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:

\[ H_{\text{atom}} = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 r^2. \]  

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

\[ U = 3NkT, \]  

and so the specific heat at constant volume is

\[ c_V = 3Nk = 3R \text{ per mole}, \]  

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,

\[ U = \frac{\hbar\nu}{2} \coth \frac{\beta\hbar\nu}{2} = \frac{\hbar\nu}{2} + \frac{\hbar\nu}{e^{\beta\hbar\nu} - 1}, \]  

and then for one oscillator

\[ c = \frac{\partial U}{\partial T} = \frac{\partial \beta}{\partial T} \frac{\partial U}{\partial \beta} = -\frac{1}{kT^2} \left[ \frac{(\hbar\nu)^2 e^{\beta\hbar\nu}}{(e^{\beta\hbar\nu} - 1)^2} \right] \]
\[
= k \left( \frac{h \nu}{kT} \right)^2 \frac{1}{(e^{\beta h \nu/2} - e^{-\beta h \nu/2})^2}
\]
\[
= k \left( \frac{h \nu \beta}{2} \right)^2 \frac{1}{(\sinh \beta h \nu/2)^2}.
\] (7.5)

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 \( \nu_{\text{max}} \), 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

\[
dN = 3 \frac{V 4 \pi dp p^2}{h^3} = \frac{12 \pi V \nu^2 d\nu}{v_s^3}.
\] (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),

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

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

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

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

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

\[
k \Theta = h \nu_{\text{max}}.
\] (7.10)

Then the specific heat is

\[
c = \frac{12 \pi kV}{v_s^3} \left( \frac{2kT}{h} \right)^3 \int_0^{h \nu_{\text{max}}/2kT} dx \frac{x^4}{\sinh^2 x}
\]
\[
= 72Nk \left( \frac{T}{\Theta} \right)^3 \int_0^{\Theta / 2T} dx \frac{x^4}{\sinh^2 x},
\]
\[
= 9Nk \left( \frac{T}{\Theta} \right)^3 \int_0^{\Theta / T} dy \frac{y^4 e^y}{(e^y - 1)^2},
\] (7.11)
7.1. ALTERNATIVE DERIVATION OF THE NUMBER OF MODES

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

\[
c = 3Nk f \left( \frac{\Theta}{T} \right),
\]

(7.12)

where the Debye function is

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

(7.13)

Here, the limiting values of the Debye function are

\[
f(z) \to \begin{cases} 1, & z \to 0 (T \to \infty), \\ \frac{\pi^4}{6}, & z \to \infty (T \to 0). \end{cases}
\]

(7.14)

The latter is true because

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

(7.15)

where generally

\[
\int_0^\infty dt \frac{t^n}{e^t - 1} = \int_0^\infty dt t^n \frac{e^{-t}}{1 - e^{-t}}
\]

\[
= \int_0^\infty dt t^n \sum_{k=1}^{\infty} e^{-kt} = \sum_{k=1}^{\infty} \int_0^\infty dt t^n e^{-kt}
\]

\[
= \sum_{k=1}^{\infty} \frac{1}{k^{n+1}} \Gamma(n+1) = \zeta(n+1) \Gamma(n+1),
\]

(7.16)

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

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

(7.17)

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

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

(7.18)

The Debye function is shown in Fig. 7.1. In reality, this is not particularly realistic, because the \( \nu \) 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

\[
\psi(0) = \psi(M).
\]

(7.19)
Because a plane wave has the form
\[ \psi(x) = e^{ipx}, \]
(7.20)
the periodicity condition implies
\[ e^{ipMa} = 1, \]
(7.21)
so the possible wavenumbers are
\[ p_k = \frac{2\pi}{Ma}k, \quad k = 1, 2, \ldots, M. \]
(7.22)
In three dimensions, the number of modes, for a given polarization, is
\[ dN = d^3k = \left( \frac{Ma}{2\pi} \right)^3 d^3p = \frac{V}{(2\pi)^3} d^3p. \]
(7.23)
But the relation between \( p = |p| \) and the wavelength is given by
\[ e^{ip\lambda} = e^{i2\pi}, \Rightarrow p = \frac{2\pi}{\lambda} = 2\pi \frac{\nu}{v_s}, \]
(7.24)
which implies
\[ dN = \frac{V}{v_s^3} \pi \nu^2 d\nu, \]
(7.25)
which is Eq. (7.6), apart from the factor of three reflecting the three polarizations of sound waves.