2. Interatomic Force Models
Topic 2.1 - Origins, Mie potential, van der Waals potential

- Depending on the nature of the atom or molecule, we can get
  - => gases
  - => liquids
  - => solids (with different crystal structures)

- Basic Properties:

  Both attractive and repulsive forces are present.

  Repulsive force has shorter range than attractive force.

  Forces decrease with increasing separation between the atoms.

  In solids and liquids the atoms are almost touching;

  $\therefore$ solids and liquids are difficult to compress

Attractive Forces

- **Always** basically electrostatic: 4 main types: ionic, covalent, metallic and van der Waals

IONIC (e.g. Na^+Cl^-)

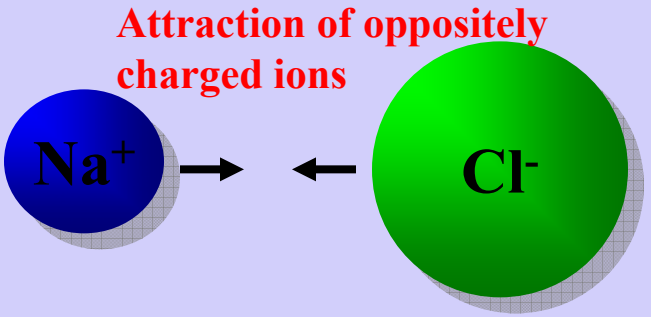
In ionic materials there is a complete transfer of electrons between atoms

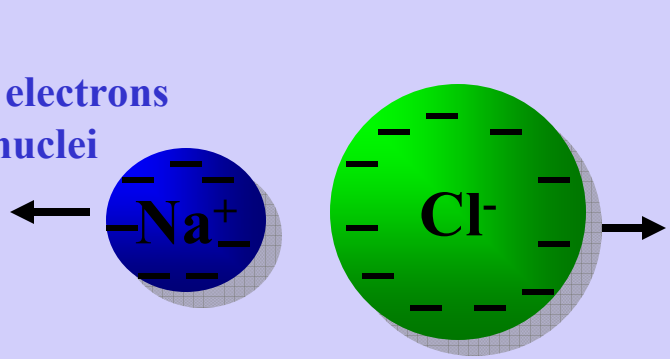
=> +ve and –ve ions

=> Coulomb forces: attractive or repulsive

$\therefore$ attractive forces dominate

Coulomb force $\therefore F \sim 1/r^2$





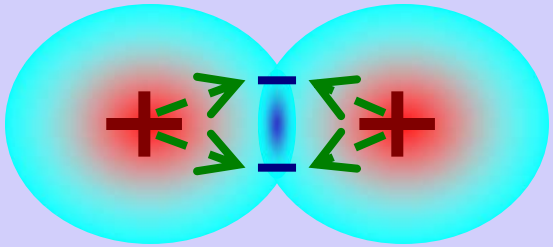
Attractive force cont.

COVALENT (e.g. diamond)

In covalent materials atoms share electrons.

+ve nuclei are attracted to the electrons between them and hence to each other

=> attractive forces between atoms

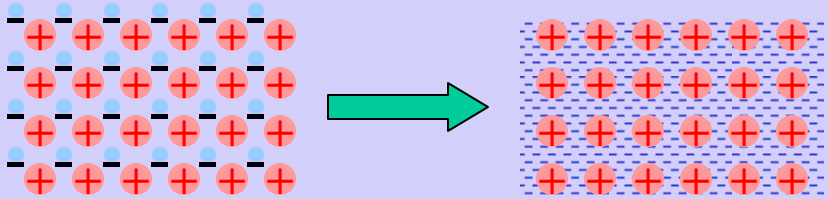


METALLIC (e.g. Na)

Metals consist of a lattice of +ve ions in a gas of free electrons.
attraction between ions and electrons (not unlike covalent bonds but electron are shared between many atoms)

=>attractive force

e.g. sodium has bcc crystal structure → each atom touches 8 others. Electrons from outer shells are shared between all of them.



Attractive force cont.

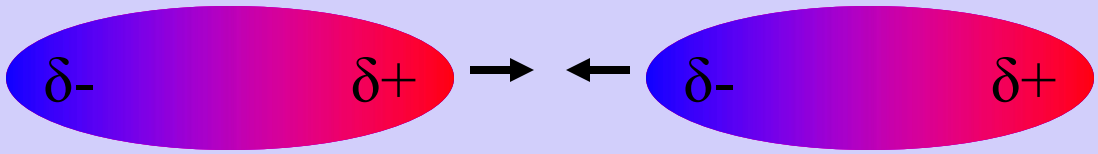
VAN DER WAALS (e.g. Ar, N_2, HCl)

VdW forces arise from an attraction between the dipole moment (either permanent or instantaneous) of one atom (molecule) and that (either permanent or induced) of another

theory => $$F \propto \frac{1}{r^7}$$

occur between all types of atoms or molecules, **including** neutral* atoms or molecules.

(*when, although it is a weak force it is important because other attractive forces are absent)



Example of Van der Waals' forces

- Van der Waals' forces give a gecko an ability to climb!

K. Autumn et al., PNAS 2002, *99*, 12252-12256

Repulsive Force

- Has both ELECTROSTATIC and QUANTUM-MECHANICAL origins.
  As atoms get close together their electron clouds overlap.

(i) +ve nuclear charges no longer screened => Coulomb repulsion

(ii) Electrons near to each-other cannot have the same quantum number
(Pauli Exclusion Principle)

$\therefore$ cannot have the same energy and position

$\therefore$ some electrons have to change (increase) their energy
=> repulsion

i) and ii) combined => $F \propto e^{-r/a}$

or more conveniently $F \propto \frac{1}{r^n}$ where n = 10 – 13

Interatomic forces: Representation

- Consider force F between an atom (or molecule) at the origin and another a distance r away.
  - require $F \to 0$ as $r \to \infty$, $\therefore F \propto 1/r^p$

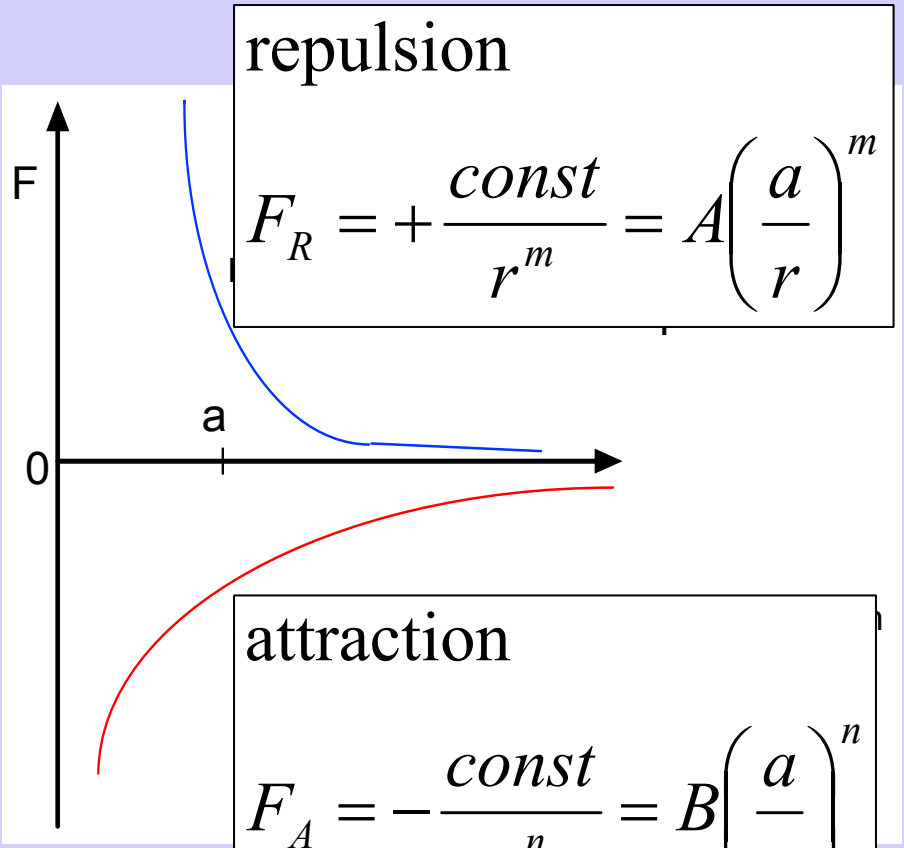
- **Sign convention:** repulsive force + ve ; attractive force – ve

Total force $F(r)=F_R(r)+F_A(r)$
m (typically 13) > n
n: 2 for ionic, > for VdW

F_R dominates at short distance (r<a)
F_A dominates at longer distances (r>a)

At r = a, F(a)=0, I.e.when $|F_R| = |F_A|$

a ≡ equilibrium separation



Interatomic potential energies

- Instead of F(r) it is often more convenient to use V(r), the potential energy of the two atoms (molecules).
- V(r) is the work done (on the system) in bringing one atom from ∞ to r (where $V(\infty)\equiv 0$),

$$\therefore \quad V(r) = -\int_{\infty}^{r} F(r)\,dr \quad \text{or} \quad F(r) = -\frac{dV(r)}{dr}$$

- N.B. System changes to minimize V.

- If $F(r) = const\left(\frac{a}{r}\right)^{m}$ then $V(r) = const'\left(\frac{a}{r}\right)^{m-1}$

The Mie potential

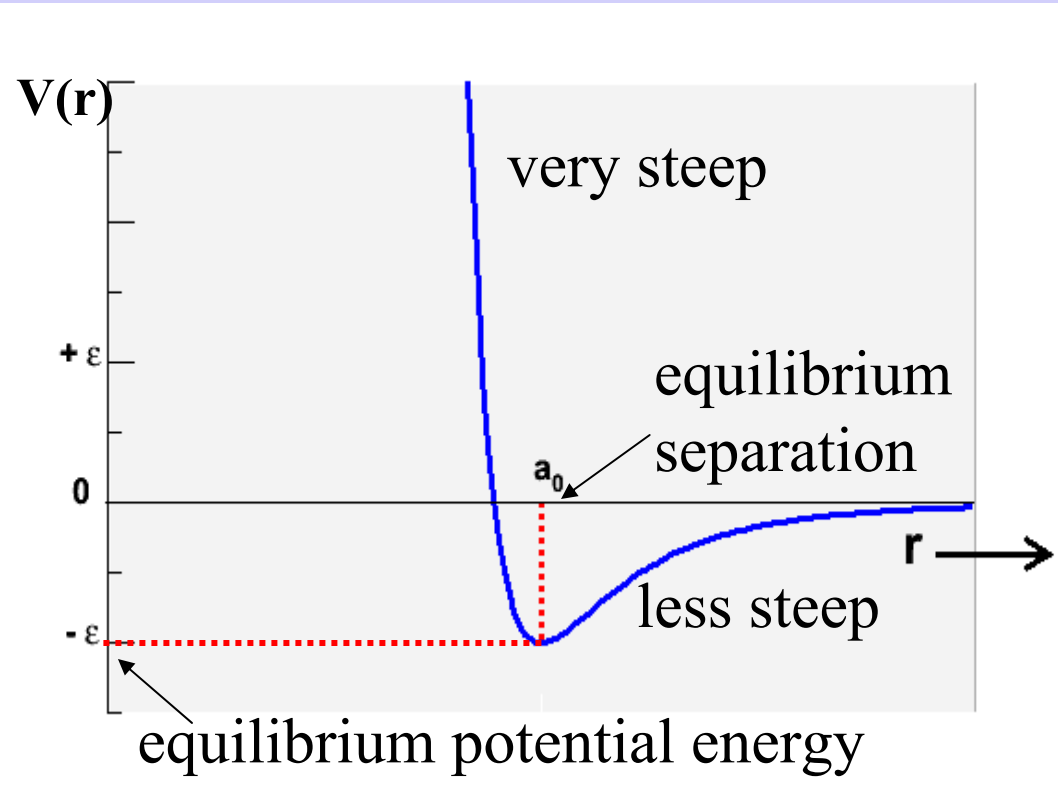
- In 1907 Mie proposed a very simple form of the inter-atomic potential

$$V(r) = \frac{A}{r^m} - \frac{B}{r^n}$$

- A,B,m,n are constants.
  first term is repulsive
  second attractive.
  $m > n$

- At equilibrium,

$$\frac{dV}{dr} = 0 \quad \therefore \quad F = 0$$



The Lennard-Jones 6-12 Potential (van der Waals solid)

- A good approximation to the potential energy.

$$V(r) = \varepsilon\left[\left(\frac{a_0}{r}\right)^{12} - 2\left(\frac{a_0}{r}\right)^{6}\right]$$

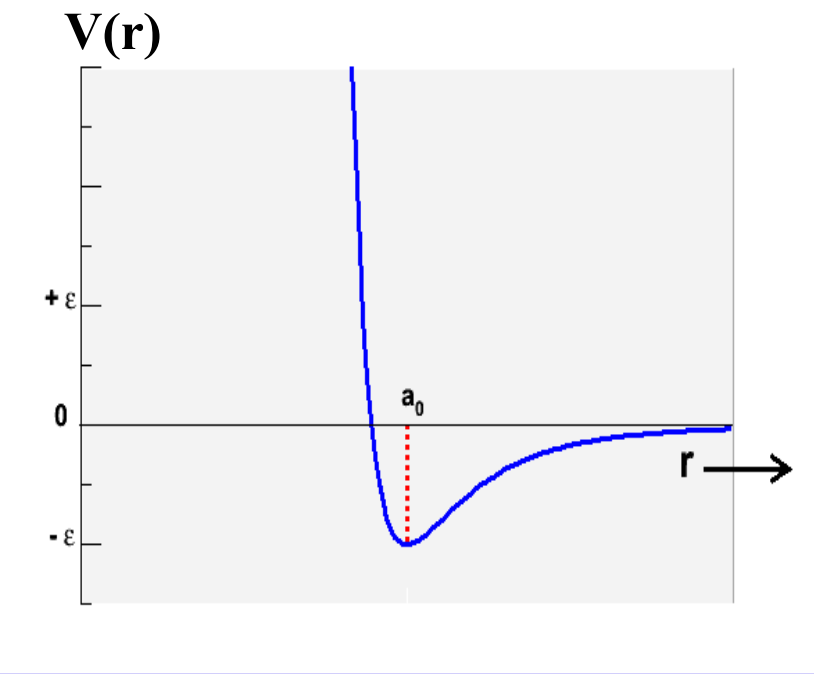
(equivalent to Mie potential with m=12, n=6, $A=\varepsilon a_0^{12}$, $B=2\varepsilon a_0^{6}$)

- At $r = \infty$ $V(r) = 0$

  At $r = a_0$, (equilibrium separation):

  $V(r) = -\varepsilon$, $F = -dV/dr = 0$

- The L-J 6-12 potential describes the interaction between two isolated atoms (molecules)



L-J potential: in solids or liquids

- The forces described by L-J 6-12 are very short range.

$$\text{e.g. } V(a_0) = -\varepsilon, \qquad V(2a_0) \sim -\varepsilon/30$$

$\therefore$ to a good approximation, only NEAREST NEIGHBOUR interactions need to be considered.

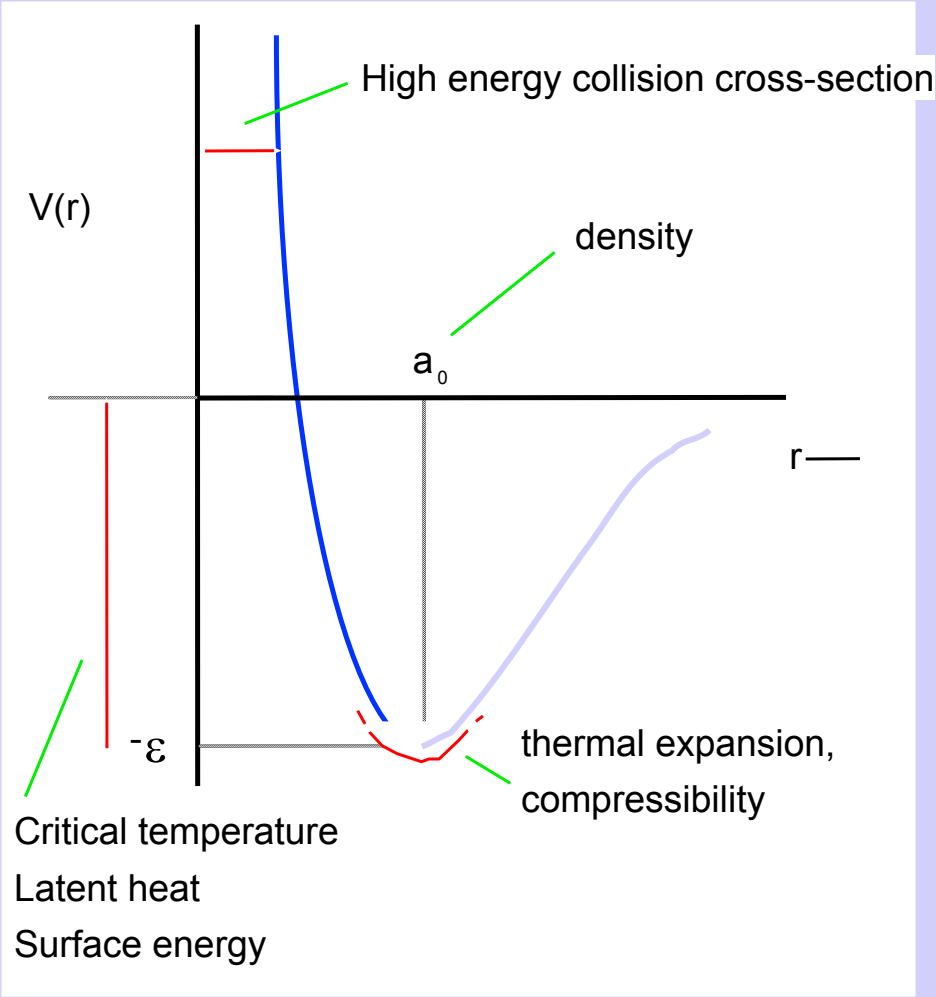
=> Concept of **Coordination number** n,
the number of NEAREST NEIGHBOURS of any particular molecule

- **SOLIDS**
  n has a definite value (dependent on structure)
  e.g. for close-packed structure (hcp or fcc) n = 12,
  for bcc n = 8 etc

- **LIQUIDS**
  n has an average value, typically 1 – 2 smaller than in solids

Consequences of L-J potential:

- Many properties of macroscopic assemblies (liquids and solids) of neutral atoms/molecules can be derived from the L-J 6-12 potential of two isolated atoms/molecules.



- We will consider density, critical temperature, latent heat, mechanical properties (compressibility) and thermal expansion.

2 Interatomic Force Models

2.2. Interatomic potential for an ionic crystal

- Between ions there are repulsive forces, van der Waals forces (as for neutral molecules) and Coulomb forces

  $\therefore$ potential energy between an isolated pair of ions, charge e, separation r

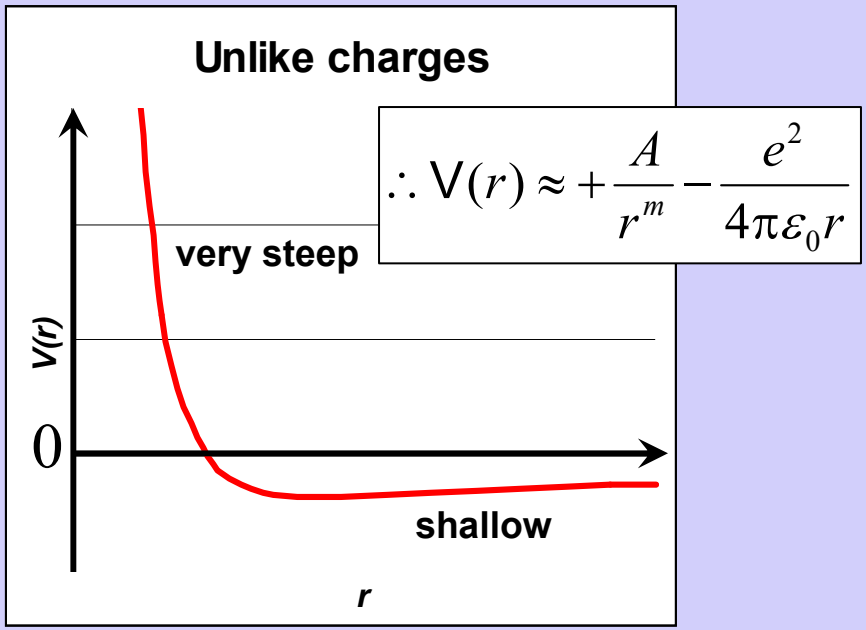
$$V(r) = +\frac{A}{r^m} - \frac{B}{r^n} \mp \frac{e^2}{4\pi\varepsilon_0 r} \qquad \left(m \approx 12,\ n \approx 6\right)$$

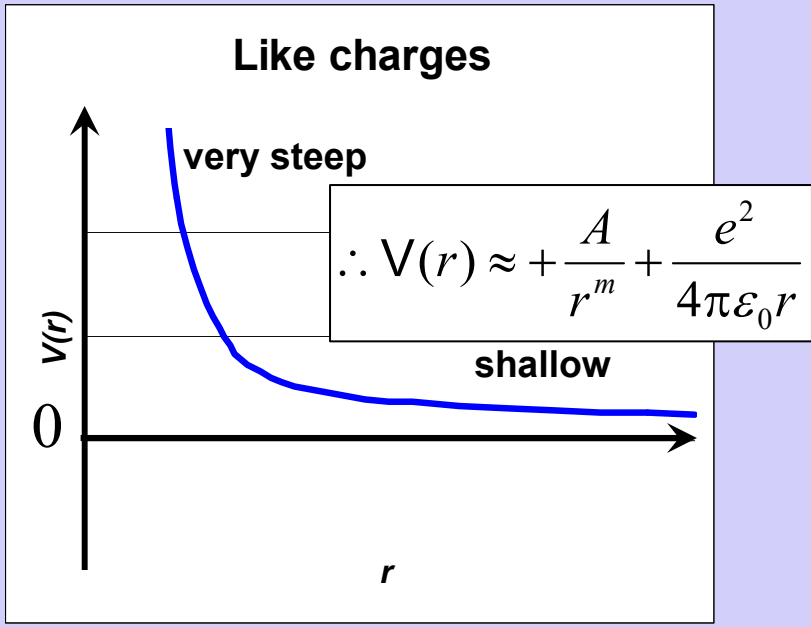
- 1st term repulsive, 2nd term VdW, 3rd term Coulomb
- VdW term is negligible compared with Coulomb term (~0.01 - 0.1eV compared to 10 eV).

$$\therefore V(r) \approx +\frac{A}{r^m} \mp \frac{e^2}{4\pi\varepsilon_0 r}$$

Ionic inter-atomic potential in solids

Two important differences (complications) compared with neutral molecules (L-J 12-6 potential)



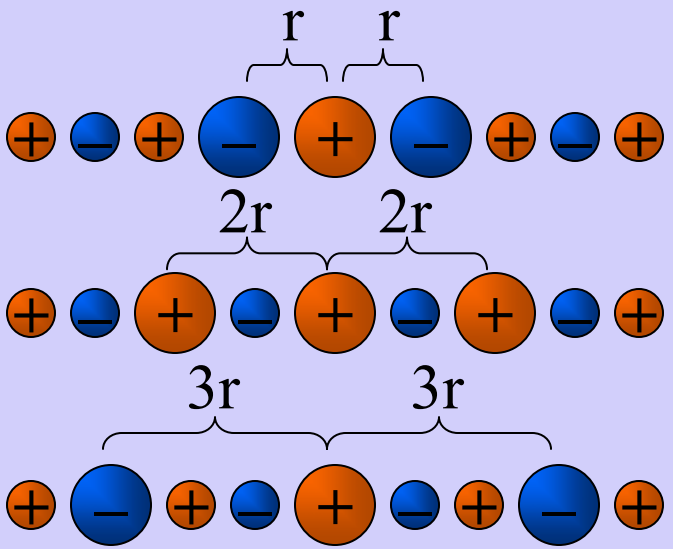


i) *V(r)* not the same between all ions (like and unlike charges)

ii) *V(r)* not short range ∴ nearest neighbour approximation won't work

Madelung constant for ionic crystals

- Consider a line of ions: …⊕⊖⊕⊖⊕⊖⊕⊖⊕…
- the **electrostatic potential energy of a single ion**



due to 2 nearest neighbours $-\frac{2\cdot e^2}{4\pi\varepsilon_0 r}$

due to 2 next-to-nearest neighbours $+\frac{2\cdot e^2}{4\pi\varepsilon_0 (2r)}$

due to 2 next-to-next-to-nearest neighbours $-\frac{2\cdot e^2}{4\pi\varepsilon_0 (3r)}$

$$\Rightarrow -\frac{e^2}{4\pi\varepsilon_0 r}\left[2\left(1-\tfrac{1}{2}+\tfrac{1}{3}-\tfrac{1}{4}+....\right)\right]$$

Madelung constant

Now: $\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} \ldots.$ (Taylor expansion)

Hence: $1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \ldots = \ln 2 = 0.69$

and the electrostatic potential is: $\frac{-\alpha e^2}{4\pi\varepsilon_0 r}$ where $\alpha = 2 \cdot 0.69 = 1.38$

α is the **MADELUNG CONSTANT** which depends on the particular arrangement of ions. (typicaly 1-2)

for the above 1D line α = 1.38; for 3D NaCl structure α = 1.75

N.B. the result of the summation is the same for any ion in the lattice.

Interatomic potential for ionic crystals

$\therefore$ Electrostatic potential energy per pair of ions in an ionic crystal equals p.e. of an isolated pair of neighbouring ions multiplied by the Madelung constant α.

- Including the p.e. due to the short range repulsive forces the p.e. per pair of ions in the crystal as a function of nearest neighbour separation r

$$V(r) = +\frac{A}{r^m} - \frac{\alpha e^2}{4\pi\varepsilon_0 r}$$

- Using $dV/dr=0$ at $r=a_0$, gives

$$A = \frac{\alpha e^2}{4\pi\varepsilon_0}\frac{1}{m}a_0^{m-1}$$

Interatomic potential of ionic crystals

Therefore:

$$V(r) = \frac{\alpha e^2}{4\pi\varepsilon_0 a_0}\left[\frac{1}{m}\left(\frac{a_0}{r}\right)^m - \frac{a_0}{r}\right]$$

- At $r=a_0$, $V(a_0)= -\varepsilon$, therefore

$$\varepsilon = \left(1-\frac{1}{m}\right)\frac{\alpha e^2}{4\pi\varepsilon_0 a_0}$$

This is the binding energy per pair of ions.

Next Lecture

3: Thermal Properties:
Topic 3.1 Thermodynamic aspects of stability