

EART265 Order of Magnitude Phys & Chem
Lecture Outline 2
Properties of Materials

Many macroscopic properties, such as latent heat, surface tension, bulk modulus and so on, can be related to atomic properties.

Atom size, spacing and energy

All atoms have (roughly) the same radius: $1 \text{ \AA} (=0.1 \text{ nm})$.

The number of atoms in one kg is N_A/μ where μ 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 $a \sim 1 \text{ \AA}$.

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 \AA .

Consider a hydrogen atom (one proton orbited by one electron). The potential energy (due to charge) is given by

$$E_1 \sim -C \frac{e^2}{a} \quad (1)$$

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 Δx is the position uncertainty and Δp is the momentum uncertainty. This gives us the kinetic energy

$$E_2 \sim \frac{\hbar^2}{a^2} \frac{1}{m_e}$$

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

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 :

$$a \sim \frac{\hbar^2}{C e^2} \frac{1}{m_e} \sim 1 \text{ \AA}$$

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

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

The binding energy is fundamental to processes involving stretching or breaking of bonds, such as chemical reactions, thermal expansion and latent heat. Binding energies of molecules are a bit smaller than that calculated above because the spacing is larger; a good ballpark figure is 3 eV.

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

Example Use the calorific value of a chocolate bar to estimate the binding energy of an H-C bond

Example Estimate the temperatures required to initiate fusion inside a star

Example Estimate the surface tension of water and the size of raindrops on Titan.

Example Estimate the latent heat of vapourization of water, and the temperature at which vapourization should occur

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} s (100 attoseconds).

The **mean free path** λ is an important quantity which controls how often particles interact with each other. We can derive λ 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 $= \frac{3}{2}kT$. 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 κ 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 higher than the thermal speed, but the mean free path $\sim a$ is smaller, resulting in smaller diffusivities in solids and liquids (typical values are $10^{-6} - 10^{-7} \text{ m}^2 \text{ s}^{-1}$).

Example If the energies associated with the nucleus are $\sim 1 \text{ MeV}$, what are the characteristic size, speed, timescale and density of the nucleus?

Example Derive an expression for the **Fermi velocity** of an electron, in terms of \hbar, a and m_e .

Example What wavelength of light is associated with electron exchange?

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

Thermal and vibrational properties

Making use of equation (1), we can show that a change in atomic radius Δa requires energy:

$$\Delta E \sim \frac{Ce^2\Delta a}{a^2} \sim E_c \frac{\Delta a}{a}$$

Assuming that this extra energy is thermal (kT) we derive

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

where α 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

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

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

For solids and liquids, C_p (per mole) is similar to that of gases, but κ and ρ are different. We end up deriving a thermal conductivity of $\sim 0.1 - 1 W m^{-1} K^{-1}$.

Thermal conductivity in metals is higher. Why? Because the electrons are another way of carrying heat, and electrons travel ~ 300 times faster than atoms, and have a longer mean free path. On the other hand, each electron has a smaller heat capacity than each atom. It turns out that metals have a conductivity of $\sim 100 W m^{-1} K^{-1}$.

Example Use the concept that pressure = work per unit volume to determine the bulk modulus of a typical solid

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

Example Estimate the electrical conductivity of metals.

Example Discuss the factors limiting ant size

Useful numbers

charge on electron $e = 1.6 \times 10^{-19} C$

proportionality constant for Coulomb attraction $C \approx 10^{10}$ (SI units)

Planck constant $\hbar = 10^{-34}$ in SI units

typical atomic radius 1 Å

typical binding energy 3 eV