

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

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

which implies

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

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