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PHYS3009: Force and Function at the Nanoscale
Week 20 – 12:00pm Friday – 07 February 2025

valid for 15 minutes from 11:55am
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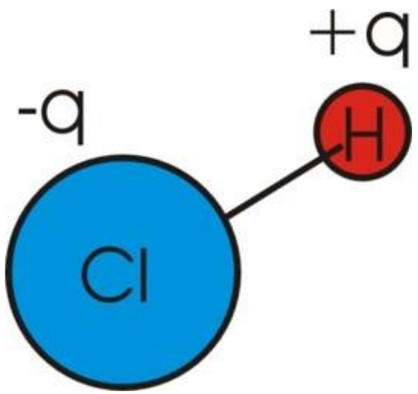
Dispersion interactions

Force & function at the nanoscale

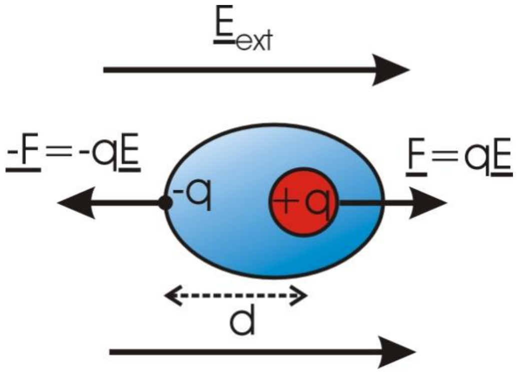
Dipoles

We’ve looked at a number of different types of dipole:

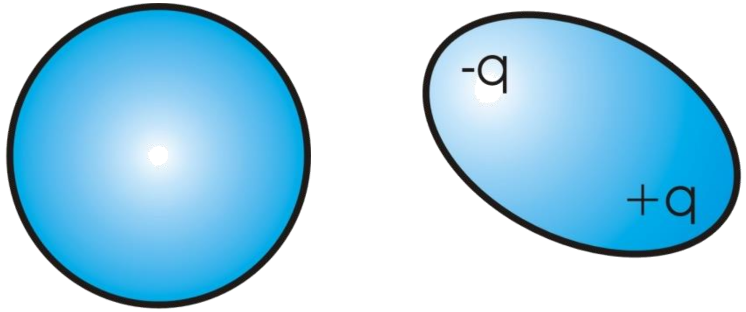
Permanent



Induced



Instantaneous

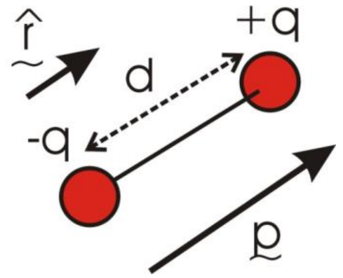


Dispersion interactions

1. Two neutral atoms
2. Fluctuations in the electron cloud result in what kind of dipole?
3. What does the dipole generate at a point x?
4. This causes what kind of dipole in a neighbouring neutral atom?
5. Why do they now attract one another?

Summary of key results

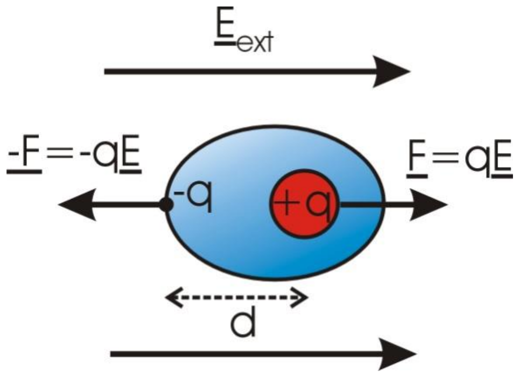
Dipole moment $$\boldsymbol{p} = qd\,\hat{\boldsymbol{r}}$$



Electric field due to a dipole $$\boldsymbol{E} = \frac{qd}{2\pi\varepsilon\varepsilon_0}\frac{1}{x^3}\boldsymbol{i}$$

Potential energy of a dipole in an E field $$\boxed{U_{dipole} = -\boldsymbol{p}.\boldsymbol{E}}$$

Dipole induced by an E field $$\boxed{\boldsymbol{p} = \alpha\boldsymbol{E}_{ext}}$$



Polarisability $$\alpha = 4\pi\varepsilon_0 d^3$$

Problem 4.1 – Dispersion Interaction Potential

When the distance between atoms in a dipole d<<x the magnitude of the electric field at a point x due to the point dipole, E, reduces to the form:

$$E = \frac{qd}{2\pi\epsilon_0 x^3}$$

where ε_o is the permittivity of free space (Fm^{-1})

An atom is placed at the point (x,0). If the polarisability of the atom is α, show that the energy associated with the dipole that is induced in this atom has the form

$$U = \frac{-C}{x^6}$$

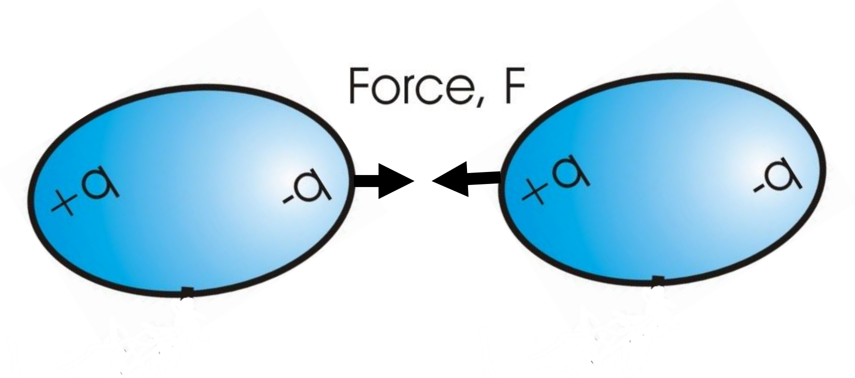
And derive an expression for C in terms of, α, *q*, *d*, ε *and* ε_o.

(Hint: recall that U=-***p*.*E*, *p*** = α ***E***)

Dispersion forces

Attractive dispersion force between two **atoms**/molecules is given by

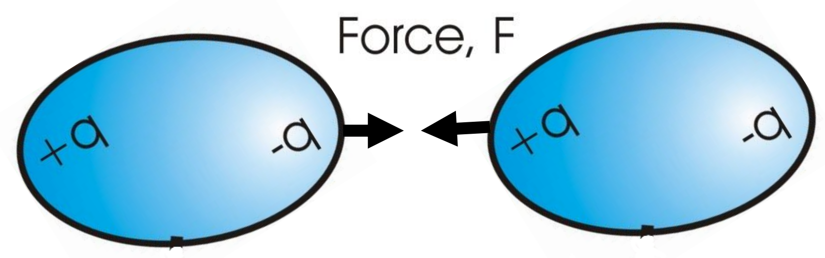
$$F(x) = -\frac{dU}{dx} = -\frac{6\alpha(qd)^2}{(2\pi\varepsilon\varepsilon_0)^2}\frac{1}{x^7} = -\frac{6C}{x^7}$$



So why don’t atoms and molecules collapse in on one another?

The form of the dispersion potential predicts that interactions get stronger as atoms and molecules get closer together

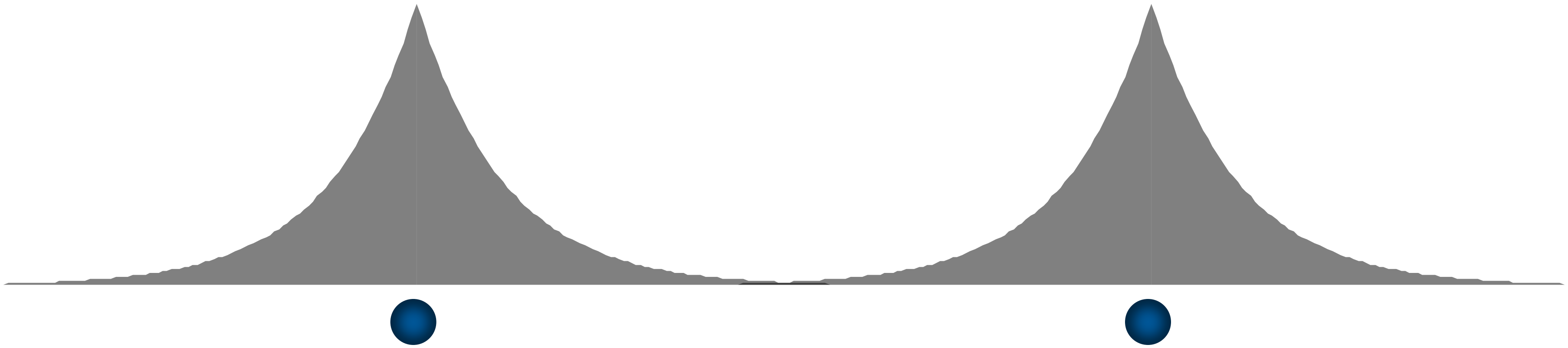
$$F(x) = -\frac{6C}{x^7}$$



So why don’t they continue to attract and collapse into each other?

There has to be a repulsive part of the potential that acts at even shorter ranges

Repulsive interaction - *The Pauli exclusion principle*



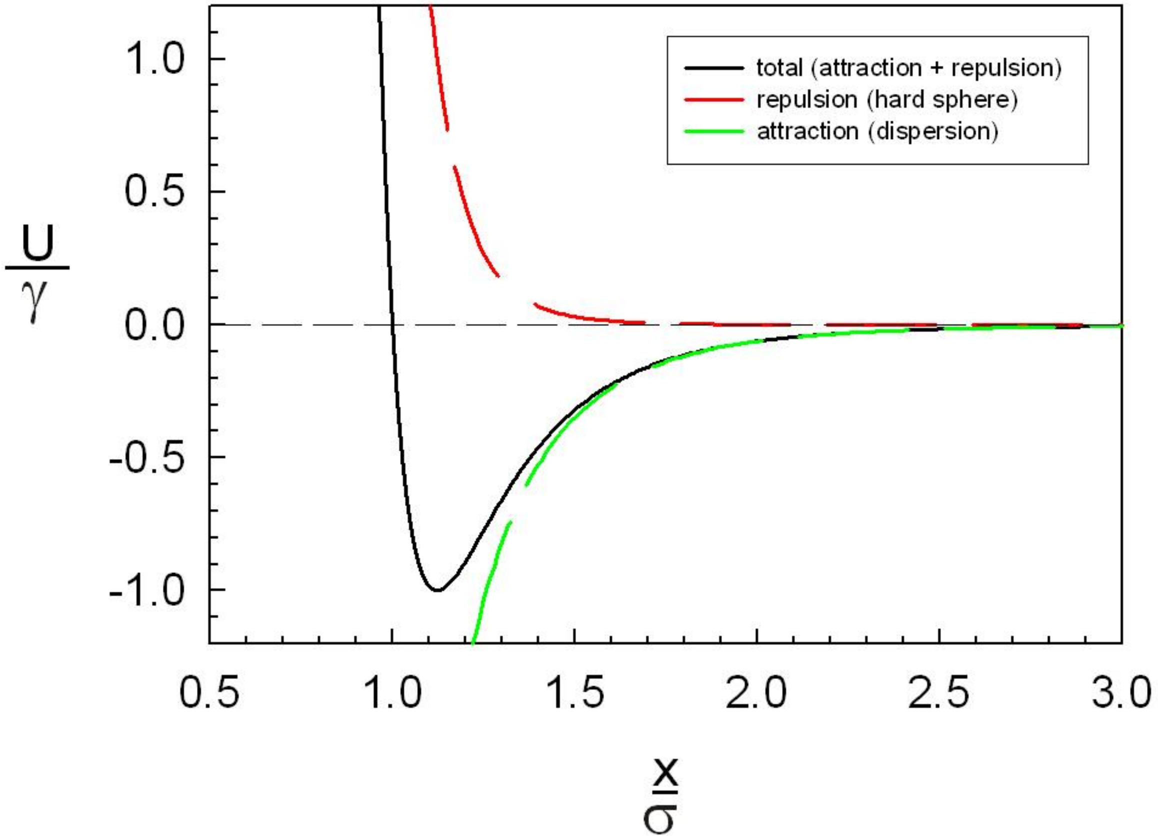
“Two or more electrons may not occupy the same quantum state.”

When two atoms get too close, their electron clouds overlap

This interaction can be represented by an empirical potential of the form,

$$U(x) = +\frac{B}{x^{12}}$$

The ‘6-12’ potential – Lennard Jones



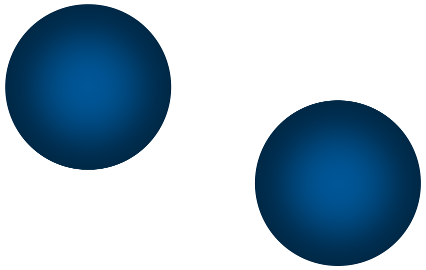
The total interatomic/molecular potential is given by summing the attractive and repulsive potentials

The use of this form gives rise to the ‘Lennard-Jones’ or ‘6-12’

$$U(x) = +\frac{B}{x^{12}} - \frac{C}{x^{6}} = 4\gamma\left[\left(\frac{\sigma}{x}\right)^{12} - \left(\frac{\sigma}{x}\right)^{6}\right]$$

Problem 4.2 What are the range of dispersion interactions?

Thermal motion of atoms and molecules tends to disrupt the effects of dispersion interactions



When U becomes comparable to thermal energies dispersion interactions become less important. Calculate the range of interaction for dispersion forces?

Typical values of $\alpha = 9 \times 10^{-40}\ C^2m^2J^{-1}$ and $p = qd = 5 \times 10^{-30}\ Cm$ for individual atoms at T=300 K. $k_B = 1.38 \times 10^{-23}$

$$|U(x)| = \frac{\alpha(qd)^2}{(2\pi\varepsilon\varepsilon_0)^2}\frac{1}{x_{range}^6}$$

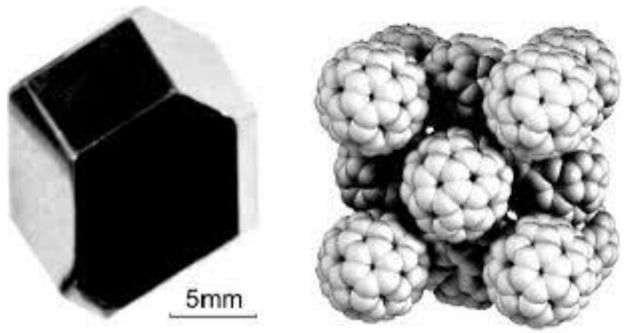
Estimate of interaction range

$$x_{range} \approx \left(\frac{\alpha (qd)^2}{(2\pi \varepsilon \varepsilon_0)^2 kT} \right)^{1/6}$$

$$x_{range} \sim 0.3\ nm$$

Compare this with the radius of an atom ~ 0.1 nm

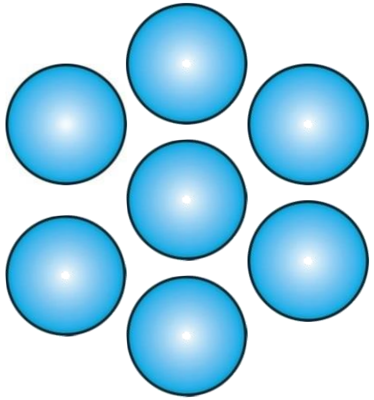
Dispersion interaction between atoms is short range, but strong enough to hold them in close contact against thermal agitation (simple liquids and organic solids).



Solid C_{60}
Fullerite

Why do we care about such weak interactions?

What happens when many atoms/molecules come together?



If central atom/molecule has N nearest neighbours, then total interaction energy

$$\mathbf{U_{tot} \sim N\,U}$$

Dispersion interactions are always attractive, so the energy of interaction increases as more atoms/molecules are brought together.

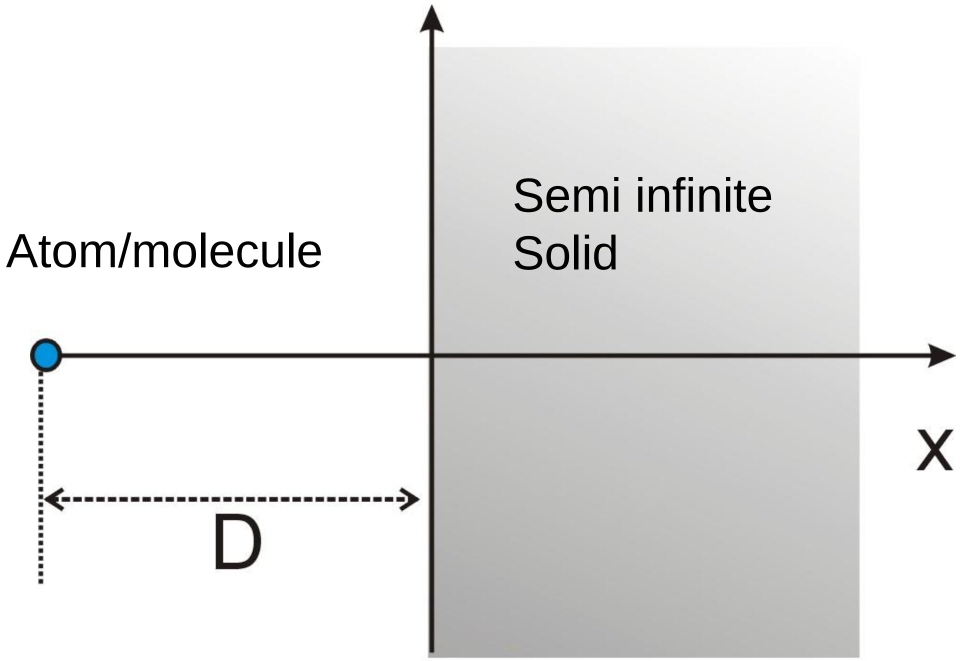
Explains why dispersion forces are capable of holding together simple organic liquids and solids (which have no other interactions).

Adding up Interactions

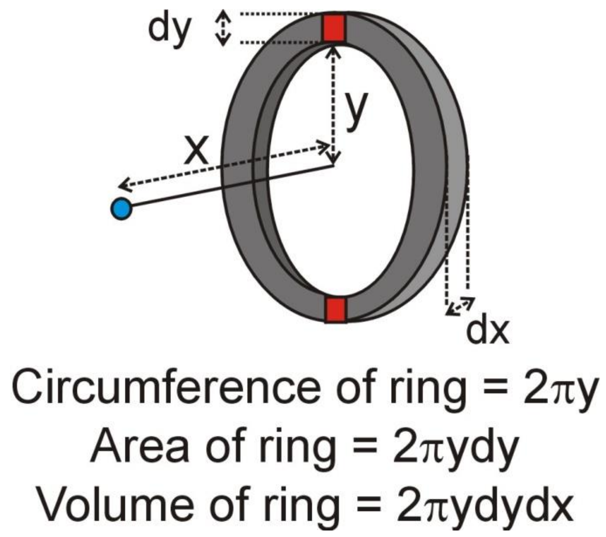
The additive nature of short range dispersion interactions means that interactions between individual atoms/molecules and macroscopic bodies (solids) can be significant.

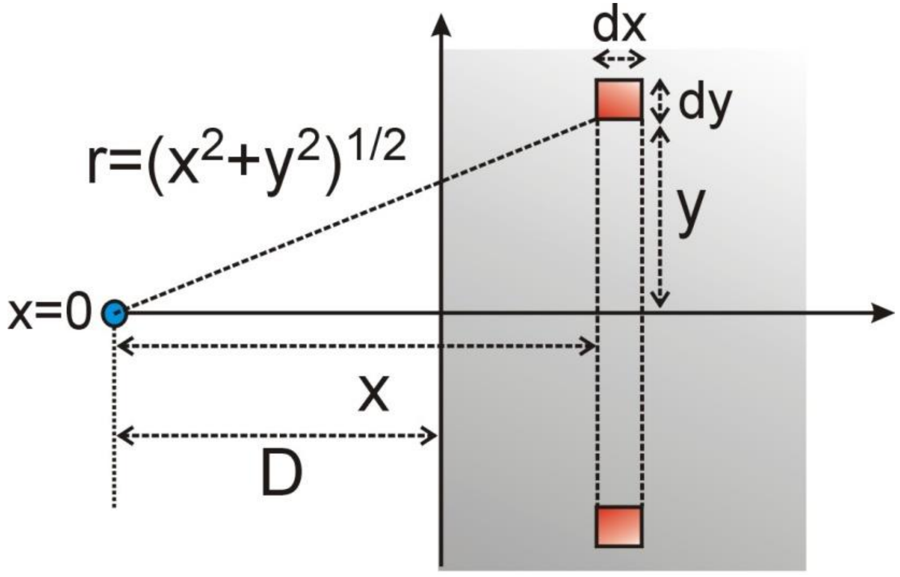
<u>A general strategy:</u>

1. Consider symmetries
2. Divide into elemental volumes
3. Integrate between limits



Detailed picture



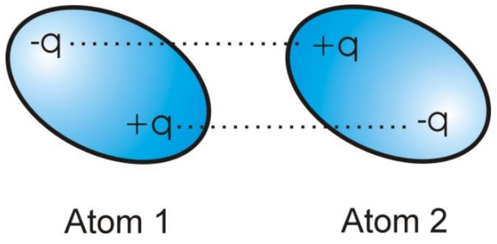


$$U(x) = -\frac{C}{x^6}$$

$$U(D) = -\frac{\pi n C}{6D^3}$$

Summary of key results

Dispersion interactions arise due to instantaneous dipole fluctuations



The potential energy due to attractive dispersion interactions between atoms and molecules has the form

$$U(x) = -\frac{\alpha(qd)^2}{(2\pi\varepsilon\varepsilon_0)^2}\frac{1}{x^6} = -\frac{C}{x^6}$$

Range of dispersion forces between atoms is ~ 0.3 nm

The **total interaction (dispersion + hard sphere repulsion)** between neutral atoms and molecules can be described in terms of a Lennard-Jones potential

$$U(x) = 4\gamma\left[\left(\frac{\sigma}{x}\right)^{12} - \left(\frac{\sigma}{x}\right)^{6}\right]$$