Microscopic and nanoscale forces are important in a number of areas of nanoscience, nanotechnology and biology.

These forces start to become important on the nanometre length scale.

The relevant energy scale on these small length scales is the thermal energy.
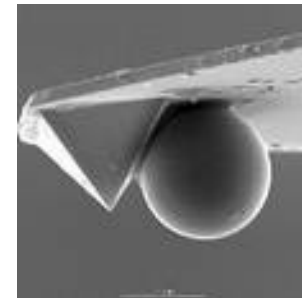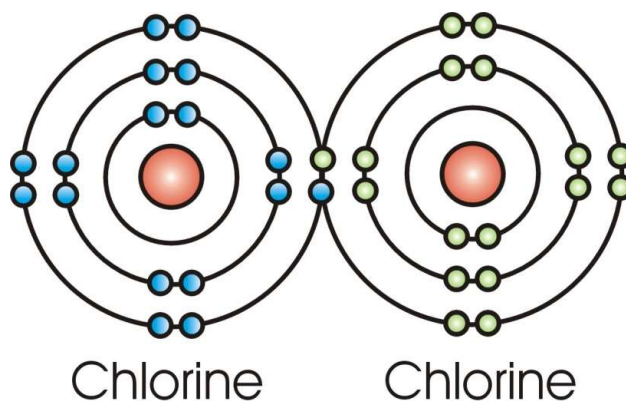
$$U_{thermal} \approx kT$$

Covalent bonds are highly directional and are chemical in origin (e.g. π bond created by overlap of p electron orbitals)

Chlorine   Chlorine

These interactions originate from the sharing of **valence** electrons to facilitate the filling of electronic shells within atoms → stable structures

The directionality of the bonds is caused by the mutual repulsion of the electrons in different bond orbitals

Covalent forces (bonds) operate over short distances 0.1-0.2 nm

The energies associated with the formation of these bonds are typically 2 to 8 eV per bond (that's on the order of 100 times kT at room temperature)
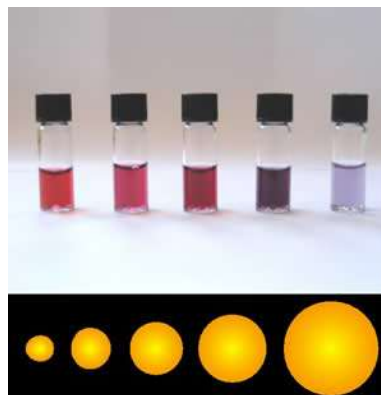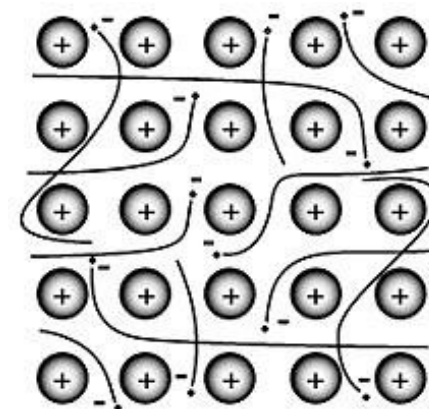
You will learn more about these in the 3rd year Solid State module

Sharing of electrons between metal atoms gives rise to another form of bonding.

However, in metallic bonds, the electrons become delocalised throughout the material in such a way that they are shared between many nuclei.
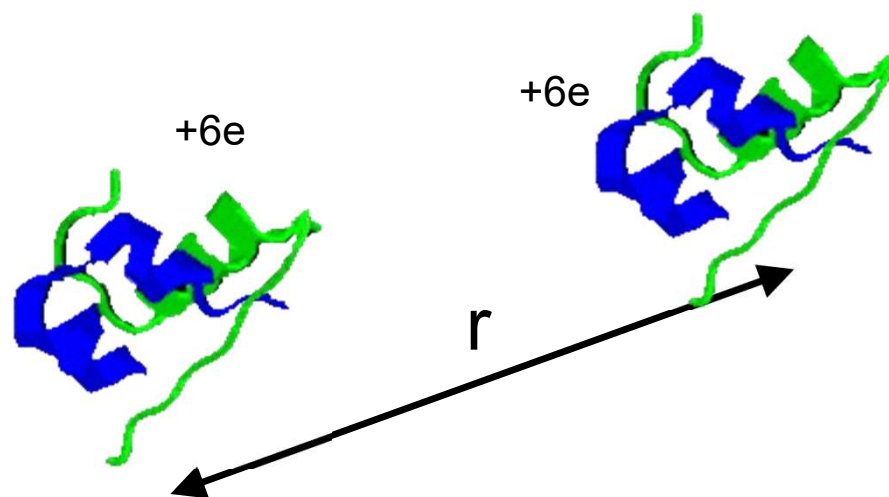
You have already met Coulomb interactions in the first year module
'Newton to Einstein'

Some atoms and molecules may acquire a net charge and
will interact via electrostatic forces

+6e

+6e
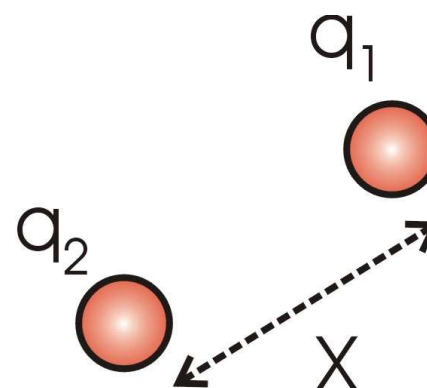
r

The **potential energy** of two molecules having charges q_1 and q_2 that are separated by a distance, x, is given by

$$U(x) = \frac{q_1 q_2}{4\pi\varepsilon\varepsilon_o x}$$

$\varepsilon_o = 8.85 \times 10^{-12}\ C^2 N^{-1} m^{-1}$

ε = relative permittivity

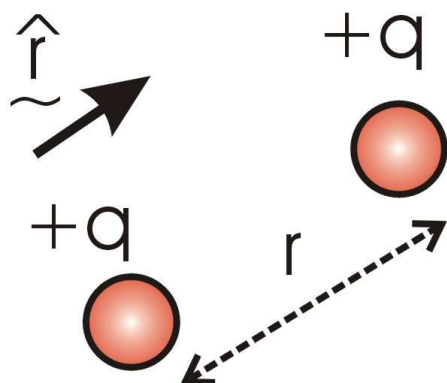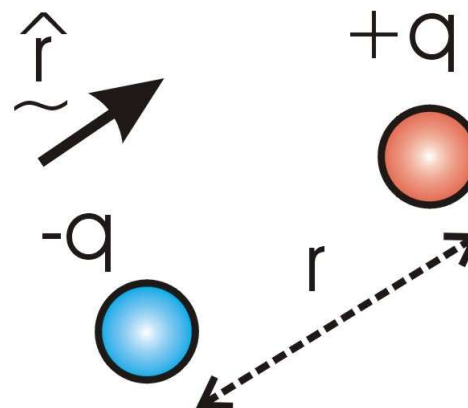Inverse power law dependence (x^{-n}) is typical of many different types of potential

When the potential energy is negative the interaction is favourable

Potential energy $U < 0$

When the potential energy is positive, interactions are unfavourable

Potential energy $U > 0$

We can obtain an estimate of the range X_{range} below which the interaction between two atoms/molecules matters

$$|U(x)| = kBT$$

Problem: A positively charged sodium ion Na$^+$ and a negatively charged Chloride ion Cl$^-$ are 20nm apart in a vacuum. Is the Coulomb force between them significant?

$$U(x) = \frac{q_1 q_2}{4\pi\varepsilon_o X_{range}}$$

$e = 1.602 \times 10^{-19}$C
$\varepsilon_0 = 8.854 \times 10^{-12}$ Fm^{-1}
$k_B = 1.38 \times 10^{-23}$ m^2 kg s^{-2} K^{-1}
$T = 20°C$

Rearranging gives

$$X_{range} = \left| \frac{q_1 q_2}{4 \pi \varepsilon \varepsilon_o kT} \right|$$

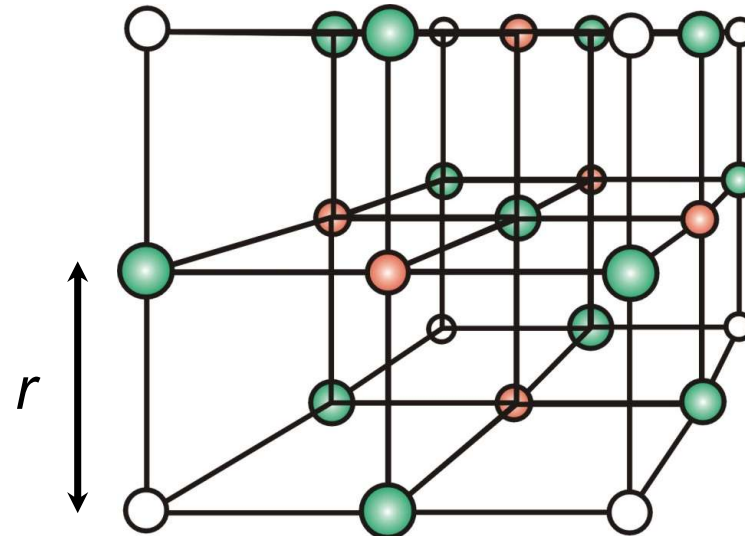$x \geq X_{range}$ electrostatic interactions become unimportant

$x < X_{range}$ electrostatic interactions start to influence atoms/molecules

Electrostatic interactions are responsible for the formation of ionic crystals

For example, consider NaCl (salt)

We can calculate the (cohesive) energy per ion pair holding the crystal together by summing up the contributions to the potential energy from all neighbours

$$U_{coh} = -\frac{e^2}{4\pi\varepsilon\varepsilon_0 r}\left(\frac{6}{1} - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \cdots\right) = -\frac{\alpha e^2}{4\pi\varepsilon\varepsilon_0 r}$$

where α is called the Madelung constant (α =1.748 for NaCl and anything else that has the same crystal structure)

e is the electronic charge (1.6 x 10^{-19}C)

However, if $|U(x)|$ > kT this **does not** mean the interaction is stable indefinitely

The probability of 2 objects which are held together by an attractive interaction escaping due to thermal fluctuations is given by the Boltzmann probability.

$$P(x) \propto exp^{-U/k_B T}$$

Proportional

Potential of interaction

The ratio U/kT determines how likely 2 objects are to stay "stuck" to one another.

For a covalent bond U/kT ~ 100. → e^{-100} = 3.7x10^{-44} → "Stable" or "Strong"

Suppose U/kT ~ 2 → e^{-2} = 0.13 → Probability is "Significant" but "Weak"

1) Calculate the cohesive energy of a NaCl crystal in

a) water ($\varepsilon = 80$)

b) toluene ($\varepsilon = 2.38$)

$$U_{coh} = -\frac{e^2}{4\pi\varepsilon\varepsilon_0 r}\left(\frac{6}{1} - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \cdots\right) = -\frac{\alpha e^2}{4\pi\varepsilon\varepsilon_0 r}$$

$\alpha = 1.748$, $\varepsilon_0 = 8.854 \times 10^{-12} Fm^{-1}$, $k_B = 1.38 \times 10^{-23} m^2 kgs^{-2}K^{-1}$, T=293K

the nearest neighbour spacing between Na$^+$ and Cl$^-$ ions is r = 0.282 nm.

2) Use your answers to parts a) and b) to explain why ionic crystals dissolve in water, but not in organic solvents.

3) Why does heating the water help the salt dissolve faster?

The force, *F,* on an object can be related to the gradient in its potential energy, *U,* with respect to distance, x, by the formula

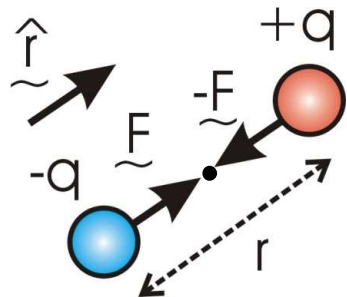$$F(x) = -\frac{dU}{dx}$$

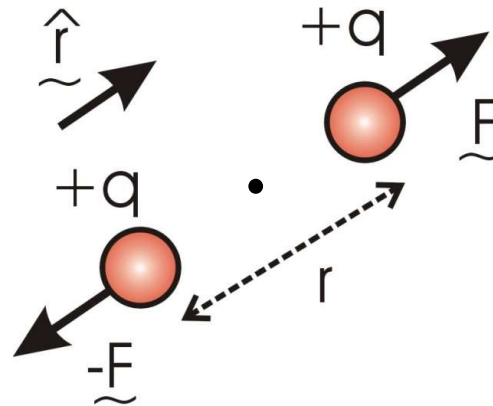This is an extremely important formula in physics and we will use it a lot.

Negative forces are attractive

$|\underline{F}| < 0$

Positive forces are repulsive

$|\underline{F}| > 0$

The **force acting between** two point charges q_1 and q_2 separated by a distance, x, is given by

$$F(x) = -\frac{dU}{dx} = \frac{q_1 q_2}{4\pi\varepsilon\varepsilon_o x^2}$$

The sign of the force depends upon the signs of the charges

If $q_1 q_2 < 0$ **force is attractive** (negative sign)

If $q_1 q_2 > 0$ **force is repulsive** (positive sign)

The range of an interaction determines whether it is important at different distances

How likely an interaction is to be disrupted by thermal fluctuations defines them as "strong" or "weak"?

$$P(x) \propto exp^{-U/k_BT}$$

The force can be calculated from the derivative of the potential:

$$F(x) = -\frac{dU}{dx}$$