

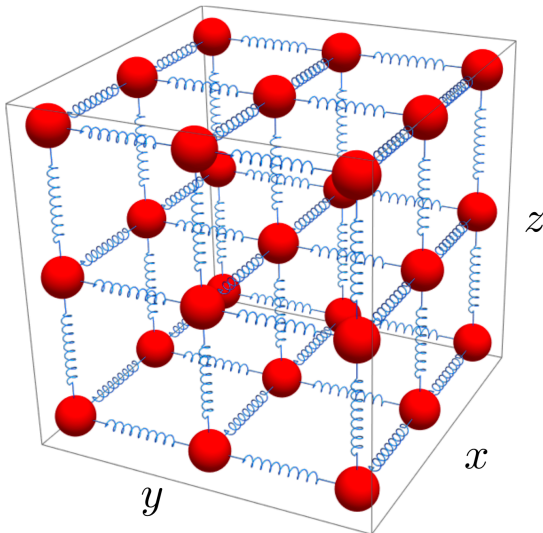
8 Einstein's model of a simple solid

Here we apply the Boltzmann distribution to the vibrational energy of atoms in a solid. In so doing we use a fundamental model of quantum physics—the quantum harmonic oscillator.

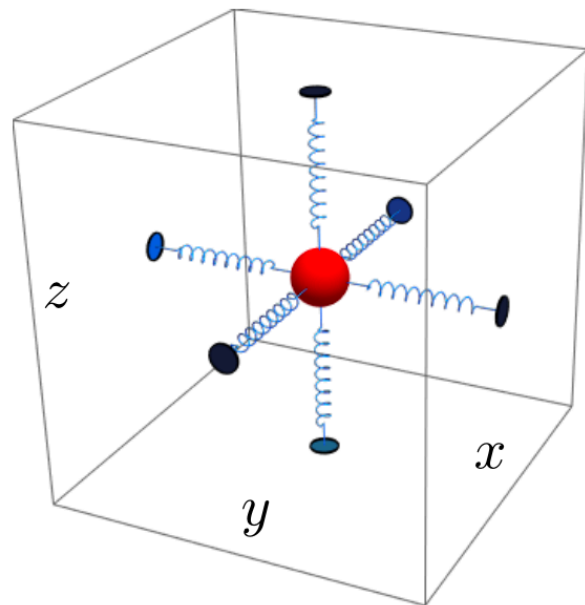
8.1 Simple model of a solid

See Mandl 6.2

Recall from your first year Properties of Matter course that in a crystalline solid, atoms sit on the sites of a regular array (lattice). A model for the vibrational motion of the atoms about their equilibrium positions (lattice sites) is to consider the atoms attached to each other by springs (see Figure 1a). However this is a (strongly) interacting system since energy is stored in interaction potentials (the springs) between atoms.



(a) Model of crystal solid as atoms connect by harmonic springs.



(b) Model of each atom as independent harmonic oscillator

We seek a weakly interacting system that models the behaviour. A simple approximation is illustrated in Figure 1b. Each atom sits in its own harmonic potential and the motion of atoms independent of the others. This is the Einstein model.

Let us first consider the system classically. Each oscillator has energy

$$\varepsilon = \frac{1}{2}\kappa x^2 + \frac{1}{2}mv^2$$

where x is the displacement from equilibrium position. Thus in 3d the system has $N \times 3 \times 2$ quadratic contributions (N particles, 3 dimensions, P.E. + K.E.) to the energy. The equipartition principle then implies that the energy and heat capacity of the system should be

$$\overline{E} = 6N \times \frac{1}{2}kT = 3NkT$$

$$C_V = \frac{\partial \overline{E}}{\partial T} = 3Nk$$

If you have forgotten the equipartition principle you can find it in your first year Properties of Matter notes. However we will understand it at a deeper level in a few chapters' time.

The prediction for the heat capacity was well borne out experimentally for many monoatomic solids and is known as the Dulong–Petit law. However diamond has a smaller heat capacity than the Dulong–Petit law predicts. Einstein showed that this is a quantum effect.

To understand why at a qualitative level quantum effects are important in diamond. Recall that diamond is very hard. This means that the ‘spring constant’ of the classical oscillator modelling each atom in Figure 1 is very large. Therefore the frequency of the oscillators is very large and the typical displacements very small. This last fact implies that quantum effects have to be taken into account—roughly speaking, from the uncertainty principle if the displacements are very small then we know the atoms’ positions with high accuracy, therefore there must be uncertainty in the momenta (velocities).

8.2 Statistical mechanics of the quantum harmonic oscillator

From quantum mechanics recall that a one dimensional harmonic oscillator has energy levels

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

where $n = 0, 1, 2 \dots$. The ground state energy $n = 0$ is $\frac{1}{2}\hbar\omega$. The generalisation to a three-dimensional oscillator is easy

$$\varepsilon_{3d} = \left(n_x + n_y + n_z + \frac{3}{2}\right) \hbar\omega$$

Einstein’s model is a system of N 3d quantum oscillators all with the same frequency ω in thermal equilibrium; ω is chosen to fit the experimental data.

From the statistical mechanics of weakly interacting systems we have $Z = [Z(1)]^N$. Now since the energy of an oscillator is a sum of three similar contributions we will have a further factorisation (see chapter 6.3) and

$$Z = [Z(1)]^N = [Z_{1d}(1)]^{3N}$$

where $Z_{1d}(1)$ is the partition function for a single 1d oscillator. The task reduces to the calculation of $Z_{1d}(1)$

$$Z_{1d}(1) = \sum_{n=0}^{\infty} \exp\left(-\beta\hbar\omega\left[n + \frac{1}{2}\right]\right)$$

To evaluate the sum recall the geometric series

$$\sum_{n=0}^{\infty} a^n = \frac{1}{1-a}$$

Thus

$$Z_{1d}(1) = \frac{\exp\left(-\frac{x}{2}\right)}{1 - \exp(-x)}$$

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

8.3 Thermodynamic properties

We now turn the handle to crank out the thermodynamics variables. First note

$$\overline{E} = 3N\overline{\varepsilon} = 3N\hbar\omega\left(\overline{n} + \frac{1}{2}\right)$$

It is easiest to calculate ε directly from the relation

$$\begin{aligned}\overline{\varepsilon} &= -\frac{\partial}{\partial\beta} \ln Z_{1d}(1) = -\frac{dx}{d\beta} \frac{\partial}{\partial x} \ln Z_{1d}(1) \\ &= -\hbar\omega \frac{\partial}{\partial x} \left[-\ln(1 - \exp(-x)) - \frac{x}{2} \right]\end{aligned}$$

$$= \hbar\omega \left[\frac{\exp(-x)}{1 - \exp(-x)} + \frac{1}{2} \right]$$

and we see

$$\bar{n} = \frac{\exp(-x)}{1 - \exp(-x)} = \frac{1}{\exp(x) - 1}$$

🔥 Expand to see an alternative derivation

Aside: An alternative derivation is to use the Boltzmann distribution P_n for the levels n of a 1d oscillator explicitly

$$\bar{n} = \sum_{n=0}^{\infty} P_n n = \frac{1}{Z_{1d}(1)} \sum_{n=0}^{\infty} n \exp \left[-x \left(n + \frac{1}{2} \right) \right]$$

then use the identity

$$\sum_{n=0}^{\infty} n a^n = a \frac{d}{da} \sum_{n=0}^{\infty} a^n = a \frac{d}{da} \frac{1}{1-a} = \frac{a}{(1-a)^2}$$

The mean total energy is given by

$$\bar{E} = 3N\hbar\omega \left[\frac{\exp(-x)}{1 - \exp(-x)} + \frac{1}{2} \right]$$

and the heat capacity is given by

$$C_V = \left(\frac{\partial \bar{E}}{\partial T} \right)_V = \left(\frac{\partial x}{\partial T} \right)_\omega \left(\frac{\partial \bar{E}}{\partial x} \right)_\omega$$

Note that here the ‘constant volume’ constraint on the partial derivative is the same as the ‘constant ω ’ constraint. This is because the only way volume (or any other variable except temperature) can enter into the model is through the parameter ω .

We find

$$C_V = -3N \frac{\hbar\omega}{kT^2} \frac{d}{dx} \left[\frac{1}{\exp(x) - 1} \right] = 3Nk \frac{x^2 \exp(x)}{(\exp(x) - 1)^2}$$

8.4 High and low temperature behaviour

To define the high temperature and low temperature regimes we define a characteristic temperature T^* defined by $x = 1$ i.e. when kT equals the excitation energy $\hbar\omega$

$$T^* = \frac{\hbar\omega}{k}$$

Thus in the high temperature regime $T \gg T^*$ ($x \ll 1$) we find

$$\bar{n} \approx \frac{1}{1 + x + \dots - 1} \approx \frac{1}{x} = \frac{kT}{\hbar\omega}$$

$$\bar{E} \approx 3NkT + \frac{3}{2}N\hbar\omega$$

we see that \bar{n} and hence $\bar{\varepsilon}$ and \bar{E} increase linearly with temperature. Moreover the heat capacity becomes

$$C_V = \left(\frac{\partial \bar{E}}{\partial T} \right)_V \approx 3Nk$$

and we recover the Dulong–Petit law.

In the low temperature regime $T \ll T^*$ ($x \gg 1$) we have

$$\bar{n} \approx \exp(-x)$$

$$\frac{C_V}{3Nk} \approx x^2 \exp(-x)$$

The mean energy level \bar{n} tends to zero meaning most oscillators are in the ground state; the heat capacity is very much less than $3Nk$.

Thus when $x = \frac{\hbar\omega}{kT}$ is large, quantum effects, in particular the effect of a discrete gap between the ground state and first excited state, become important. The Einstein model quite successfully explained the experimentally observed heat capacity of diamond (see Mandl 6.2). However the very low temperature behaviour of the heat capacity was still not quite right. In fact a T^3 dependence appeared to emerge. This can be explained by an elaborated version of the Einstein theory known as the Debye theory.

When $x = \frac{\hbar\omega}{kT}$ is small we recover the ‘classical’ results i.e. results where Planck’s constant does not appear in the thermodynamic quantities (except as an arbitrary constant in the energy). Quite generally high temperature is the classical limit (if indeed one exists).