Many macroscopic properties, such as latent heat, surface tension, bulk modulus and so on, can be related to atomic properties. Thus, based on macroscopic properties that you know, you can infer microscopic quantities of interest (e.g. atomic spacing). Conversely, given known atomic properties (such as characteristic bond energy) you can infer macroscopic properties.

**Atom size, spacing and energy**

All atoms have (roughly) the same radius: 1 Å (=0.1 nm).

The number of atoms in one kg is \( N_A / \mu \) where \( \mu \) is the mass number (in kg) and \( N_A \) is Avogadro’s number. Assuming a typical density of \( \rho = 3000 \text{ kg m}^{-3} \) we have the volume of one atom \( \sim (2a)^3 \sim \mu / N_A \rho \) where \( a \) is the atomic radius. This gives us \( a \sim 1 \text{ Å} \).

Most of the atom is empty space; the nucleus is only a very small fraction of the total volume (see below).

Gas densities are typically \( 10^{-3} \) of solid densities, implying that the inter-atom spacing in gases is roughly 10 Å.

**Binding energy**

We’ll define the binding energy as the energy required to break *inter*-molecular bonds. *Intra*-molecular bonds are stronger: boiling water breaks the bonds between water molecules, but doesn’t decompose a water molecule into H and O. The binding energy is fundamental to processes such as chemical reactions, thermal expansion and latent heat. Intra-molecular bonds are typically a few eV; binding energies for liquids are a few tenths of an eV; solid binding energies are roughly 1 eV. See the “Binding Energies” handout for more details.

You can estimate typical binding energies \( E_c \) by consideration of e.g. a bar of chocolate. If an 0.1 kg bar has a calorific value of 200 kCal (800 kJ) then the implied binding energy is a few eV (1 eV \( \approx 2 \times 10^{-19} \text{ J} \)) per atom.

A very useful conversion is that 10 eV/molecule \( \approx 1 \text{ MJ/mole} \).

**Example** Fabric colours get bleached by UV light. Estimate Planck’s constant (\( h \), not \( \hbar \)).
Example The latent heat of vapourization of water is about 2 MJ/kg. What’s the implied binding energy? Also estimate the surface tension of water.

Speed and mean free path

Once we’ve calculated the binding energy, we can calculate the speed of an atom or an electron in a solid assuming binding energy \( \approx \) kinetic energy:

\[
v \sim \left( \frac{E_c}{m} \right)^{1/2}
\]

The speed of an atom controls the sound speed of the material. For a typical intermediate-mass solid the sound speed is \( \approx 2 \text{ km s}^{-1} \). Note that the sound speed in a gas is different because the atoms are not bound to each other and move at a rate controlled by their temperature.

The speed of an electron is faster by a factor of \( \sqrt{m/m_e} \) or roughly 300. Chemical reactions involve transfer of electrons; the timescale for a chemical reaction to occur is \( \sim a/v \) or roughly \( 10^{-16} \text{ s} \) (100 attoseconds).

The mean free path \( \lambda \) is an important quantity which controls how often particles interact with each other. We can derive \( \lambda \) by considering the volume swept out during an interaction with one other particle:

\[
n\pi a^2 \lambda \sim 1
\]

where \( n \) is the number density of molecules \( (\rho N_A/\mu) \). Note that this quantity is independent of molecular speed, and proportional to density. For solids, the mean free path \( \sim a \), as expected. For gases, the density is \( 10^3 \) times lower and so the mean free path \( \sim 10^{-7} \text{ m} \).

Gas transport processes (e.g. heat, sound or chemistry) depend on molecules colliding with each other. The thermal velocity of the gas molecules depends on their temperature:

\[
v \sim \left( \frac{3kT}{m} \right)^{1/2}
\]

where gases have a thermal energy \( \approx \frac{3}{2}kT \) and \( k \) is Boltzmann’s constant (= \( R/N_A \)). For gases, the thermal velocity is also the sound speed, \( \approx 400 \text{ m s}^{-1} \) for \( N_2 \) at 300 K. For solids, the sound speed is much larger than the thermal velocity (because the energy associated with bonds is higher than the thermal energy at room temperature).

The diffusivity of gases \( \kappa \) is given by

\[
\kappa \sim v\lambda
\]

or roughly \( 10^{-4} \text{ m}^2 \text{ s}^{-1} \).

For solids and liquids, heat is conducted not by molecular collisions, but by molecular vibrations (phonons). The vibration speed is roughly 3 times higher than the thermal speed (because the binding energy is larger - see below), but the mean free path \( \sim a \) is \( 10^3 \) times smaller, resulting in smaller diffusivities in solids and liquids (typical values are \( 10^{-6} - 10^{-7} \text{ m}^2 \text{ s}^{-1} \)).

Example How long does it take perfume to diffuse across a room?

Thermal and vibrational properties
The potential energy $E$ due to charge of a proton-electron pair depends on their separation $a$: $E \sim 1/a$. This implies that a change in atomic radius $\Delta a$ requires energy:

$$\Delta E \sim E_c \frac{\Delta a}{a}$$

where we have assumed that the potential energy represents a significant fraction of the total binding energy $E_c$. Assuming that this extra energy is thermal ($kT$) we derive

$$\frac{\Delta a}{a} = \frac{k}{E_c} T = \alpha T$$

where $\alpha$ is a macroscopic quantity known as the **thermal expansivity** ($K^{-1}$). We can immediately see that a binding energy of 1 eV gives rise to a thermal expansivity $\sim 10^{-4}$ K$^{-1}$.

The force between two particles is $F \sim E_c/a$. We can define an atomic “spring constant” $k_{spring}$ using $F = k_{spring}a$ (see the Oscillators chapter) which gives us

$$k_{spring} \sim \frac{E_c}{a^2}$$

The vibration frequency $f$ is given by

$$f \sim \sqrt{\frac{k}{m}} \sim \sqrt{\frac{E_c}{ma^2}} \sim \frac{v_{sound}}{a}$$

The thermal conductivity $K$ is given by $\kappa \rho C_p$ where $C_p$ is the specific heat capacity and $\kappa$ is the thermal diffusivity. Consideration of an ideal gas shows that $C_p \sim R$ (actually $3R$) per mole. Using the results for gas diffusivity from above, we get a typical thermal conductivity for a gas of $\sim 10^{-2}$ W m$^{-1}$ K$^{-1}$.

We’ll talk more about thermal conductivity of materials when we start to consider heat transfer.

**Example** Given the latent heat of solid nitrogen, how would you go about determining its bulk modulus? [This is a real example. It helps to remember that pressure = work per unit volume.]

**Example** What wavelength of light is required to cause dissociation of a water molecule?

### Solid-state diffusion and rheology

In reality, at any given temperature atoms exhibit a range of different vibration energies, given by the **Boltzmann distribution**. We can write the fraction of atoms $p$ having a vibrational (thermal) energy exceeding the binding energy $E_c$ as

$$p \sim \left(\frac{E_c}{kT}\right)^{1/2} e^{-E_c/kT}$$

where we are assuming that $kT \ll E_c$ (as is appropriate for a solid).

Real atomic lattices contain vacancies, which allow atoms to migrate. The probability of a particular atom jumping is $p$, so the overall diffusivity $D$ is just $p v a$, where $v \sim (E_c/m)^{1/2}$ is the sound speed as before.

So we can write the diffusivity as

$$D \sim \frac{E_c a}{(mkT)^{1/2}} e^{-E_c/kT}$$
The exponential term shows that diffusion is a strong function of temperature, and will be very slow for \( T \ll E_c/k \). Note also that it is the binding energy (termed the activation energy in this context) which controls the temperature sensitivity. The pre-exponential term (also called \( D_0 \)) shows that atomic mass matters: thus, hydrogen diffuses more rapidly than other substances (a problem in power plant construction and also in olivine crystals).

Application of stress causes vacancies to migrate and results in the crystal deforming. This effect is the cause of solid-state viscosity. So we would expect viscosity to be strongly temperature-dependent (it is), and that the absolute viscosity has the same kind of dependence as \( D_0 \) (it does).

The viscosity of liquids does not exhibit the same kind of temperature-dependence as solids, but can also be calculated from first principles. If you think about (dynamic) viscosity as involving momentum transfer between rows of atoms you can see from dimensional analysis that \( \eta \sim mf/a \). This can then be rewritten as \( \eta \sim (E_c \rho/a)^{1/2} \). For typical values you get viscosities of order \( 10^{-3} \) Pa s, which is about right.

Friction is hard to derive in an order of magnitude sense. The observed fact that the frictional resistance is proportional to the force and not the stress is not readily derived by order of magnitude arguments.

**Useful numbers**
- charge on electron \( e = 2 \times 10^{-19} \) C
- Planck constant \( \hbar = 10^{-34} \) in SI units
- typical atomic radius 1 Å
- typical binding energy = 0.1 eV (liquids), 1 eV (solids), 10 eV (intra-molecular bonds)
- Earth atmospheric density (surface) 1 kg m\(^{-3}\)
- wavelength of visible light \( 3 \times 10^{-7} \) m

**Afterthought: Heisenberg and all that**
Consider a hydrogen atom (one proton orbited by one electron). The potential energy (due to charge) is given by

\[
E_1 = -C \frac{e^2}{a}
\]

where \( a \) is the proton-electron spacing, \( e \) is the charge on an electron and \( C \) is a constant \( \sim 10^{10} \) in SI units.

The kinetic energy of the electron can be assessed by using the uncertainty principle:

\[
\Delta x \Delta p \sim \hbar
\]

where \( \hbar = 10^{-34} \) in SI units. Here \( \Delta x \) is the position uncertainty and \( \Delta p \) is the momentum uncertainty. We can use this to obtain the kinetic energy

\[
E_2 \sim \frac{\hbar^2}{a^2 m_e}
\]

where \( m_e \) is the mass of an electron (\( \approx 1/2000 \) of a proton) and we have assumed that \( \Delta x \sim a \) and the momentum \( \sim \Delta p \).

The kinetic energy can also be converted to an effective temperature \( T \) using \( E_2 = kT \) where \( k \) is Boltzmann’s constant (\( = R/N_A \) where \( R \) is the gas constant).
Guessing that the kinetic and potential energies are comparable, we can solve for $a$:

$$ a \sim \frac{\hbar^2}{Ce^2 m_e} \sim 1 \text{ Å} $$

Once we’ve solved for $a$, we can obtain the **binding energy** $E_c$ (per atom or molecule):

$$ E_c \sim \left( \frac{Ce^2}{\hbar} \right)^2 m_e \sim 10 \text{ eV} $$