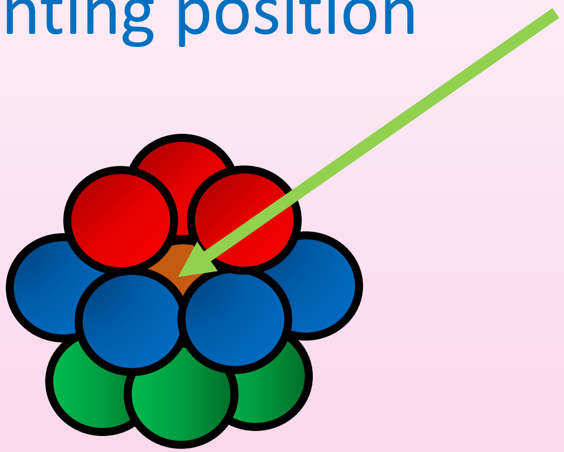
Recap from last time

Force (F) and potential (V) are intimately related – in the case of inter-atomic forces, the relationship is $F = -\frac{\mathrm{d}V}{\mathrm{d}x}$ with x representing position

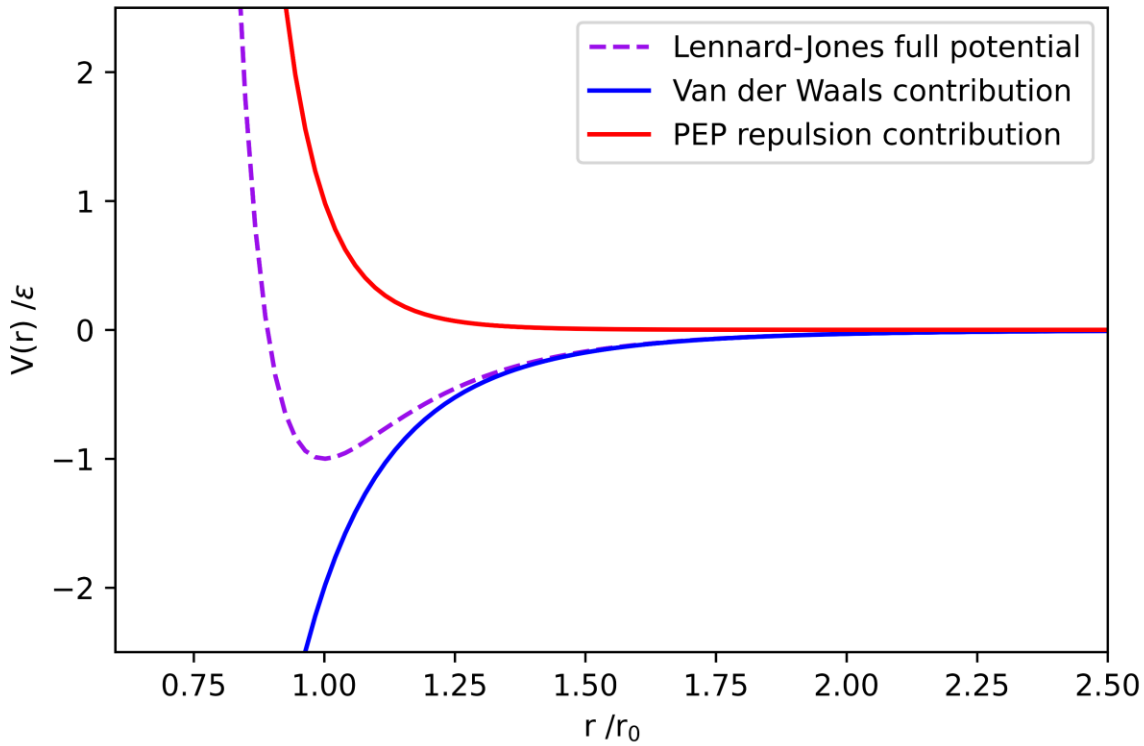
The most efficient packing for spheres is a hexagonal arrangement – 12 nearest neighbours (in a closely-packed solid)

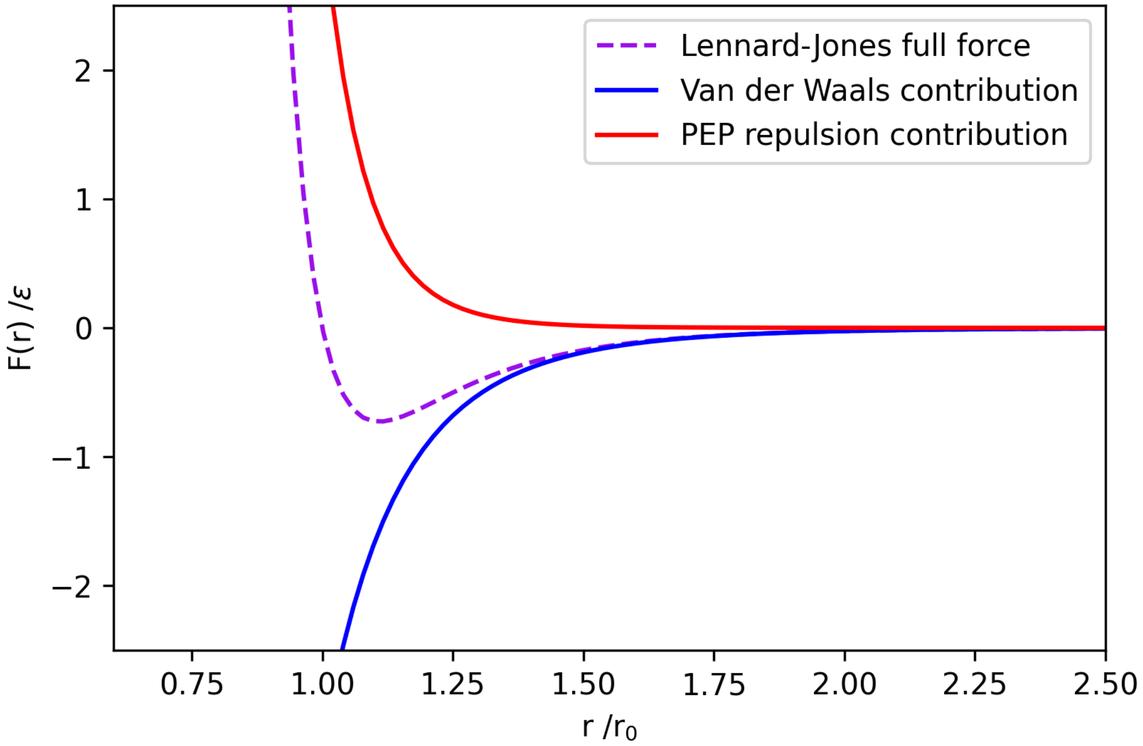


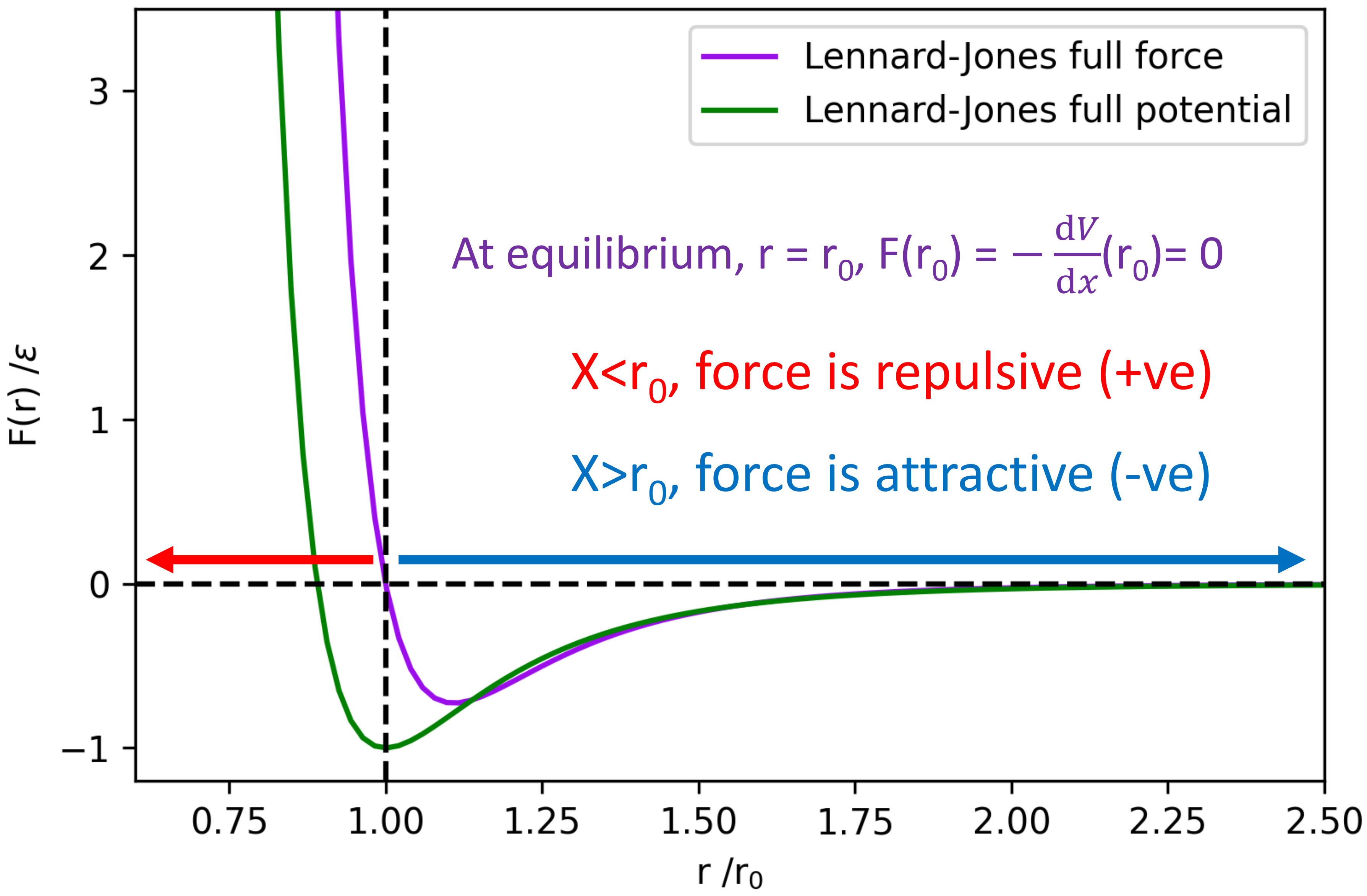
At equilibrium, neighbouring atoms sit at a distance r_0 (average bond length) away from each other, which depends on the material in a potential well of depth ε × the number of nearest neighbours

$$V(r) = \varepsilon\left[\left(\frac{r_0}{r}\right)^{12} - 2\left(\frac{r_0}{r}\right)^{6}\right]$$

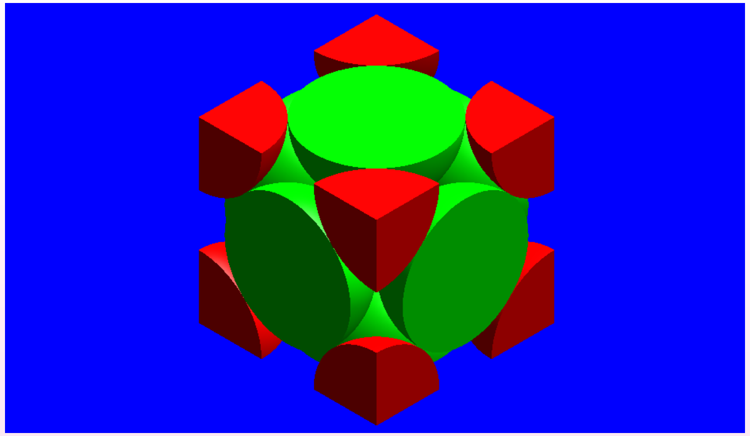
$$F(r) = 12\varepsilon\left(\frac{r_0^{12}}{r^{13}} - \frac{r_0^{6}}{r^{7}}\right)$$

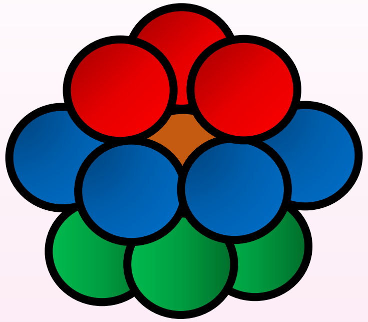


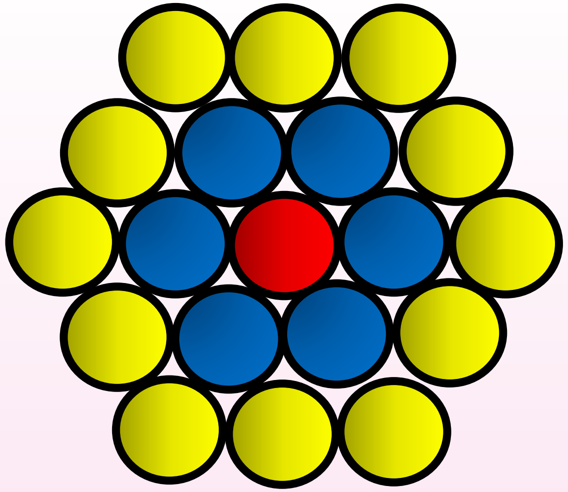




Lennard-Jones full force
Lennard-Jones full potential
At equilibrium, r = r_0, $F(r_0) = -\frac{dV}{dx}(r_0) = 0$
$X<r_0$, force is repulsive (+ve)
$X>r_0$, force is attractive (-ve)
F(r) /ε
r /r_0
3
2
1
0
−1
0.75
1.00
1.25
1.50
1.75
2.00
2.25
2.50





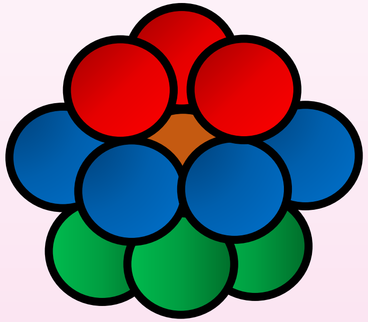


In a closely-packed FCC or HCP solid, can get a maximum coordination number (number of nearest neighbours), **n**, of 12

Inter-atomic spacing for solids: ~ 2×10^{-10} m
liquids: ~ 3×10^{-10} m
gases: ~ 40×10^{-10} m (at STP)

Liquids tend to have **n ≤ 10**

Molecular/structural binding energies



Q: To first order, how much energy do we need to remove the orange atom from the centre of the structure?

$$E = \frac{n\varepsilon}{2}$$

Q: How much energy do we need to remove 1 mole of (connected) atoms from the centre of the structure?

$$E = \frac{nN_A\varepsilon}{2}$$

where the factor of two comes from avoiding double-counting bonds (as in the diatomic system) --- or a mole consists of $N_A/2$ pairs

Measurement of an atom's size (latent heat)

Latent heat of vaporisation, L, (J/kg): the amount of heat required to completely vaporise a liquid into a gas (at a constant temperature).

Specific latent heat -> per kg

$$L = 10\, U_0/2 \times (\text{number of atoms per kg})$$

Q: How much energy do we need to remove 1 mole of (connected) atoms from the centre of the structure?

Molar latent heat -> per mol

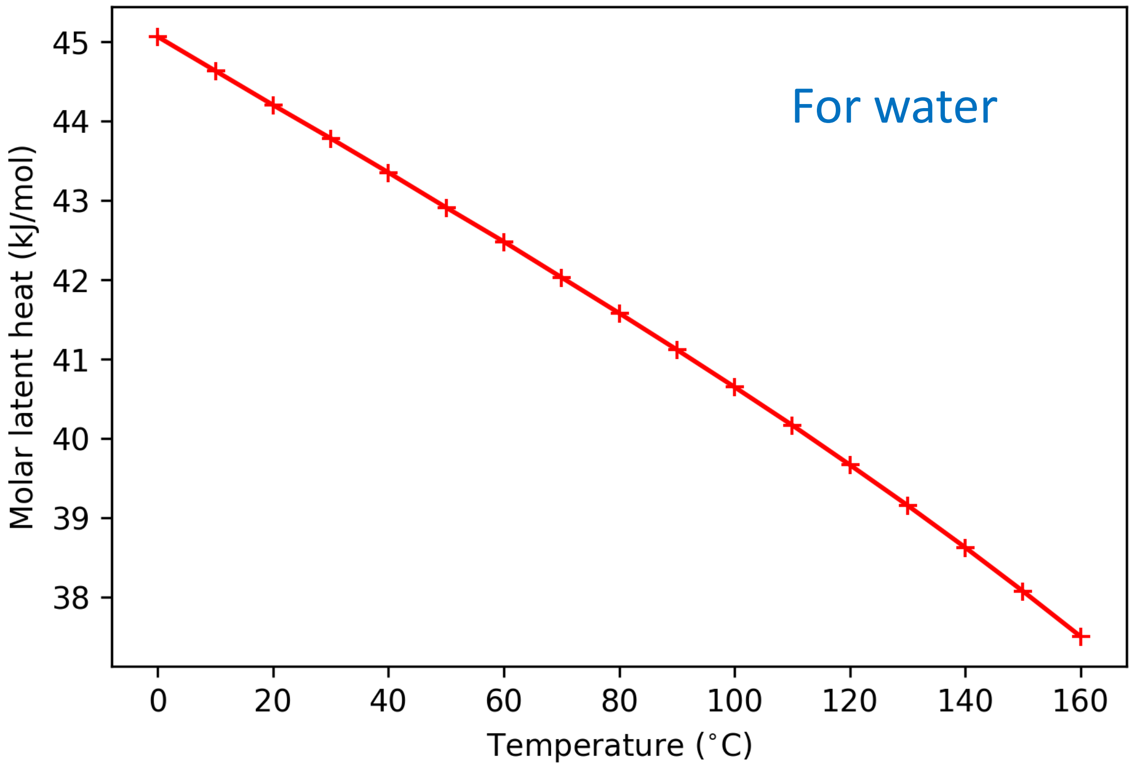
$$\text{Amount of substance (moles)} = \frac{\text{Number of particles}}{N_A}$$

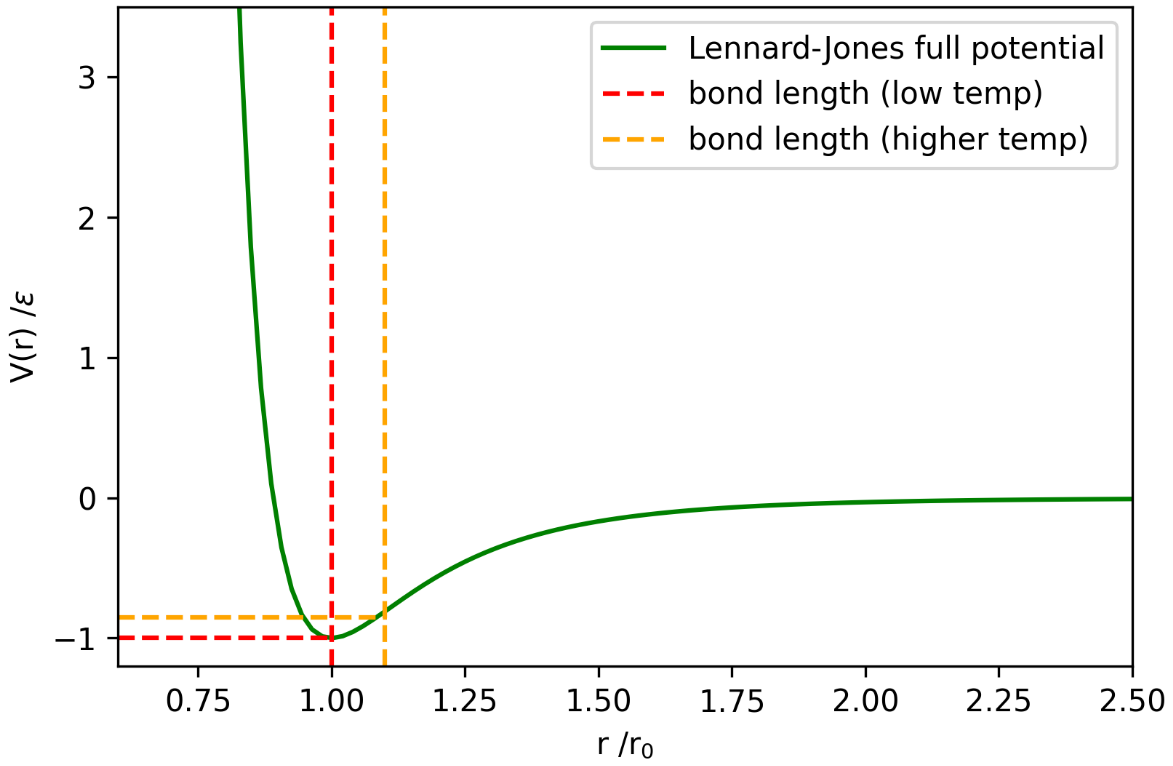
$$E = \frac{nN_A\varepsilon}{2}$$

$$N_A = \frac{atoms}{mol}$$

This assumes kinetic energy of particles is small compared to potential energy (i.e. low temperature)

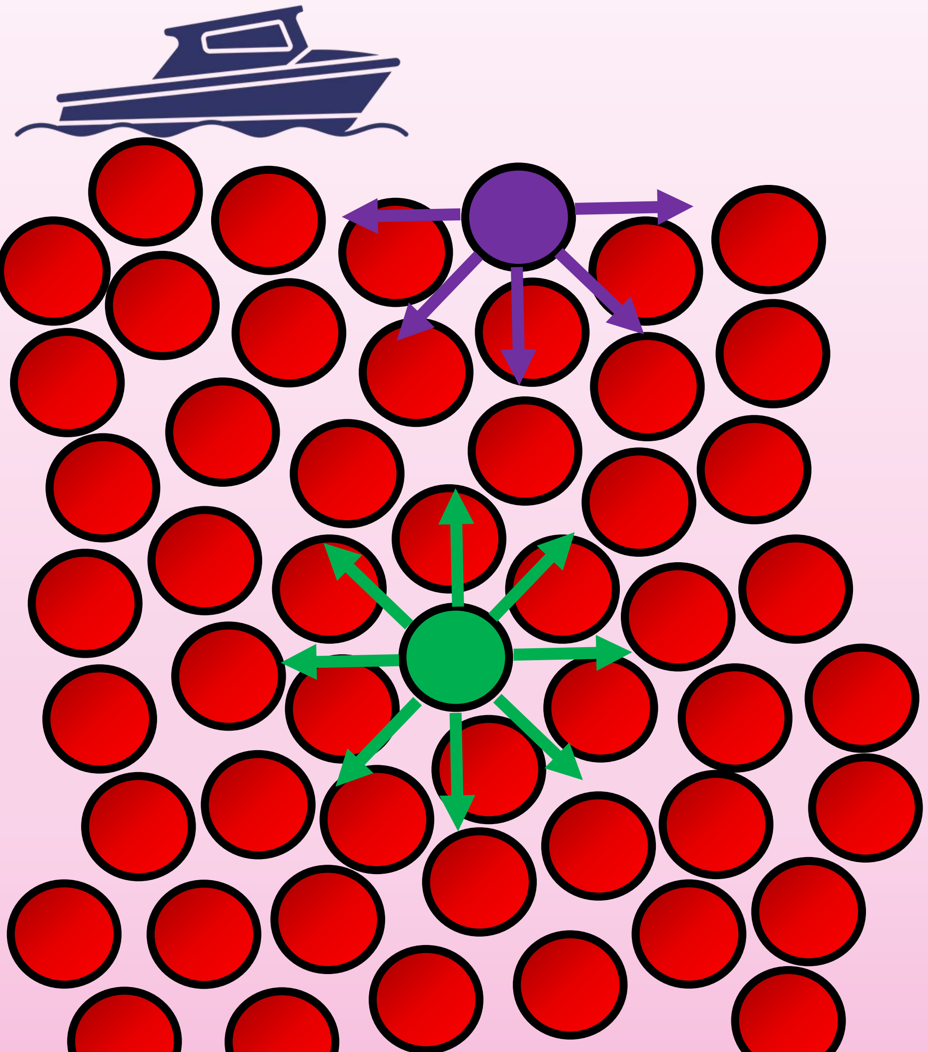
What about high temperatures?





Higher kinetic energy increases average bond length – more repulsion when close than attraction when apart

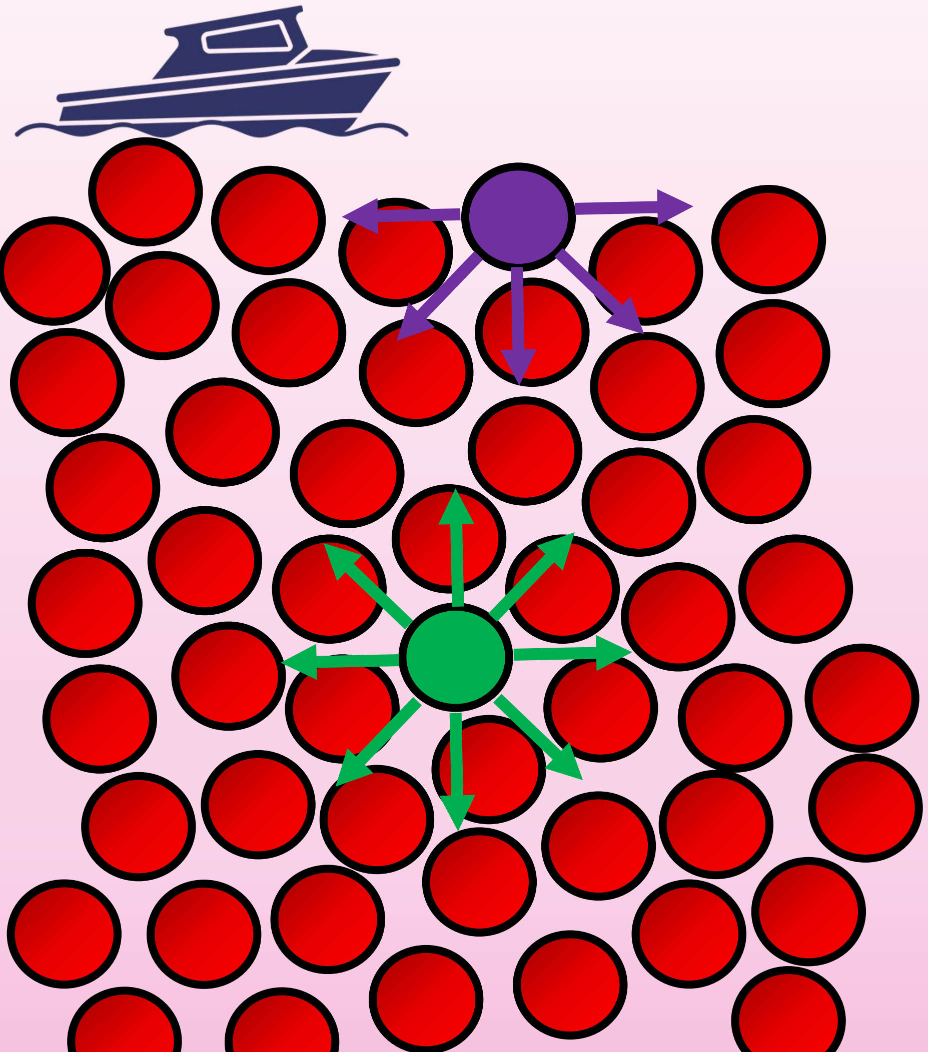
What about the surface?



Q: Does the particle at the surface or the particle deeper within the liquid experience a greater potential?

A: The particle deeper within the liquid

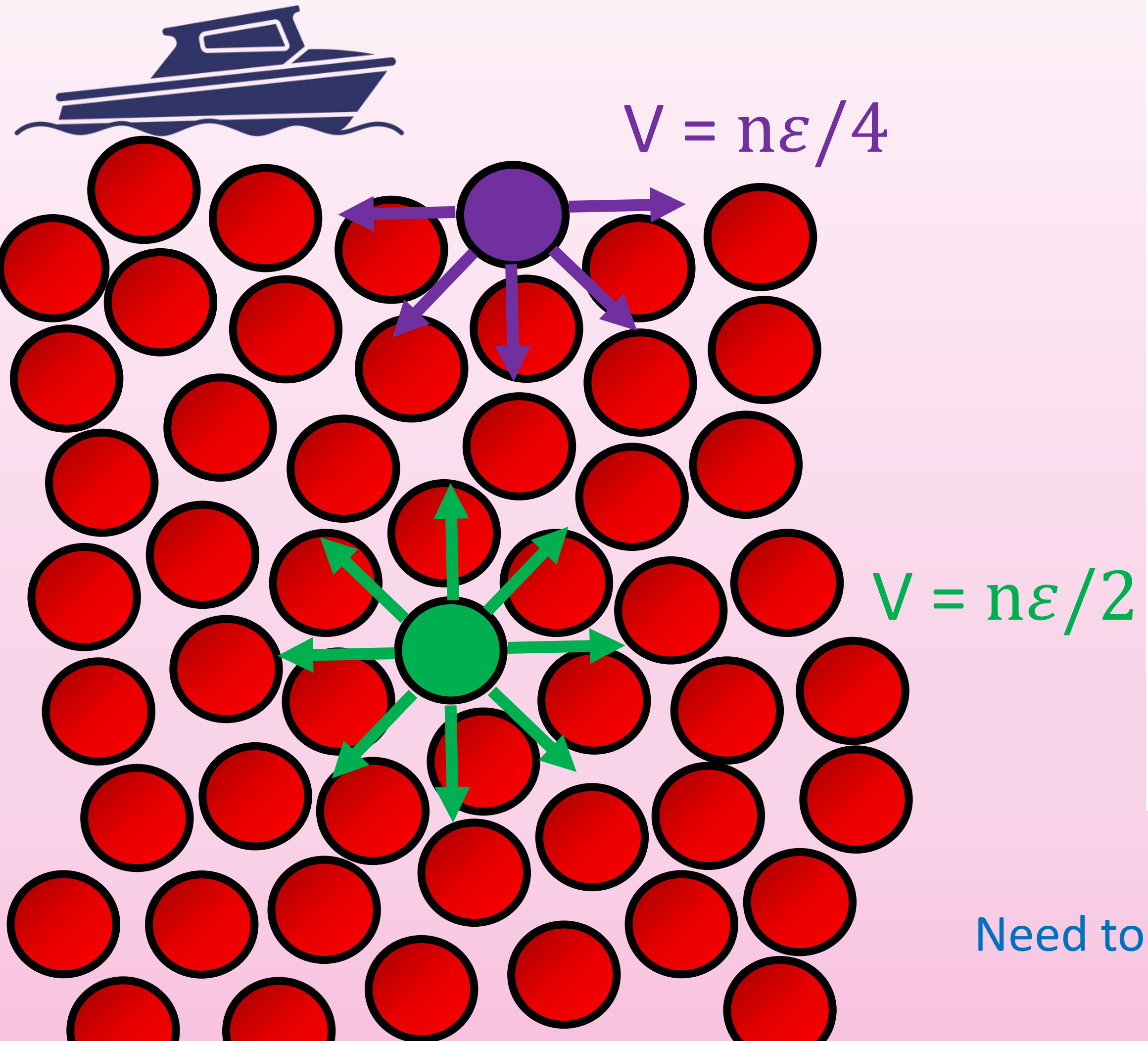
What about the surface?

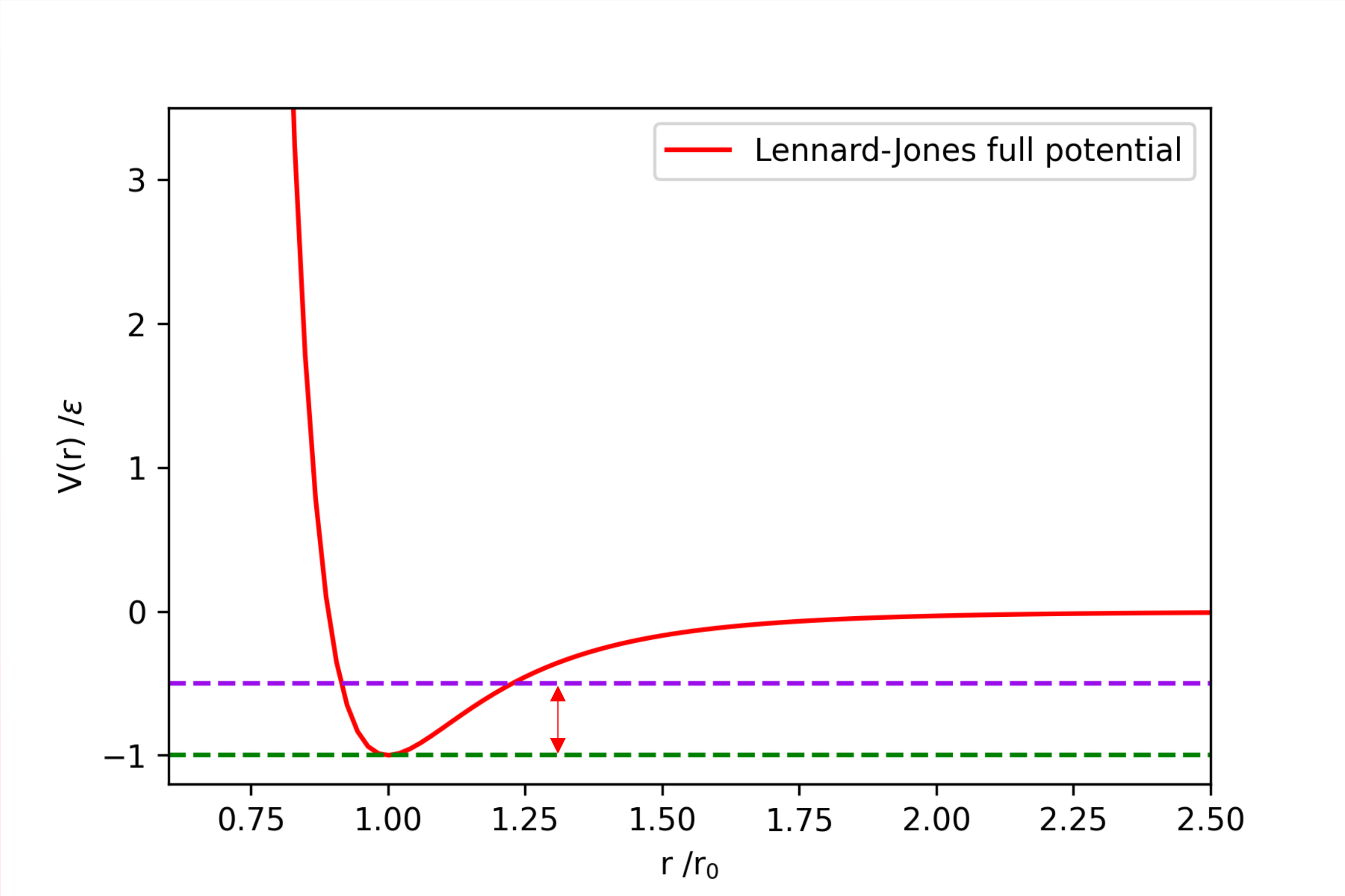


Q: What is the number of nearest neighbours for the particle on the surface if the deeper particle has 10 nearest neighbours?

A: 5 $\left(\frac{10}{2}\right)$

What about the surface?





Need to do $n\varepsilon/4$ amount of work to bring deeper particle to surface

Surface tension

Define a quantity called surface tension, γ, which is the amount of work done needed to move 1 m^2 of particles, N, to the surface of a liquid from deeper inside:

$$\gamma = \left(\frac{n\varepsilon}{2} - \frac{n\varepsilon}{4}\right) \times \mathrm{N}$$

Potential deep in liquid

Surface tension

Define a quantity called surface tension, γ, which is the amount of work done needed to move 1 m^2 of particles, N, to the surface of a liquid from deeper inside:

$$\gamma = \left(\frac{n\varepsilon}{2} - \frac{n\varepsilon}{4}\right) \times \mathrm{N}$$

Potential at surface

Surface tension

Define a quantity called surface tension, γ, which is the amount of work done needed to move 1 m^2 of particles, N, to the surface of a liquid from deeper inside:

$$\gamma = \left(\frac{n\varepsilon}{2} - \frac{n\varepsilon}{4}\right) \times \mathrm{N}$$

Number of particles per m^2

Surface tension

Define a quantity called surface tension, γ, which is the amount of work done needed to move 1 m^2 of particles, N, to the surface of a liquid from deeper inside:

$$\gamma = \left(\frac{n\varepsilon}{2} - \frac{n\varepsilon}{4}\right) \times \mathrm{N} = \frac{n\varepsilon N}{4}$$

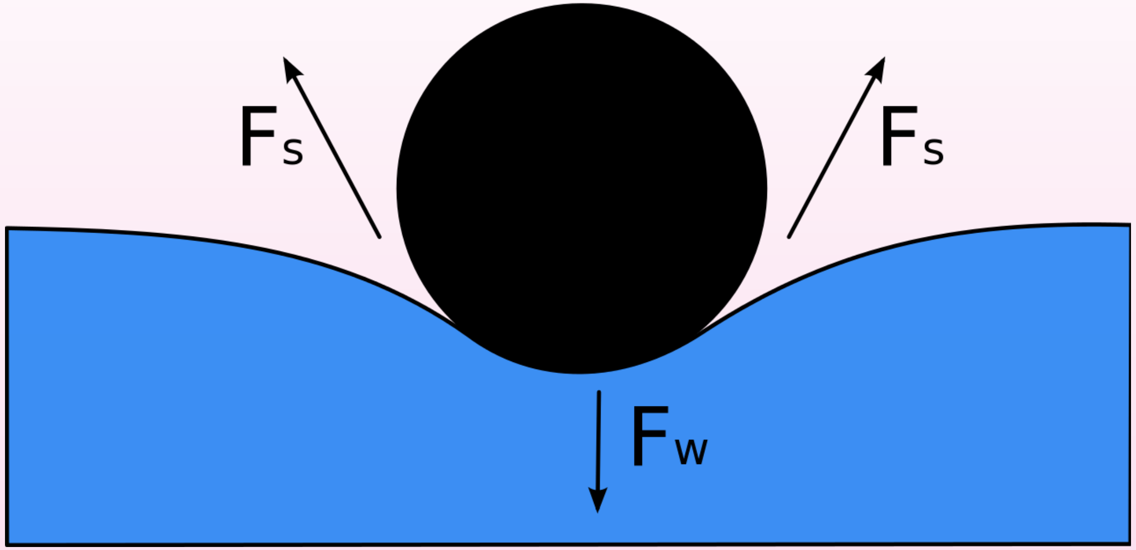
Units of energy over area

(or force over length)

Surface tension

https://www.thoughtco.com/surface-tension-definition-and-experiments-2699204

The mass of the insect wants to break the surface of the water, but the work that would need to be done to produce more surface not achievable by the gravitational potential energy



https://upload.wikimedia.org/wikipedia/commons/thumb/6/6a/Surface_Tension_Diagram.svg/1280px-Surface_Tension_Diagram.svg.png

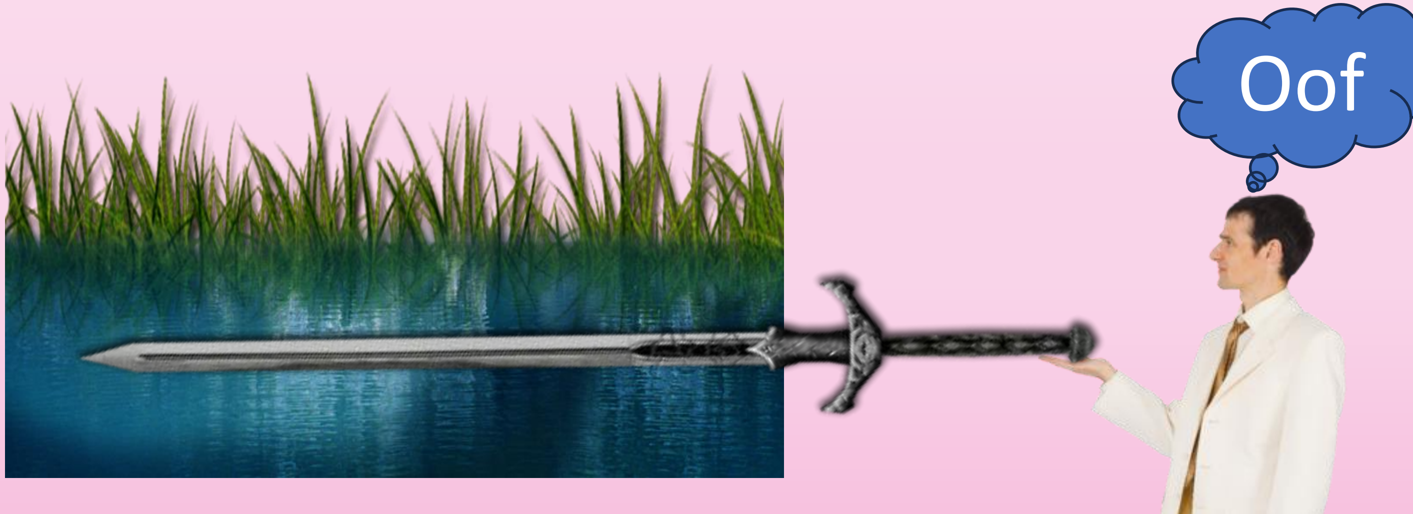
The force exerted by the liquid (tangential to its surface) that opposes the stretching of the surface is larger than the force of gravity acting on the insect

Easy to consider in terms of both forces and potentials!

Surface tension

Surface tension has units of energy over area, or force over length

The force due to surface tension acts parallel to the surface of the liquid, but perpendicular to the division we are trying to create by exerting a separate force on the liquid



Surface tension

Surface tension has units of energy over area, or force over length

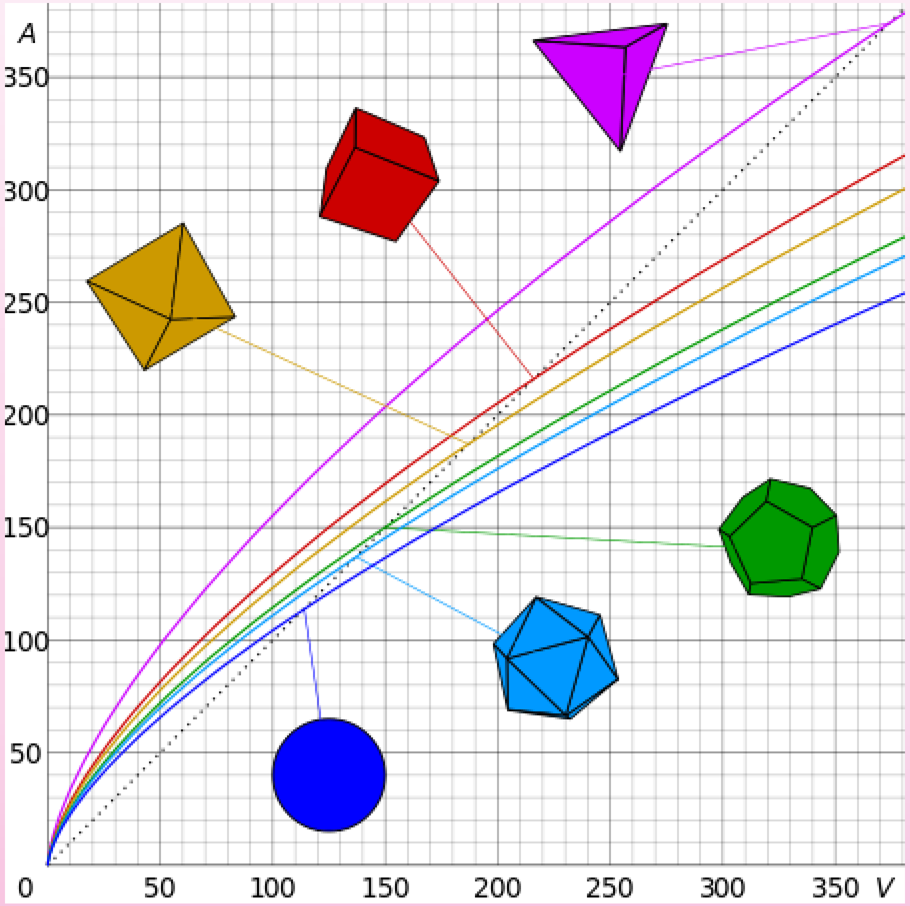
The force due to surface tension acts parallel to the surface of the liquid, but perpendicular to the division we are trying to create by exerting a separate force on the liquid

Any other consequences?

Want to minimise the amount of surface for a given volume in a liquid…

Spheres!

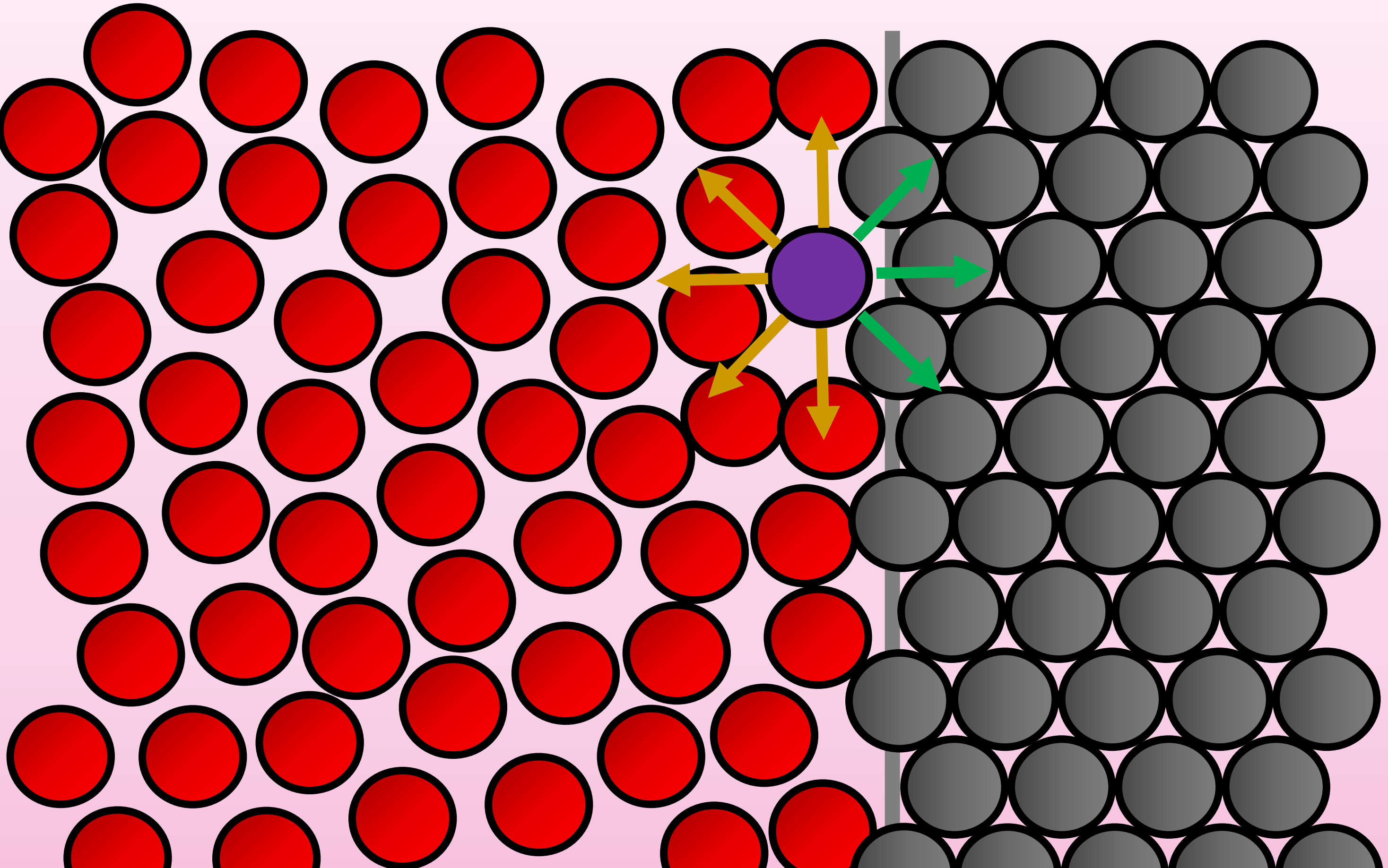
https://www.thoughtco.com/definition-of-surface-tension-in-chemistry-605713



https://i.stack.imgur.com/jZL2T.png

Surfaces revisited

Consider a liquid contained in some solid beaker

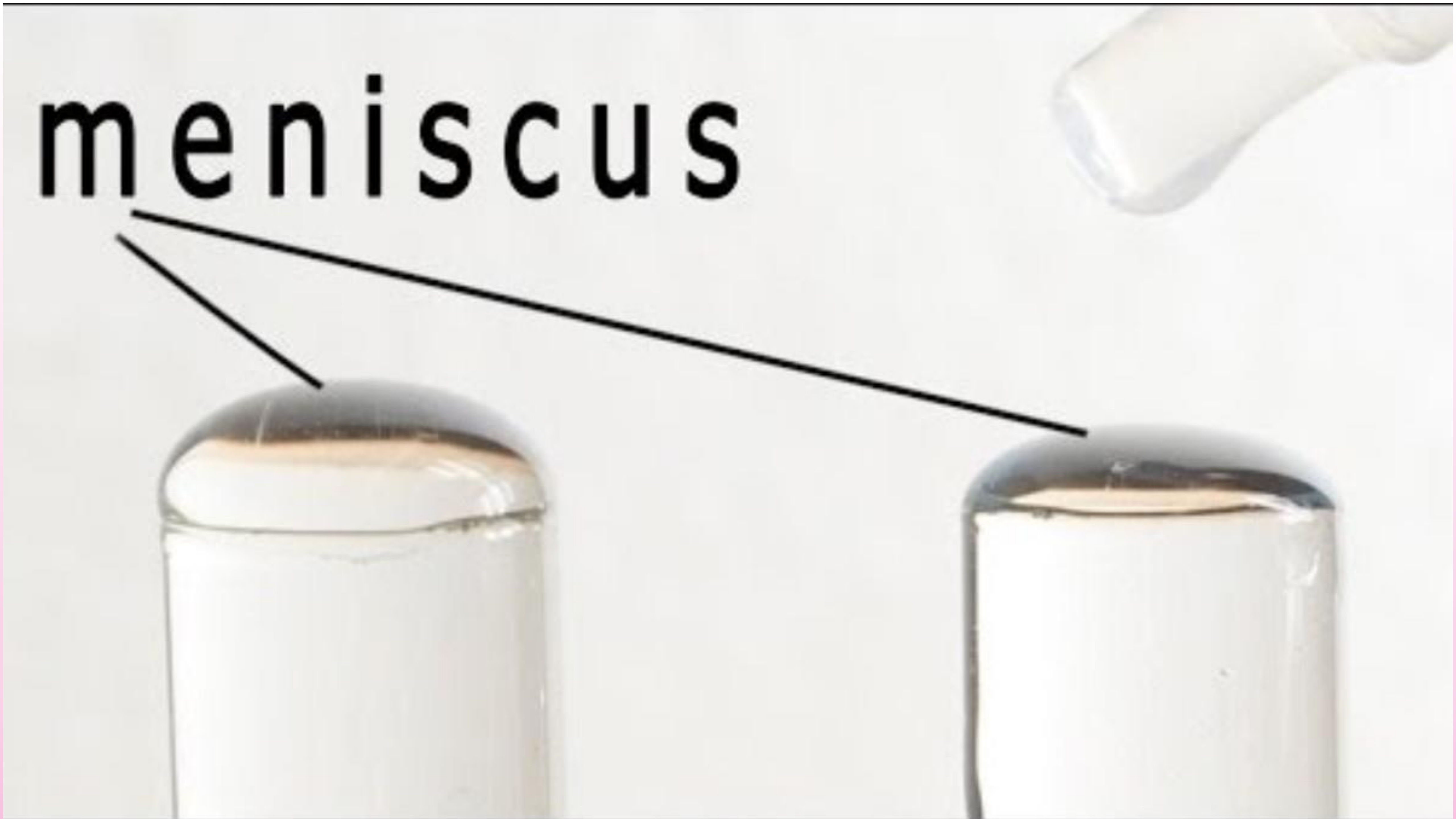


Surface particle now has two competing forces – the interatomic forces of the liquid and the beaker

Cohesion and adhesion

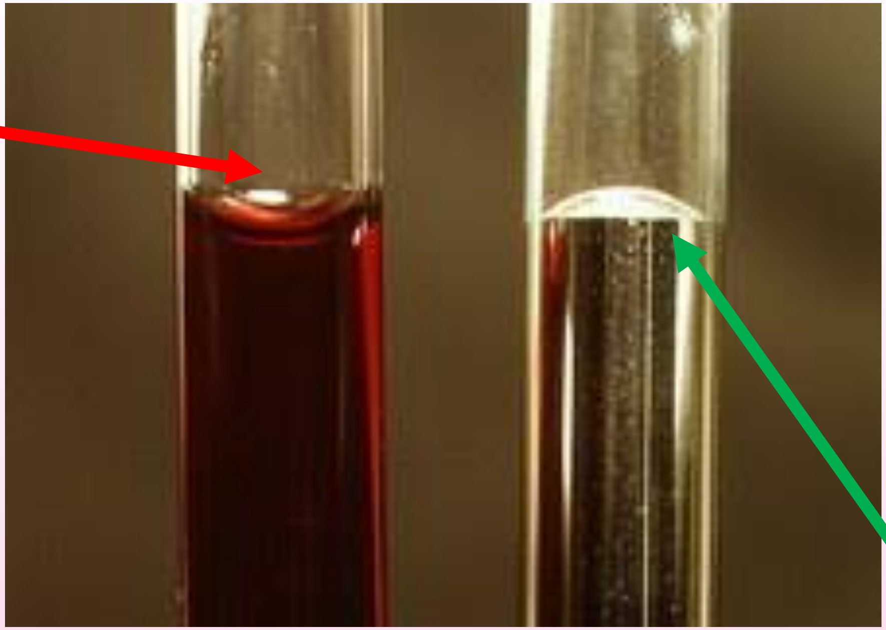
Interparticle forces between dissimilar particles

Interparticle forces between similar particles


meniscus

Wetting

Concave
(strong adhesion)



https://media.sciencephoto.com/image/a3500019/225

Convex
(weak adhesion)

Wetting is the ability of a liquid to maintain contact with a solid surface (inversely proportional to surface tension)

Most liquids are "wetter" than water!

https://en.wikipedia.org/wiki/Wetting

Strong adhesive forces cause liquid to stick to the sides of the container: concave meniscus

Strong cohesive forces causes minimisation of surface area: convex meniscus

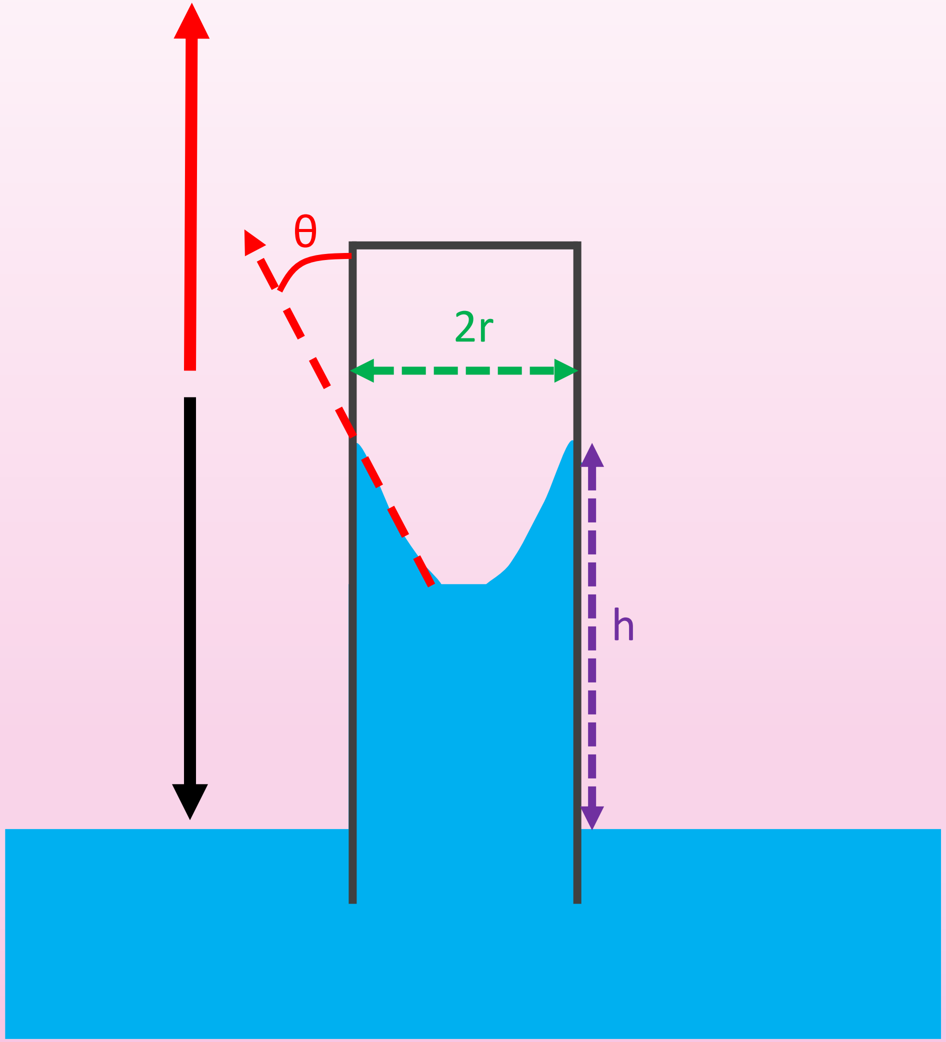
Capillary action

$$h = \frac{2\gamma \cos\theta}{\rho g r}$$

Open tube placed in contact with the surface of a liquid causes the liquid to rise up the tube

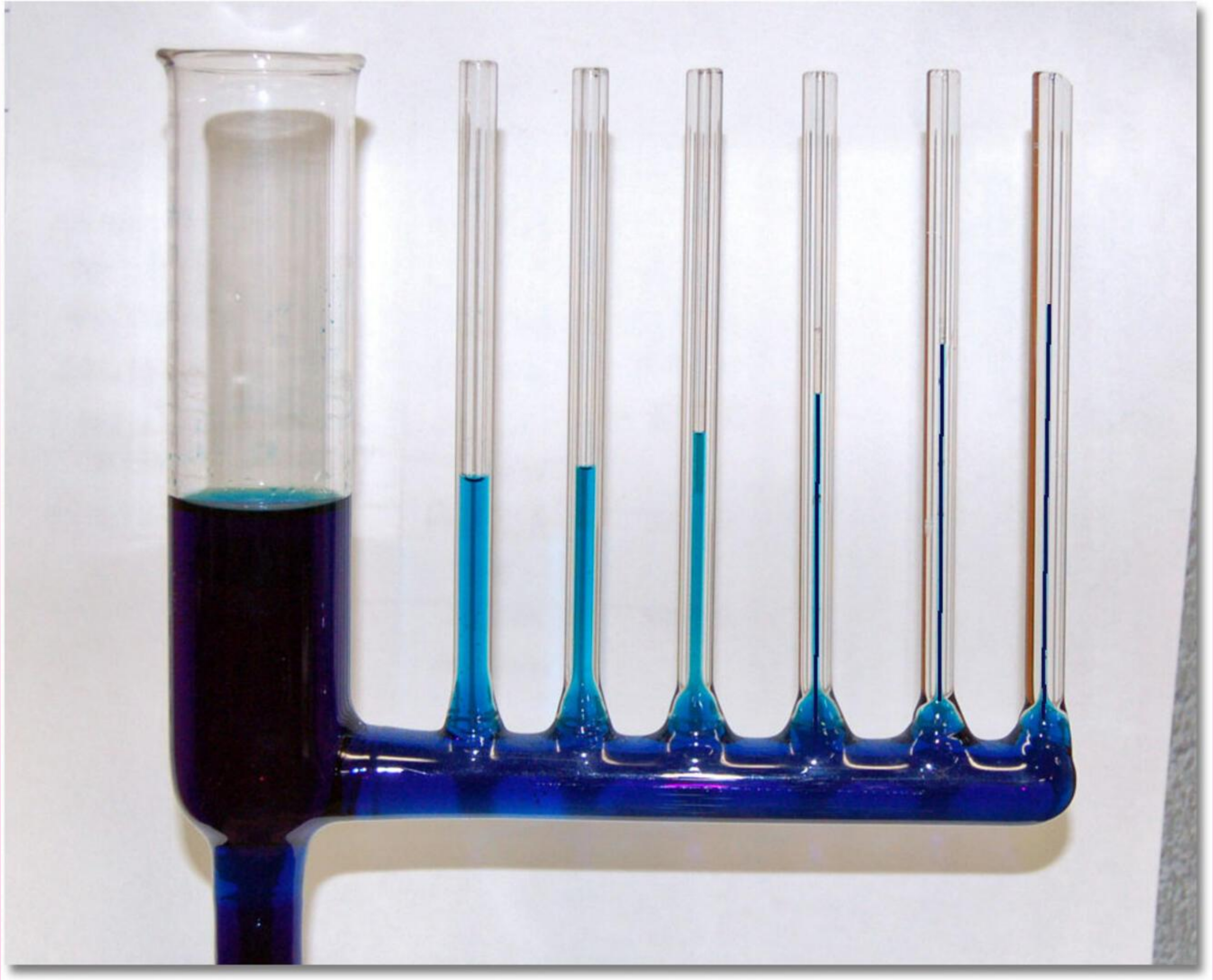
Competing forces/potentials:

1) Gravity of the liquid
2) Surface tension – total surface energy is reduced as adhesion contributes to liquid in the tube



https://scienceexperiments101.weebly.com/uploads/6/1/3/6/61367479/8158502_orig.jpg

https://www.zurich.com/en/media/magazine/2021/can-reforestation-uproot-climate-change



Credit: Dr. Keith Hayward
https://www.usgs.gov/media/images/narrower-tube-openings-allow-capillary-action-pull-water-higher

Summary

Looked at the relationship between the microscopic quantity of the energy to separate two particles and how it can be extended to macroscopic quantities (latent heats)

Discussed the underlying physics behind surface tension from microscopic behaviour

Learnt about cohesion and adhesion in the context of liquids, as well as capillary action