

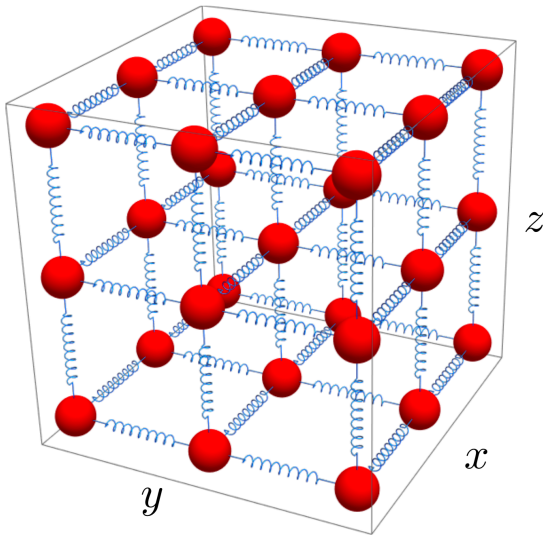
8 Einstein's model of a simple solid

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.

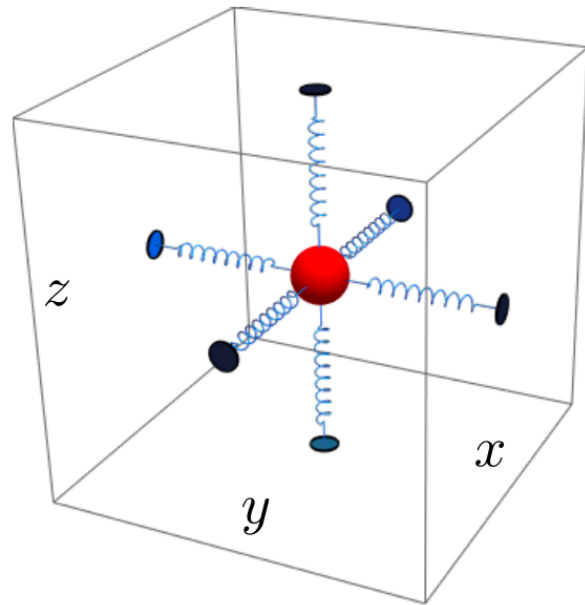
8.1 Simple model of a solid

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 theorem then implies that the energy and heat capacity of the system should be

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

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

More on the Equipartition Theorem

For each degree of freedom of a system with an energy which is quadratic in either the coordinate or the momentum, the average energy is $kT/2$ and its contribution to the heat capacity is $k/2$, at high enough temperatures.

The equipartition theorem is applicable only when the system can be described classically and is applicable only to each term in the energy that is proportional to a coordinate squared. This coordinate must take on a continuum of values from $-\infty$ to $+\infty$. Here are some examples from classical mechanical systems.

- **Vibrations:**

$$E_{vib} = \frac{1}{2}m\dot{x}^2 + \frac{1}{2}kx^2$$

Two quadratic degrees of freedom, hence $E \rightarrow kT$ as $T \rightarrow \infty$.

- **Rotations:** Two perpendicular axes about which a molecule can rotate,

$$E_{rot} = \frac{1}{2}I_1\dot{\theta}_1^2 + \frac{1}{2}I_2\dot{\theta}_2^2$$

Two quadratic degrees of freedom, hence $E \rightarrow kT$ as $T \rightarrow \infty$.

- **Translations:**

$$E_{tr} = \frac{1}{2}m(\dot{x}^2 + \dot{y}^2 + \dot{z}^2)$$

Three quadratic degrees of freedom, hence $E \rightarrow \frac{3}{2}kT$ as $T \rightarrow \infty$.

The equipartition theorem is a fundamental principle in classical physics. However, from the perspective of modern statistical mechanics, it fails when the energy level separation is significantly larger than thermal energy. In such cases, the heat capacity associated with that degree of freedom decreases, eventually approaching zero at low temperatures. This phenomenon is referred to as “freezing out” of the degree of freedom. A common example is the vibrational degrees of freedom, which are typically frozen out at room temperature.

More specifically, equipartition holds:

- for **vibrations**, when $T \gg \hbar\omega/k \approx 10^3 K$;
- for **rotations**, when $T \gg \hbar^2/Ik \approx 10 - 100 K$;
- for **translations**, when $T \gg \hbar^2/(mV^{2/3}k) \approx 10^{-14} K$.

Thus, at room temperature, only the rotational and translational degrees of freedom can be treated classically, giving $C_V = \frac{3}{2}R$ for monatomic gases and $C_V = \frac{5}{2}R$ for diatomic gases, for the molar heat capacity.

Using the equipartition theorem, we can estimate the heat capacities of various substances by counting their quadratic degrees of freedom. For example, in a solid, each atom can vibrate in three directions, leading to an expected molar heat capacity of $(3R)$. This prediction aligns with the **Dulong-Petit law**, which accurately describes the heat capacities of many solids at room temperature.

If you have forgotten the equipartition theorem, you can find it in your first year Properties of Matter notes and in the note above. 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, valid for $|a| < 1$

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

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. In essence the central weakness of the Einstein model is its neglect of collective motion of atoms (so called phonons) which exhibit a spectrum of frequencies.

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).