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# The Importance of Interfaces

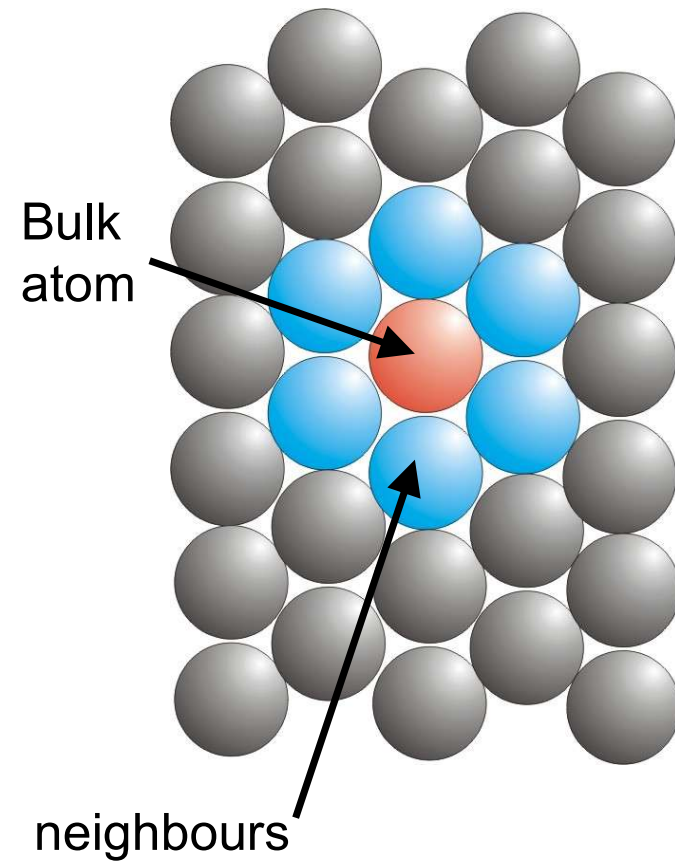


## Cohesive Energy of bulk materials

In the bulk of a material, atoms and molecules are surrounded by  $N_{Bulk}$  nearest neighbours.

If each interaction with the central atom/molecule has an energy,  $-u$ , the total interaction energy becomes

$$U_{bulk} = -N_{bulk}u$$





## Cohesive Energy near a surface

When we create a surface in material and expose it to vacuum each surface atom/molecule has fewer nearest neighbours

$$N_{surf} < N_{bulk}$$

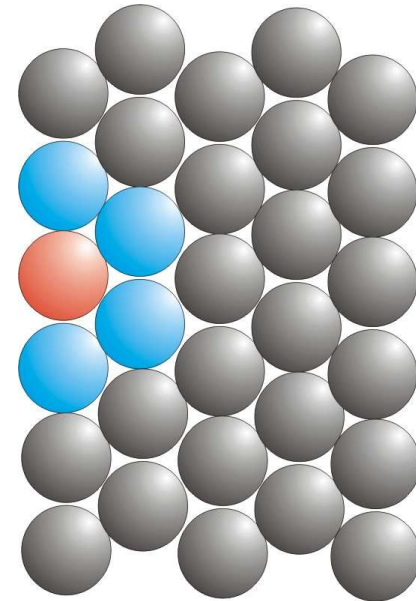
The interaction energy per atom/molecule is then

$$U_{surf} = -N_{surf}u$$

There is therefore an energy cost (ie positive, unfavourable)

$$\Delta U = U_{surf} - U_{bulk} = (N_{bulk} - N_{surf})u$$

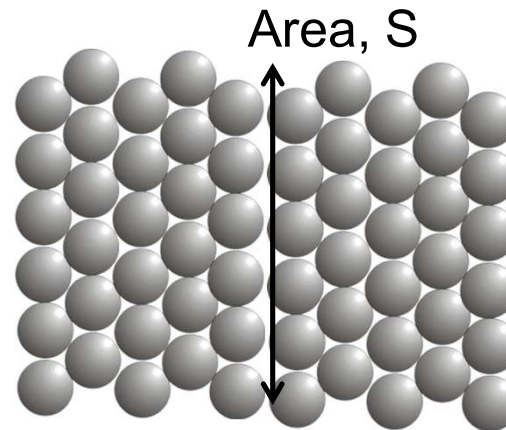
associated with each surface atom/molecule





# Surface Energy

“Surface energy is the excess energy required per unit area to create a surface in vacuum (or air)”



The energy required to create two new surfaces in a material, each having area  $S$  is

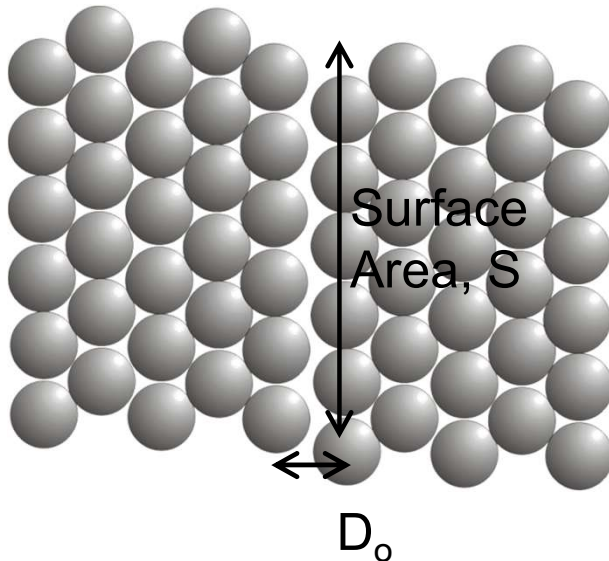
$$W = 2\gamma S$$

where  $\gamma$  is the surface energy of the material in  $\text{Jm}^{-2}$



## Calculating surface energies from dispersion potentials

The surface energy is the energy required to separate two surfaces from their inter-atomic/molecular distance and remove them to infinity



Surface energy is half this energy  
(there are two surfaces) per unit area

Recall that inter-surface potential energy,  $U$  is

$$U = -\frac{AS}{12\pi D_0^2}$$

$A$  = Hamaker constant (J)

$$\gamma = -\frac{U}{2S} = \frac{A}{24\pi D_0^2}$$



## Does this simplistic approach work?

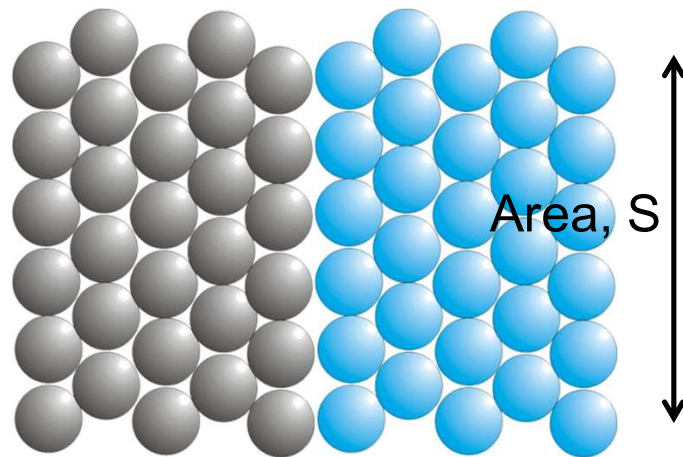
$$\gamma = -\frac{U}{2S} = \frac{A}{24\pi D_0^2}$$

Material	Measured $\gamma$ (mJm <sup>-2</sup> )	A (x10 <sup>-20</sup> J )	A/(24 $\pi$ D <sub>0</sub> <sup>2</sup> ) (mJm <sup>-2</sup> ) (D <sub>0</sub> =0.165nm)
Liquid Helium	0.12-0.35	0.057	0.28
Polystyrene	33	6.6	32.1
Benzene	28.8	5	24.4
Ethanol	22.8	4.2	20.5



# Interfacial Energy

“Interfacial energy is the excess energy per unit area required to create an interface between two different materials”



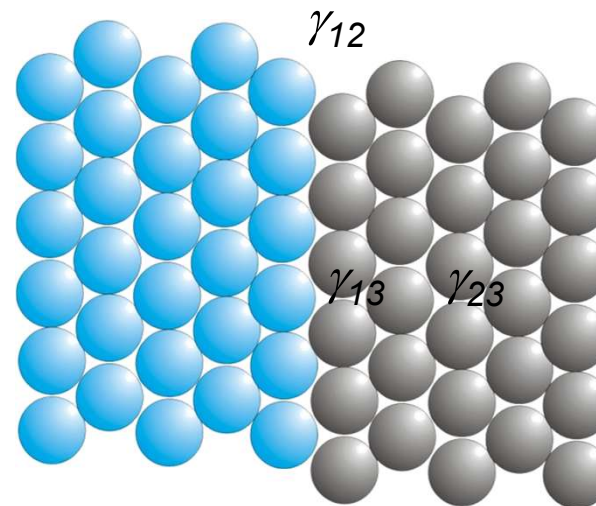
The interfacial energy between materials 1 and 2 is represented by  $\gamma_{12}$



## Work of Adhesion

The energy required per unit area to separate two surfaces of materials 1 and 2 in a third medium (medium 3) is called the *work of adhesion* ( $W$ )

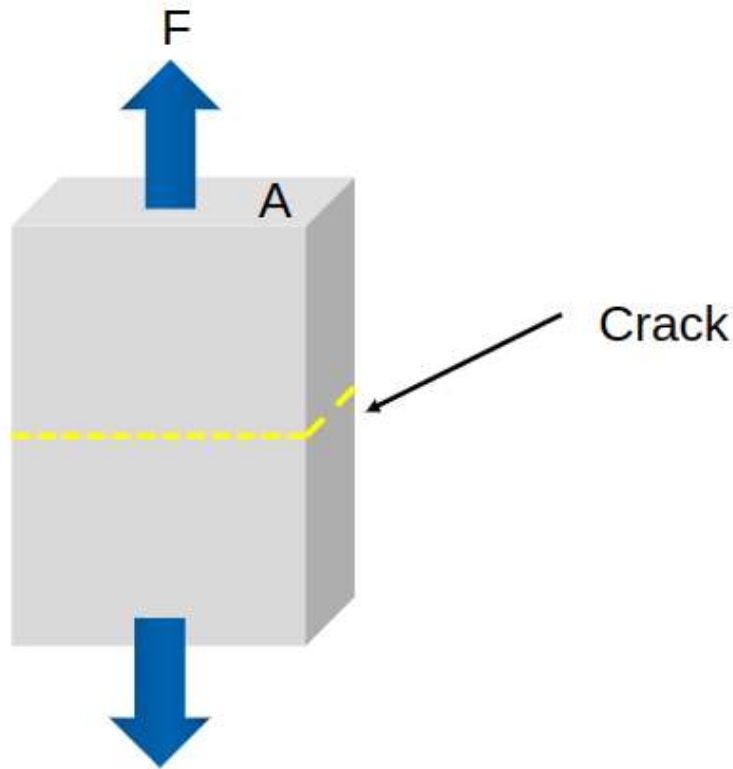
It is the energy required to break the interface between two materials and form two new interfaces



$$W = \underbrace{\gamma_{13} + \gamma_{23}}_{\text{creation of new surfaces}} - \underbrace{\gamma_{12}}_{\text{breaking of initial bonds}}$$



## Problem 1: Cracking a rectangular bar

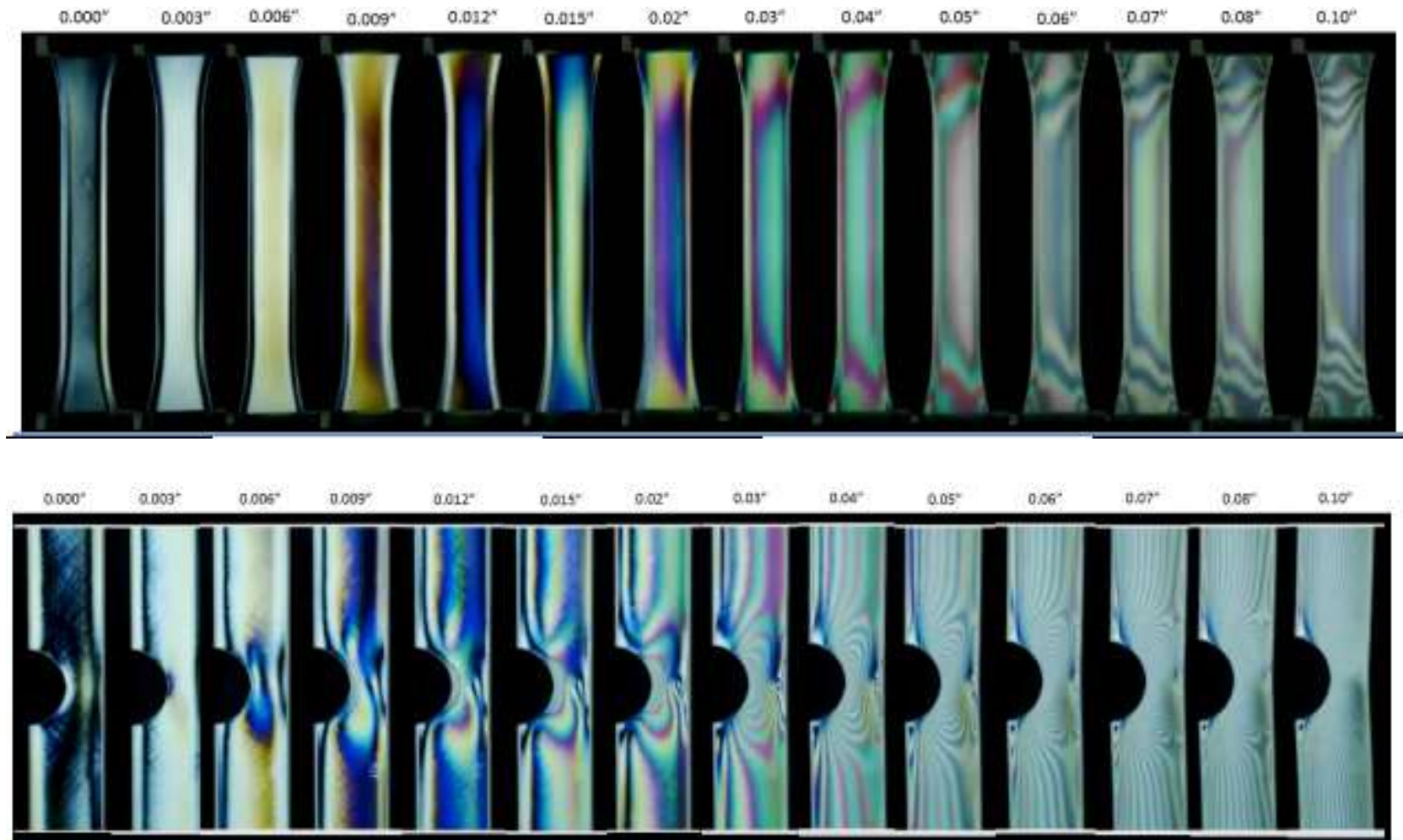


Estimate the maximum force that a bar of cross-sectional area  $A = 0.1\text{m}^2$ ,  $L=0.2\text{m}$  and Crack Young's modulus  $E = 1119\text{ GPa}$ , can sustain before cracking? The (work of adhesion) change in the interfacial energy of the bar/air interface is  $\gamma = 40\text{mJm}^{-2}$ . You may use the fact that for a bar under stress  $\sigma$ , the energy stored is:

$$U = \sigma^2 AL / 2E$$



## Stress concentration around a crack tip

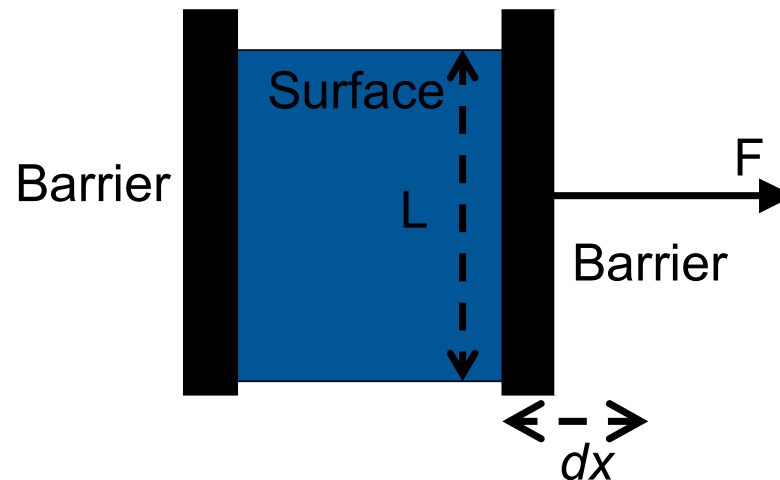




## Surface and interfacial tensions

Surface/interfacial tension is the force required per unit length to extend a surface/interface (measured in  $\text{Nm}^{-1}$ )

**The surface energy and surface tension are equivalent.** They act to prevent a surface from increasing in area. Consider...



$$dU = \gamma L dx$$

$$T = -F = \frac{dU}{dx} = \gamma L$$

$$\gamma = \frac{T}{L} \text{ Nm}^{-1}$$

$$\text{Nm}^{-1} = \text{Jm}^{-2}$$

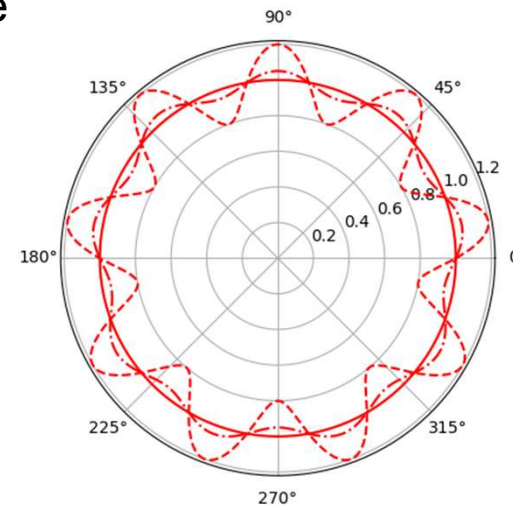
The same reasoning applies to interfacial tension and interfacial energy



# Why is a suspended droplet spherical?



A sphere represents the smallest surface area for a given volume



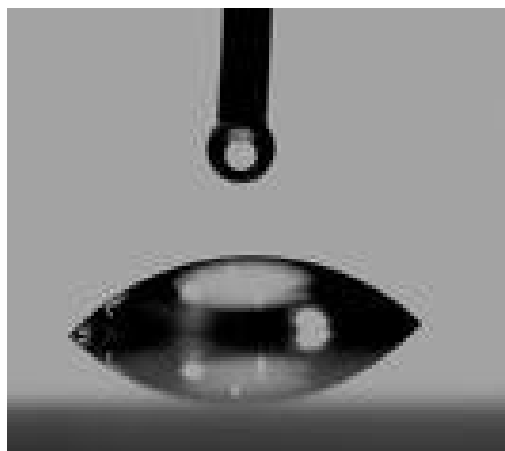
Any shape other than a sphere will have additional surface area  $dA$ . This results in an increase in the free energy  $dU$  of  $\gamma_{12}dA$ .

Surface tension thus acts to minimise the surface area through creation of a curved interface.



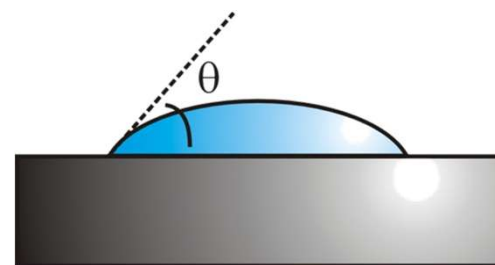
# Wetting interactions

Surface and interfacial energies determine the shape of macroscopic liquid droplets when they are placed on a surface



$$S = \gamma_{VS} - \gamma_{LS} - \gamma_{VL}$$

Partially wetting films ( $S < 0$ )



Completely Wetting film ( $S > 0$ )

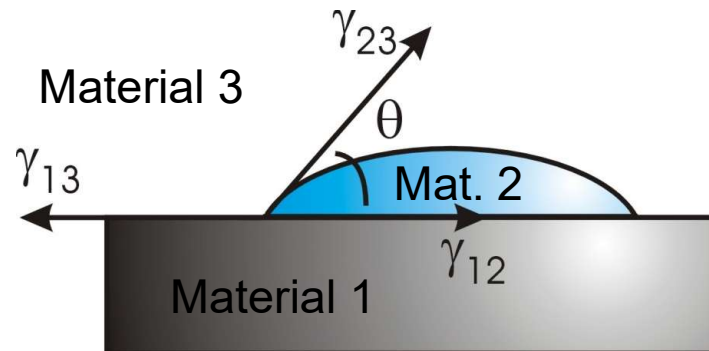




## Problem: Contact angle droplet

The contact angle made by a liquid with a surface depends on the balance of the interfacial tensions.

- By considering the balance of horizontal forces acting on a small length of contact line, derive an expression for the angle made by the droplet edge
- Calculate the angle if  $\gamma_{12} = 5\text{mJm}^{-2}$ ,  $\gamma_{13} = 15\text{mJm}^{-2}$ ,  $\gamma_{23} = 20\text{mJm}^{-2}$ ,



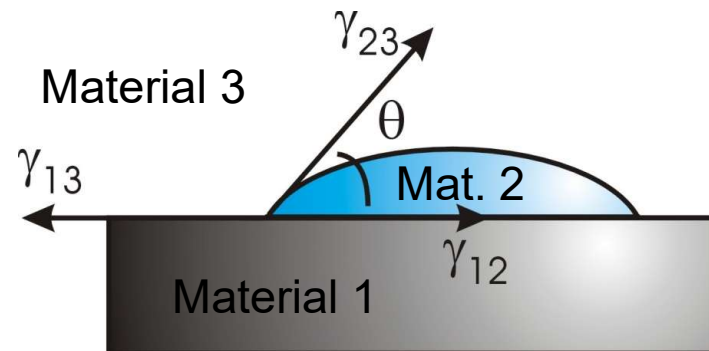
“Young-Laplace Equation”

$$\cos \theta = \frac{\gamma_{13} - \gamma_{12}}{\gamma_{23}}$$



## Cohesive v Adhesive Forces

The contact angle made by a liquid with a surface depends on the balance of the cohesive and adhesive forces



“Hydrophilic / Hydrophobic” – water makes small / large contact angle with the material



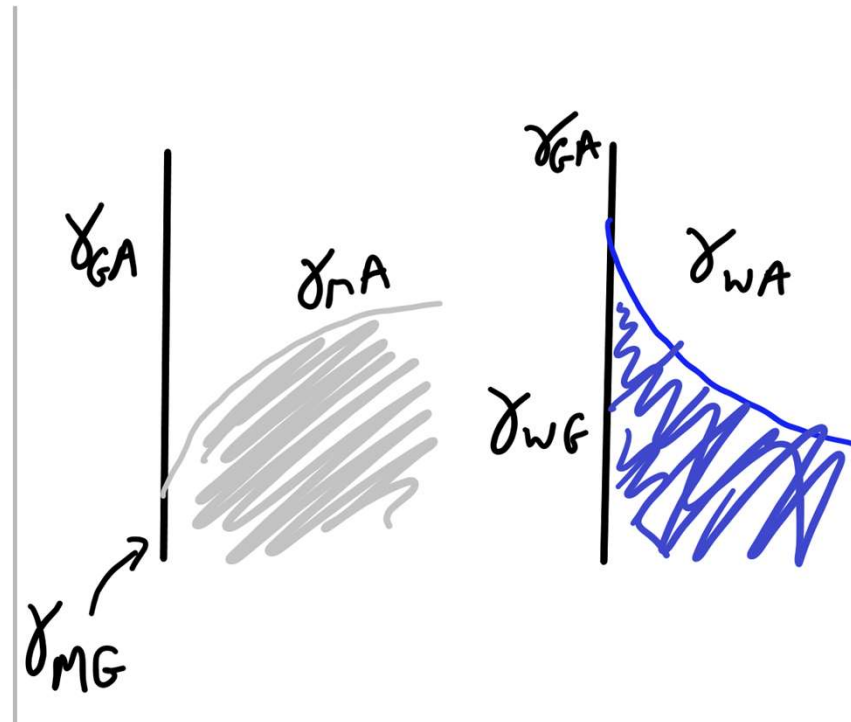
*Mercury and water in a glass tube*



## Thinking through interfacial energies



*Mercury and water in a glass tube*

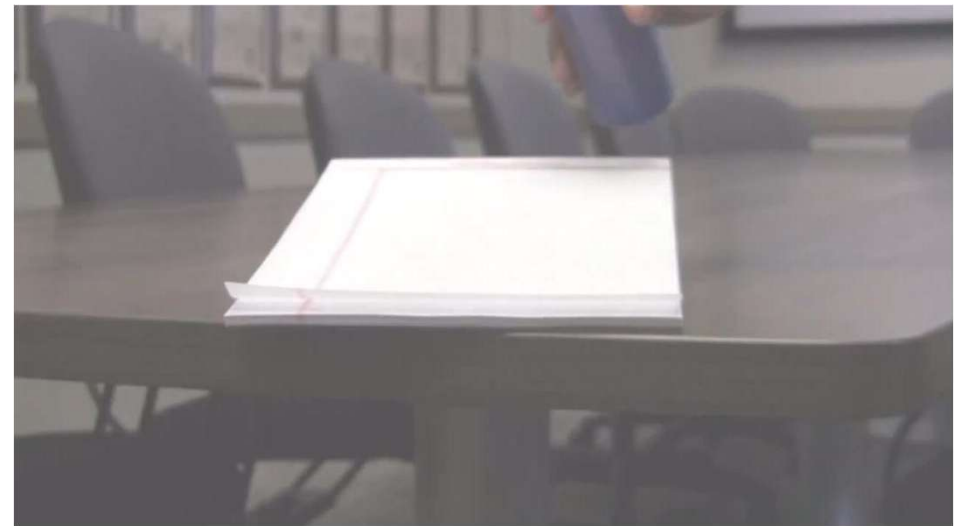
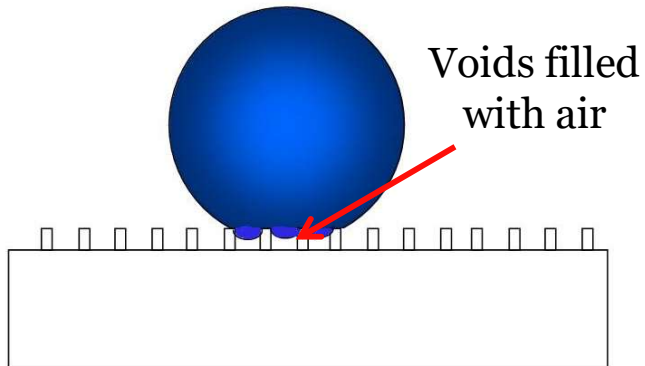


Why does water spread upwards and mercury curve downwards?



# Superhydrophobicity

Covering surfaces in small structures can change the balance of surface energies and hence the contact angle. The area of the liquid-air interface increases whilst the liquid solid-interface decreases.



It is possible to reach contact angles  $> 160^\circ$



## Summary of key concepts

In liquids the minimisation of the interfacial energies determines the shape of droplets

For a single droplet in an immiscible phase this is a sphere since this has the smallest area for a given volume.

At surfaces this is more complicated and the shape arises from a balance of the various interfacial energies.

