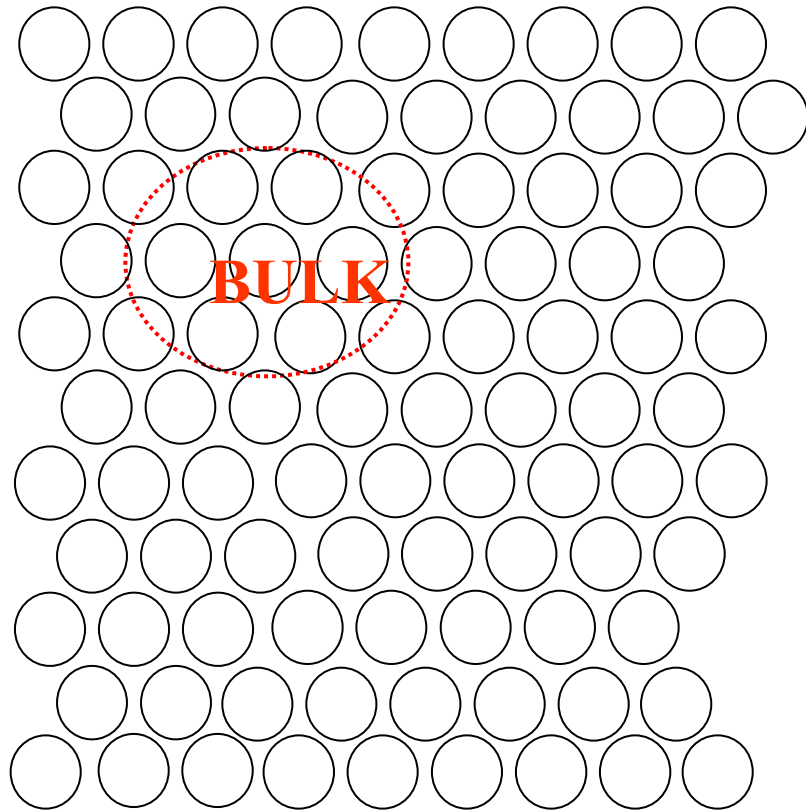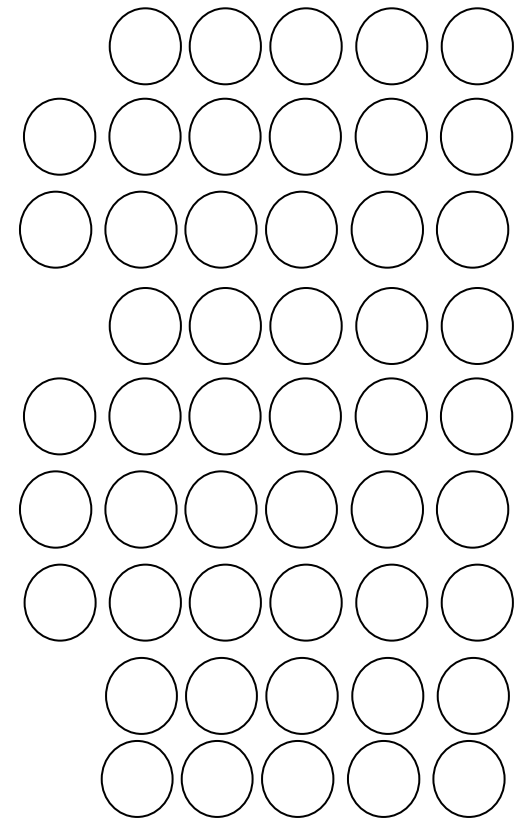# Bulk and Surface Properties of Solids

Close packed solid

Cubic lattice

BULK

SURFACE

Motivation

$$V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{n} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

Following parameters characterise interatomic interaction microscopically: σ, ε, a_0 Once these are known one can hope to model and *predict* properties of materials constructed of building blocks (atoms, molecules, ions) with these properties.

So far we have studied pairs of molecules. It is possible to study isolated pairs of molecules but this is rather difficult. Much easier to study large aggregates of molecules and make **macroscropic** measurements

Problem: how to relate macroscopic properties to microscopic pair potential?

For simplicity: assume the pair potential for the basic molecular unit is the same for all phases, i.e. gases, liquids, solids

E.g.

He, Ar, Kr, Xe   single atoms

H_2, N_2, I_2,   diatomic molecule in all phases

CCl_4,   polyatomic but 'spherical' molecule

At low T all of the above are liquid or solid: if the basic unit is neutral, we refer to these as **MOLECULAR SOLIDS** or **MOLECULAR LIQUIDS**; or in the case of ionic materials, **IONIC SOLIDS** and **IONIC LIQUIDS**

MOLECULAR SOLID: at low T the effects of molecular kinetic energy are small and properties are dominated by **potential energy**
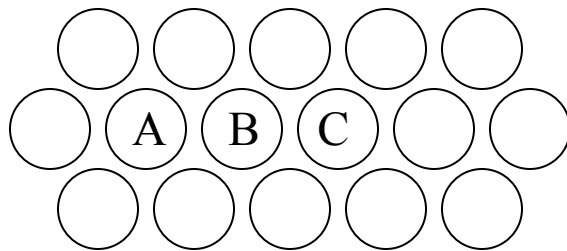
Solid/crystal
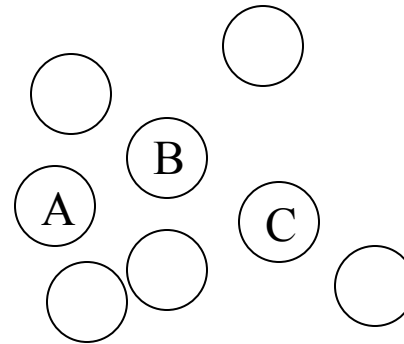
Liquid

Nearest neighbour separation$\sim a_0$
Next nearest neighbour separation$\sim 2a_0$

For vdW solid: pairs that are not nearest neighbours contribute only a few % to the potential energy so it is a good approximation to write

sum of

TOTAL POTENTIAL ENERGY is Σ POTENTIAL ENERGIES OF ALL NEAREST NEIGHBOUR PAIRS

The low temperature equilibrium state corresponds to lowest possible potential energy $\Rightarrow$ pairs want to be at separation $r = a_0 \Rightarrow$ crystal separation $\approx a_0$, liquid separation slightly larger but still close to a_0

Suppose we want to break up the material into widely separated parts? i.e. produce it in the form of a low density vapour. We have to do WORK(or supply heat) to separate the pairs. The energy we must supply to do this is called BINDING ENERGY or LATENT HEAT OF SUBLIMATION (or EVAPORATION)

In the case of a crystal, each molecule has the same number of nearest neighbours called the (FIRST) COORDINATION NUMBER, n

L = BINDING ENERGY = $\varepsilon*$(number of nearest neighbour pairs)

For 1 mole: $L_0 = \varepsilon(\frac{1}{2}nN_A) = \varepsilon\frac{1}{2}nN_A$

Molar binding energy

Avagadro's number=total number of molecules in 1 mole

In 3-dimensions:

$n = 12$ CLOSE PACKED SOLID

$n = 10$ liquid at low temperature

$n = 0$ dilute gas

To go from solid to liquid (melting) there is a small reduction in binding energy

LATENT HEAT OF MELTING$= \frac{1}{2}\varepsilon\,(n_{\text{solid}} - n_{\text{liquid}})N$

total number of molecules

If we then evaporate the material into a dilute gas,

LATENT HEAT OF EVAPORATION$= \frac{1}{2}\varepsilon\,(n_{\text{liquid}} - n_{\text{gas}})N \approx \frac{1}{2}\varepsilon\,n_{\text{liquid}}N$

E.g. Methane, CH_4: at low temperature the measured latent heat of vaporisation is $5.77(10^5)$ J.kg^{-1}

Low temperature molar density

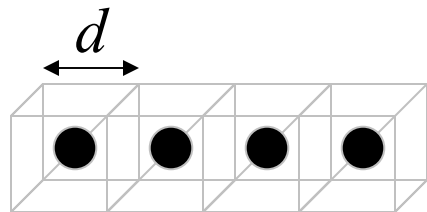Molar latent heat$=5.77(10^5)$ J.kg^{-1} 0.016 kg mol$^{-1}=9.2(10^3)$J.mol^{-1}

$= \frac{1}{2}\,\varepsilon n N_A = (10/2)\,\varepsilon\,(6.02)(10^{23})$ mol^{-1}

$\Rightarrow$

$$\varepsilon = \frac{9.2(10^3)}{5(6.02)(10^{23})}\,J = 0.31(10^{-20})J = 3.1(10^{-12})J$$

$$\varepsilon = \frac{3.1(10^{-21})}{1.6(10^{-19})} \text{eV} = 1.9(10^{-2})\text{eV} = 0.019 \text{ eV}$$

Thus we can make estimates of **microscopic** parameters from **macroscopic** data

To find the intermolecular spacing we can use the low temperature density ρ=0.42 kg l^{-1}. Assume each molecule occupies a cube of side d
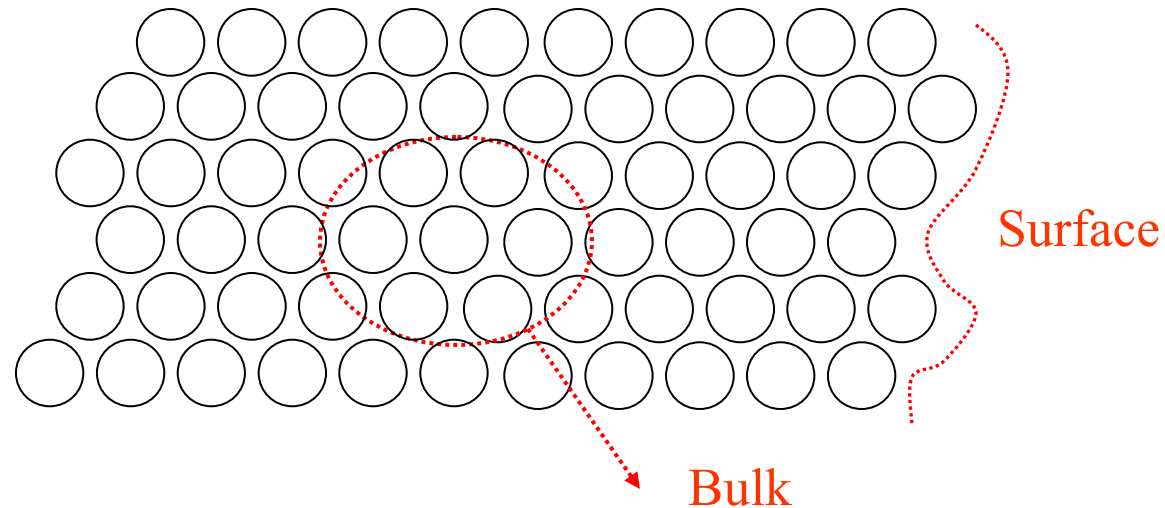

$$\rho = \frac{M}{d^3 N_A} \text{g.mol}^{-1} = \frac{1}{d^3} \frac{16\text{g.mol}^{-1}}{6.02(10^{23})\text{mol}^{-1}} = \frac{420\text{g}}{10^3 \text{cm}^3}$$

$$d^3 = \frac{16}{(420)(6.02)} 10^{-20} \text{cm}^3 = 0.63(10^{-22})\text{cm}^3 = 63(10^{-24})\text{cm}^3$$

$$d = 4.0 \ (10^{-8}) \text{ cm} = 4.0 \ (10^{-10}) \text{ m} = 0.4 \text{ nm} = 4\text{Å}$$

For materials held together by short range forces, the microscopic pair potential is related to the occurrence of SURFACE ENERGY effects

Each **surface** molecule is surrounded by $n/2$ nearest neighbours, not n (as for bulk molecules), so surface atoms are less tightly bound than bulk molecules. There is a SURFACE ENERGY DENSITY ($J.m^{-2}$) associated with the exposed surface (for simplicity suppose a very dilute gas environment just above the surface). Surface is particularly important for NANOMATERIALS.

Let N_s = surface density of molecules = number of molecules/m^2

SURFACE ENERGY DENSITY = Bulk binding energy of N_s molecules
– surface binding energy of N_s molecules

$$= \tfrac{1}{2}\ \varepsilon n\ N_s - \tfrac{1}{2}\ \varepsilon(n/2)\ N_s = \tfrac{1}{4}\ \varepsilon n\ N_s$$

If each molecule is considered to occupy a cube of side d then:

$$N_s = \frac{1}{d^2}\ \text{molecules}$$

We can find d from bulk mass densities,

$$\rho = \text{mass density} = \frac{\text{Molar mass}}{\text{Molar volume}} = \frac{M}{N_A d^3}$$

We can relate SURFACE ENERGY to another quantity: SURFACE TENSION

Imagine: making a cut in a liquid surface,, then the molecule on one side of the cut exerts a force across the cut to any object on the other side. This force is proportional to the length of the cut.

New surfaces
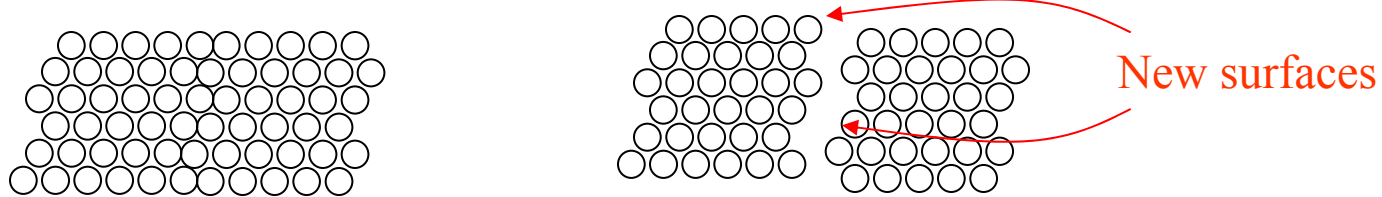
Definition: $\dfrac{\text{FORCE ACROSS CUT}}{\text{LENGTH OF CUT}} = \gamma =$ SURFACE TENSION

We can relate γ to the surface energy density as follows

Liquid film

Δx

F

l

Fixed wire

Sliding wire
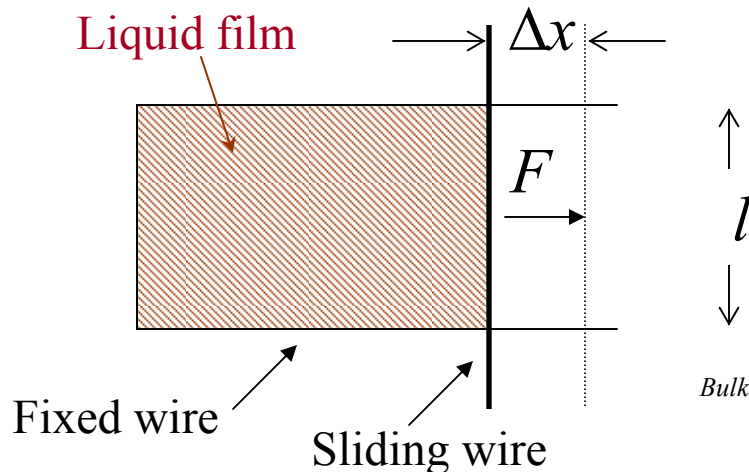
The film exerts a force on the slider in such a direction as to decrease the film area

Suppose the slide is slowly pulled a distance Δx. To do this we must perform work on the liquid

WORK = (Force)(Displacement) = $(2\gamma l) \Delta x$

= EXTRA SURFACE ENERGY

= (EXTRA AREA)(SURFACE ENERGY DENSITY)

= $2\, l\Delta x$ (SURFACE ENERGY DENSITY)

γ =SURFACE ENERGY DENSITY=SURFACE TENSION=¼ $\varepsilon n\, N^s$

There are many experimental methods to measure surface tension thus giving an alternative way to estimate ε

Example: CCl_4 at room temperature

$\gamma = 2.6(10^{-2})$ N.m^{-1} $\qquad M_r = 153 \qquad \rho = 1.6(10^3)$ kg.m^{-3}

$$\Rightarrow d^3 = \frac{M_r}{N_A \rho} = \frac{0.153 \text{kg.mol}^{-1}}{6.02(10^{23})\text{mol}^{-1}.1.6(10^3)\text{kg.m}^{-3}} = 0.159(10^{-27})\text{m}^3$$

$d = 0.54 \ (10^{-9})$ cm $= 5.4$Å

$$N^s = \frac{1}{d^2} = \frac{1}{0.29(10^{-18})\text{m}^2} = 3.4(10^{18})\text{molecules.m}^{-2}$$

$$\varepsilon = \frac{4}{n} \frac{1}{N^s} \gamma = \frac{4}{10} 0.29(10^{-18})\text{m}^2 2.6(10^{-2})\text{Nm}^{-1} = 0.3(10^{-20})\text{J}$$

$$\varepsilon = \frac{0.3(10^{-20})\text{J}}{1.6(10^{-19})}\text{eV} = 0.02\text{eV}$$

NB Many approximations have been made, e.g. assuming the density near the surface is the same as the bulk density (but is is the same ORDER OF MAGNITUDE).

The existance of the surface energy means that a liquid can LOWER its energy by MINIMISING its surface area, e.g. droplets (sphere is minimum area surface), oscillations of a droplet, foams

Exercise

Molecules of a complicated organic molecule can be considered to be disc-shaped of radius r and thickness $r/10$. When the molecules are close together face to face an energy E is required to separate them ; when they are placed end to end an energy $E/30$ is required.

(a) **Estimate** the molar latent heat of evaporation
(b) **Estimate** the surface tension
(c) Near the surface of a solid or liquid, will the molecules tend to be oriented (i) randomly, (ii) with the places parallel to the surface, or (iii) with the planes normal to the surface?

NB the equations for L_0 and γ that we have derived so far are for spherically symmetric molecules, you need to consider how the molecules are packed and do an *ab initio* calculation

Summary

- Physical meaning of bulk and surface

- Binding energy

- Coordination number

- Close packed solids

- Latent heat

- Surface energy density

- Surface tension

Next Topic: Elastic Properties of Solids