

Bonding and interatomic interactions

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We can explain material properties by looking at their atomic bonding.

Every atom has an associated electronegativity - the measure of an atoms tendency to attract electrons towards it.

H 2.1																	He —				
Li 1.0	Be 1.5															B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne —
Na 0.9	Mg 1.2															Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar —
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr —				
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe —				
Fr 0.7	Ba 0.9	La-Lu 1.1-1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn —				

When a compound consists of atoms of high and low relative electronegativity, ionic bonds form.

Electron is held by atom with high electronegativity, becoming negative by taking electron from other atom.

Held together by Coulomb potential.

These compounds are hard and brittle. They have high melting temperatures, and are insulators.

Easily dissolved into conductive solution in water.

When atoms have similar electronegativities, covalent bonds form.

A sharing of electrons between neighbouring atoms.

Described by Morse Potential

Very hard, brittle, etc.

When atoms have low electronegativity we get metallic bonding.

Electrons delocalise, leaving positive ions with electrons moving freely.

Described by models of electrons moving in a Coulombic potential of nucleus and valence electrons

Ductile and moderate melting points - conductive

Van Der Waals/Molecular bonding

Soft and weak. Low melting point.

Described by Van Der Waal potential

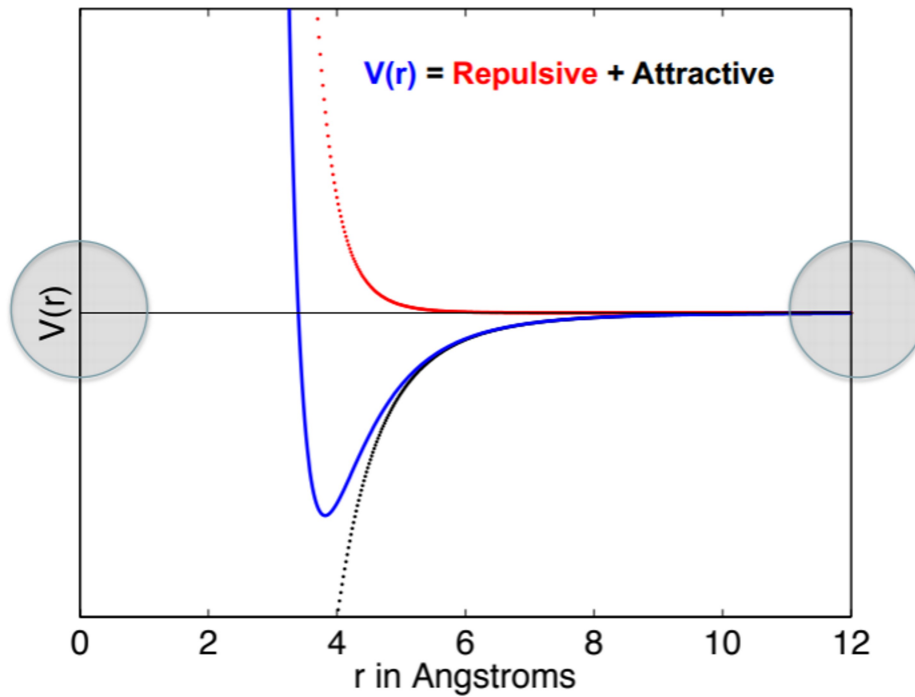
Van Der Waals forces come from induced dipoles in atoms:

Slight polarity in atom occurs from random electron movement.

This induces a matching polarity in near atoms

Slight attraction between 2 atoms

In general, interatomic potentials have the following general shape:



In van der waals forces, this can be written as:

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

σ and ϵ are constants that depend on the atom.

The r^{-6} term is the attractive force due to van der waals/ion forces.

The r^{-12} term is the repulsive force due to Pauli exclusion principle.

From this equation we can find 3 things:

The point where $V(r) = 0$

$$\rightarrow \left(\frac{\sigma}{r} \right)^{12} = \left(\frac{\sigma}{r} \right)^6 \rightarrow \left(\frac{\sigma}{r} \right)^6 = 1$$

$$\sigma = r_{V(r)=0}$$

The equilibrium separation: $\frac{dV(r)}{dr} = 0$

$$0 = 4\epsilon \left[-12 \frac{\sigma^{12}}{r^{13}} + 6 \frac{\sigma^6}{r^7} \right]$$

$$\rightarrow r = 2^{\frac{1}{6}} \sigma$$

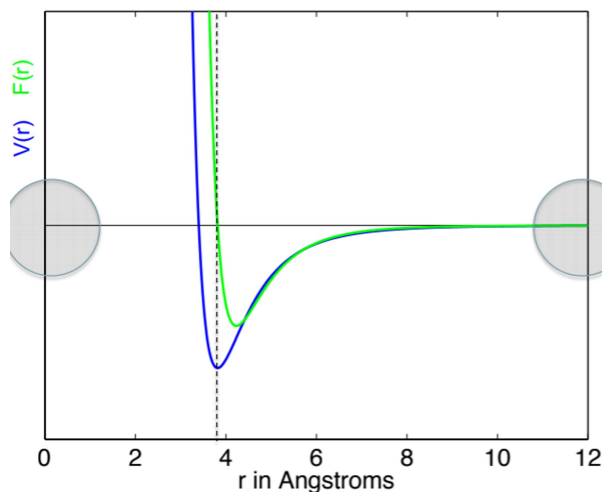
We call this r_0

This is where the atoms 'want' to be.

The depth of the well: $V(r_0)$

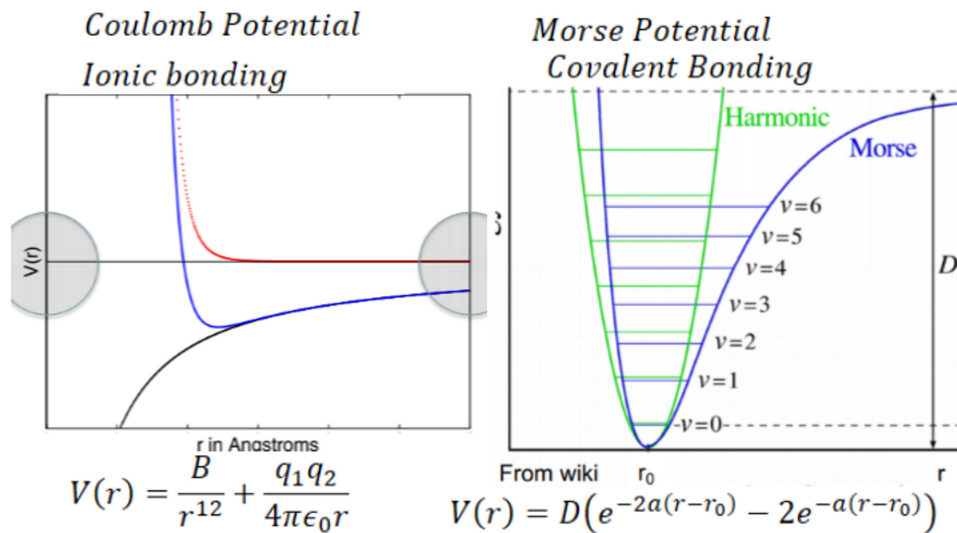
$$V(r_0) = -\epsilon$$

The force from this potential can be found knowing $F = -\frac{dV}{dr}$



- Strong repulsive force at short r
- Attractive force at large r
- Force is zero at the equilibrium separation.

For other forms of bonding, the shape looks slightly different



Thermal expansion

When an object heats up it (normally) expands. This expansion can be found by:

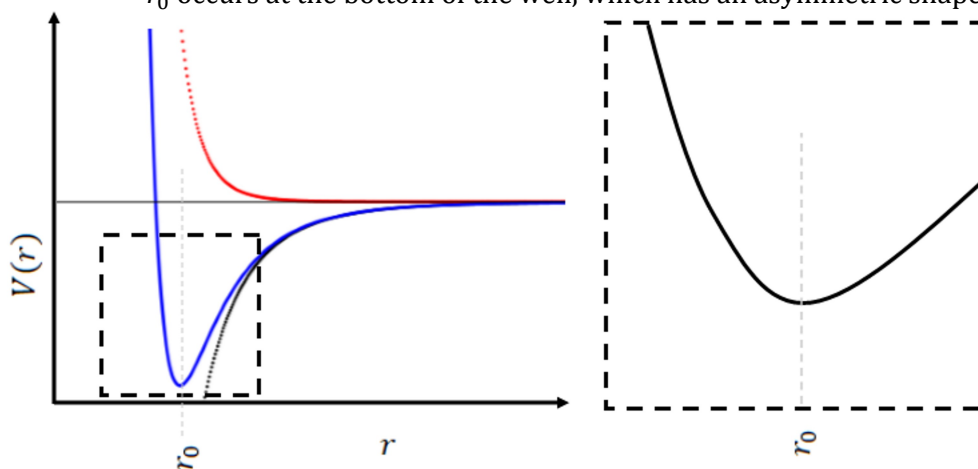
$$\frac{\Delta l}{l} = \alpha \Delta T$$

The expansion is non directional (unless stated). A change in volume comes from multiplying the change in length in each dimension.

Thermal expansion can be explained by looking at the graphs of potentials with respect to atomic separation.

When temperature is increased, the average kinetic energy of molecules increases, and so the mean distance from r_0 increases.

r_0 occurs at the bottom of the well, which has an asymmetric shape



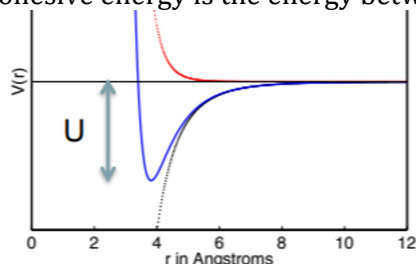
This asymmetry means that an increase in energy results in a slightly high average distance, and so an overall expansion.

When looking at potential graphs we can introduce a quantity known as the Cohesive Energy

This is defined as the energy require to separate all atoms to infinity.

It is a positive value, with the potential energy U being negative.

The Cohesive energy is the energy between the bottom of the well and $V(r) = 0$



This value relates to the melting/boiling points.

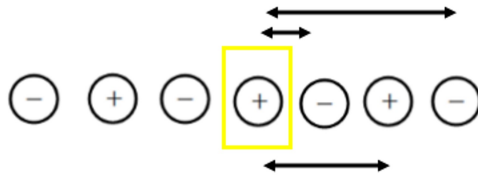
We can look at cohesive energy in ionic bonds.
 The potential of an ionic bond can be written as:

$$V(r) = \frac{B}{r^{12}} + \frac{q_1 q_2}{4\pi\epsilon_0 r}$$

We can ignore the r^{-12} term due to its insignificance

$$U = -V(r_0) \approx \frac{q_1 q_2}{4\pi\epsilon_0 r_0}$$

Imagine a chain of ions:



From the middle to the next is a distance r_0 , then to the atom after is $2r_0$, then $3r_0$...

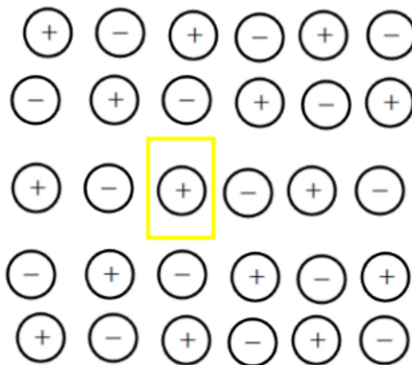
The atom will feel a potential:

$$V_c = \frac{q_1 q_2}{4\pi\epsilon_0 r}$$

As it feels this in each direction, it will have a cohesive energy of:

$$\begin{aligned} U &= 2 \times \left[\frac{-e \cdot e}{4\pi\epsilon_0 r_0} \right] + 2 \times \left[\frac{e \cdot e}{4\pi\epsilon_0 (2r_0)} \right] + 2 \times \left[\frac{-e \cdot e}{4\pi\epsilon_0 (3r_0)} \right] \dots \\ &= \frac{1}{2} \left[\frac{2e^2}{4\pi\epsilon_0 r_0} \right] \left(-\frac{1}{1} + \frac{1}{2} - \frac{1}{3} + \frac{1}{4} - \frac{1}{5} \dots \right) \\ &= -\ln(2) \times \frac{1}{2} \times \left[\frac{2e^2}{4\pi\epsilon_0 r_0} \right] \end{aligned}$$

We can do the same in 2 dimensions:



$$U = \frac{1}{2} \left(\frac{e^2}{4\pi\epsilon_0 r_0} \right) \left[4 * -\frac{1}{1} + 4 * \frac{1}{\sqrt{2}} + 4 * \frac{1}{2} + 8 * -\frac{1}{\sqrt{5}} \dots \right]$$

$$U \approx -1.57$$

If we do this for a 3D lattice we find $U = -9.78$

The shape of the potential curves between molecules relate to the properties of the substance.

Deep wells mean high cohesive energies, and so high boiling points.

The asymmetry of the well (anharmonicity) effects thermal expansion.

Defines the equilibrium separation

Linked to Young's modulus