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PHYS3009: Force and Function at the Nanoscale
Week 23 – 10:00am Tuesday – 21 February 2023





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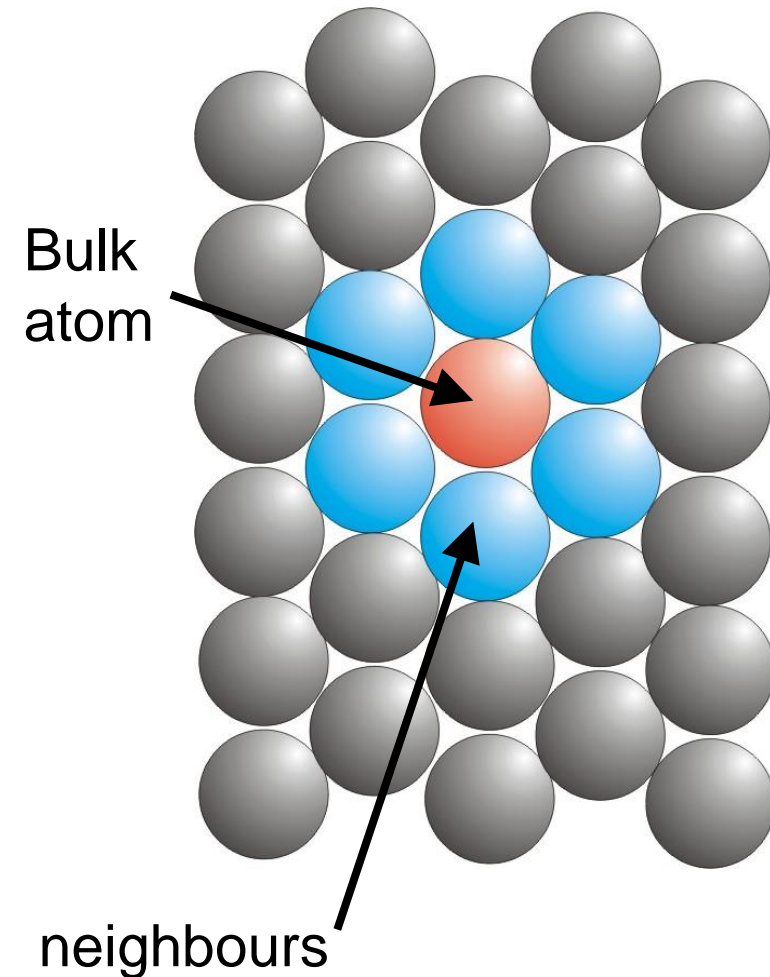
The Importance of Interfaces

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

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

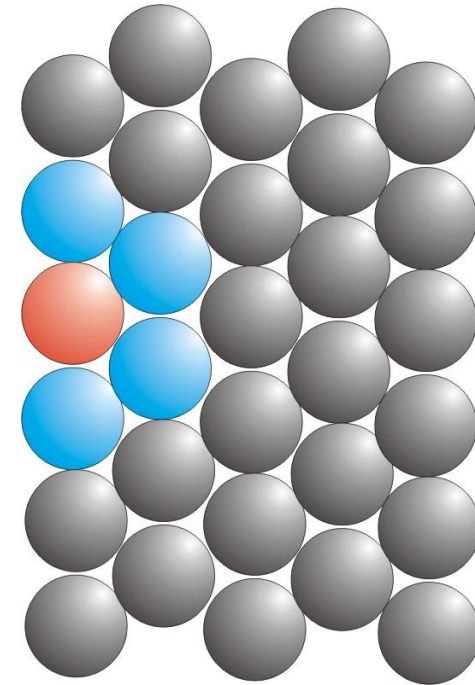
The interaction energy per atom/molecule is then

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

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

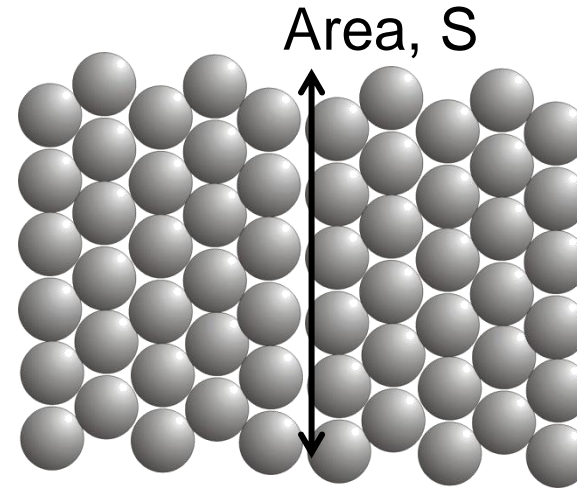
$$\Delta U = U_{surf} - U_{bulk} = (N_{bulk} - N_{surf})u$$

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)”



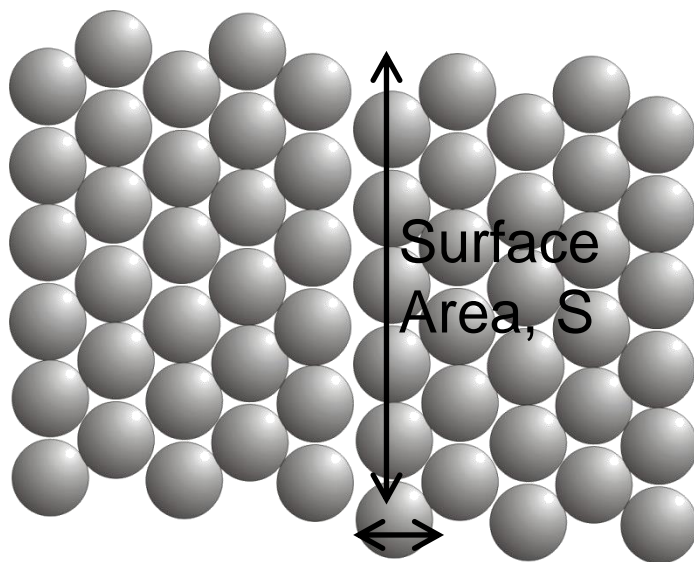
The energy required to create two new surfaces in a material, each having area S is

$$W = 2\gamma S$$

where γ is the surface energy of the material in 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?

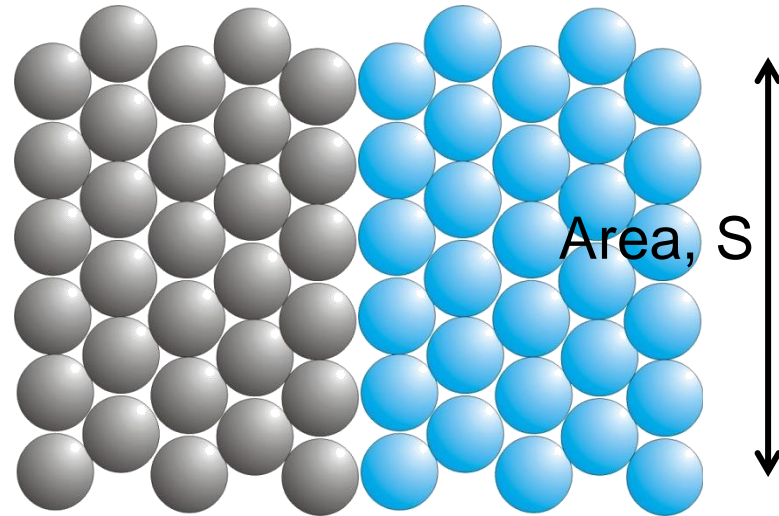
$$\gamma = -\frac{U}{2S} = \frac{A}{24\pi D_0^2}$$

Material	Measured γ (mJm ⁻²)	A (x10 ⁻²⁰ J)	A/(24 π D ₀ ²) (mJm ⁻²) (D ₀ =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”

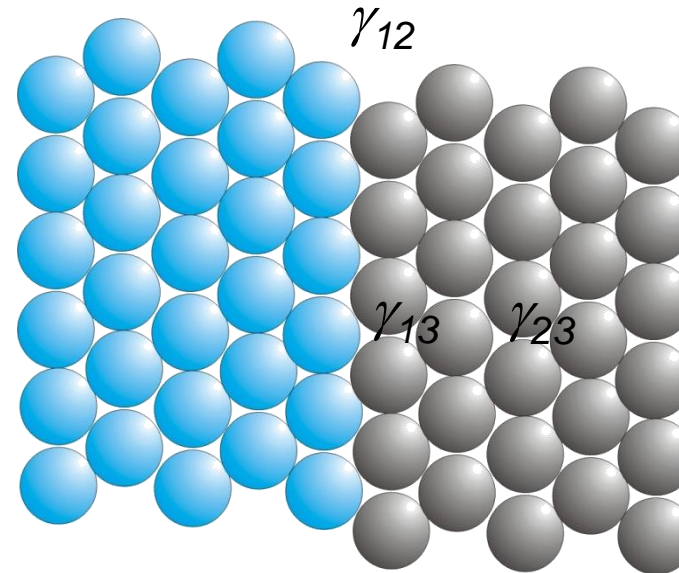


The interfacial energy between materials 1 and 2 is represented by γ_{12}

Work of Adhesion

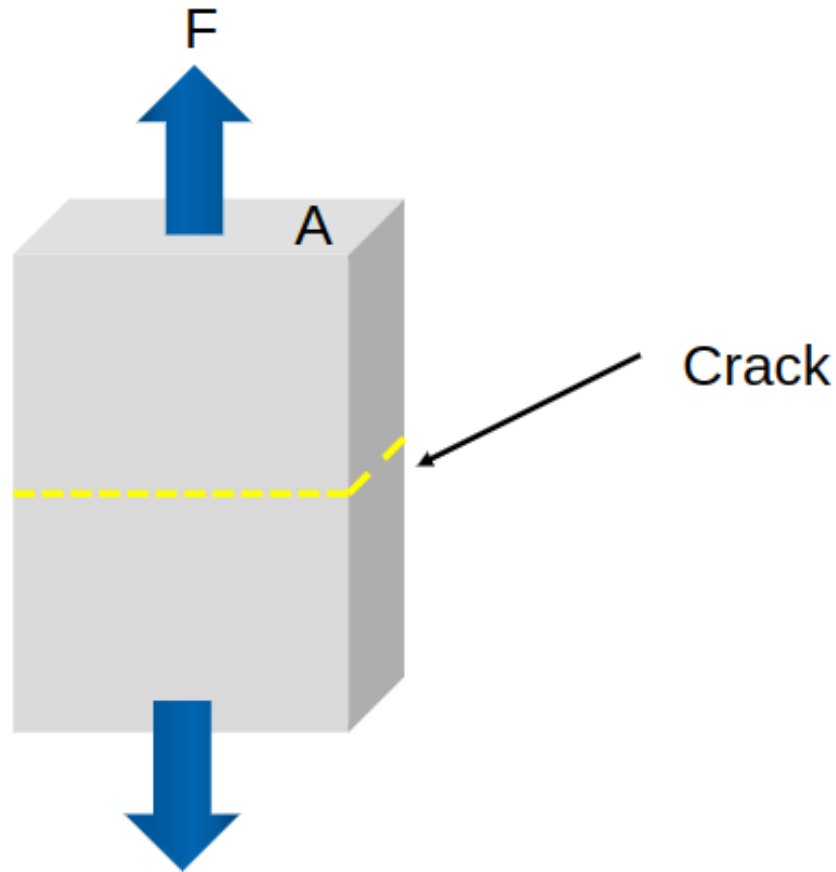
The energy required per unit area to separate two surfaces of materials 1 and 2 in a third medium (medium 3) is called the *work of adhesion* (W)

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

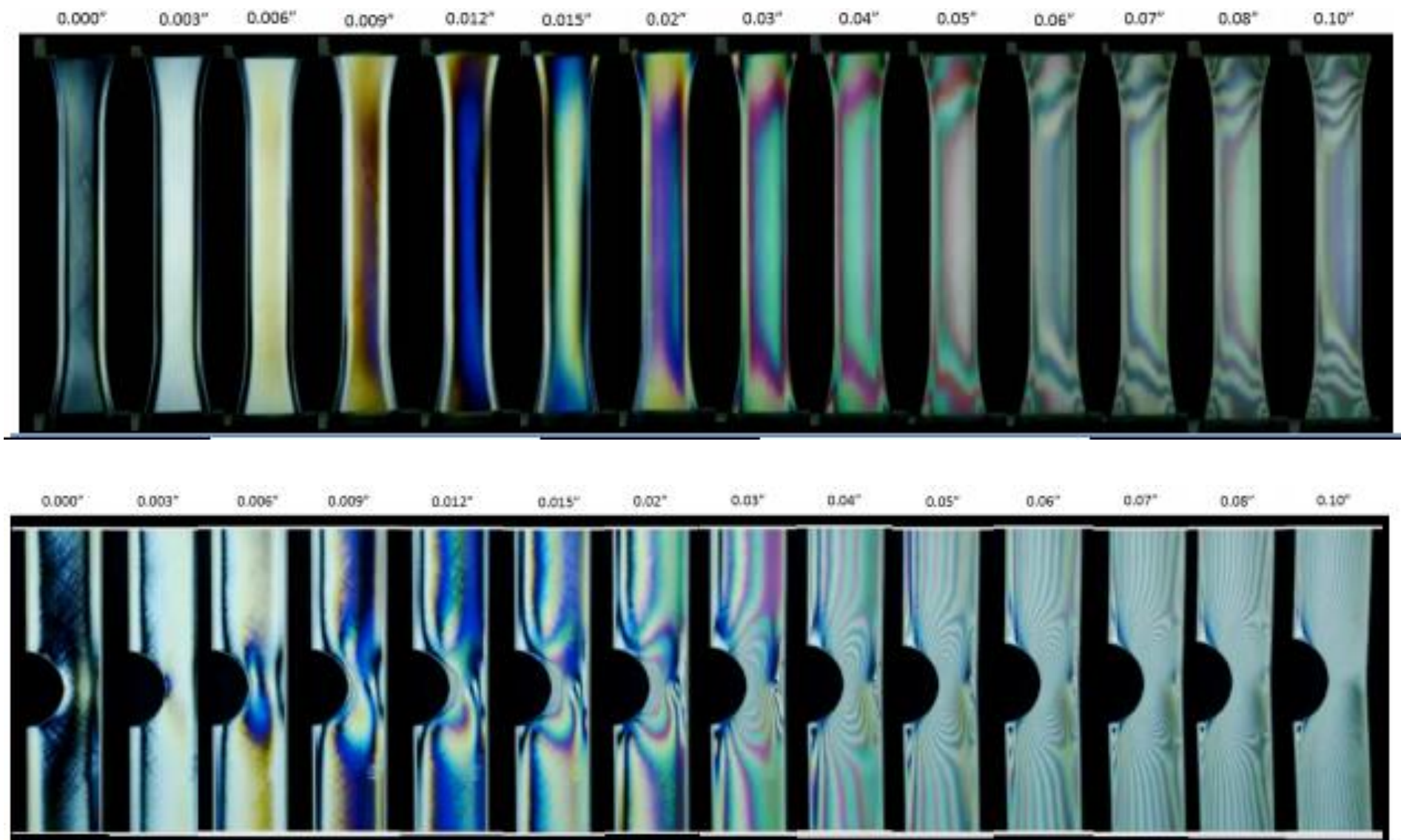


Estimate the maximum force that a bar of cross-sectional area $A = 0.1\text{m}^2$, $L=0.2\text{m}$ and Crack Young's modulus $E = 1119\text{ GPa}$, can sustain before cracking? The (work of adhesion) change in the interfacial energy of the bar/air interface is $\gamma = 40\text{mJm}^{-2}$. You may use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

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



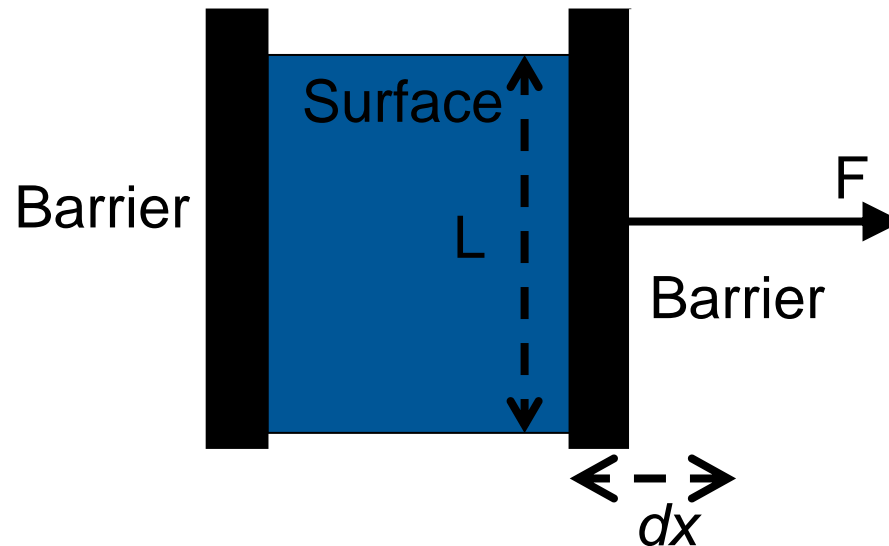
Stress concentration around a crack tip



Surface and interfacial tensions

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

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



$$dU = \gamma L dx$$

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

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

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

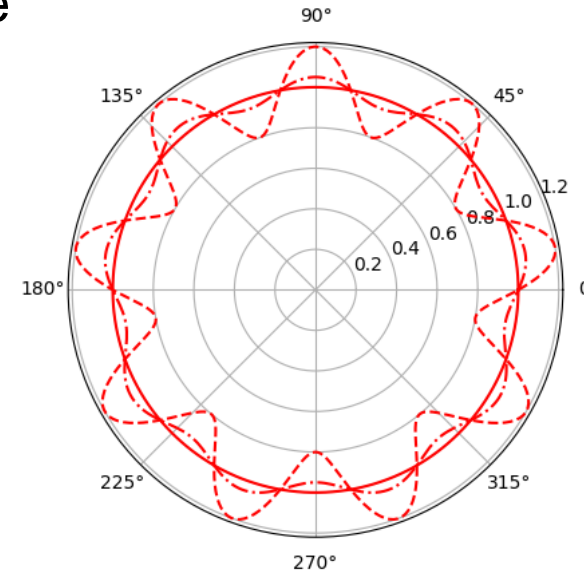
The same reasoning applies to interfacial tension and interfacial energy



Why is a suspended droplet spherical?



A sphere represents the smallest surface area for a given volume

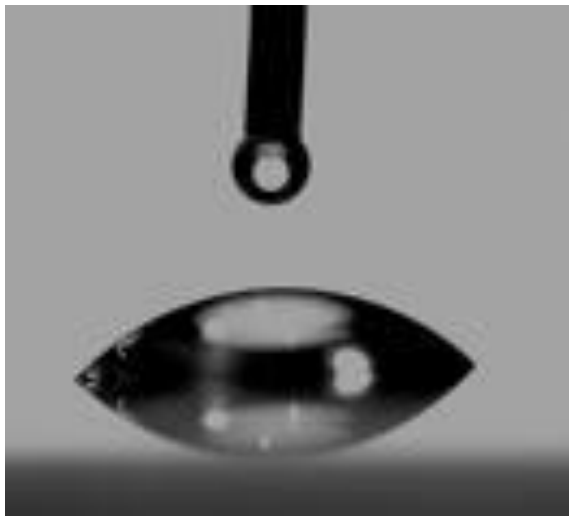


Any shape other than a sphere will have additional surface area dA . This results in an increase in the free energy dU of $\gamma_{12}dA$.

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

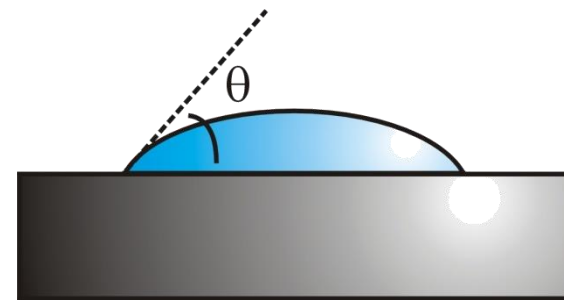
Wetting interactions

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

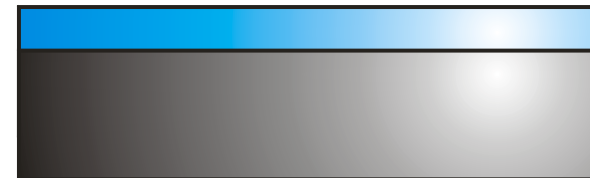


$$S = \gamma_{VS} - \gamma_{LS} - \gamma_{VL}$$

Partially wetting films ($S < 0$)



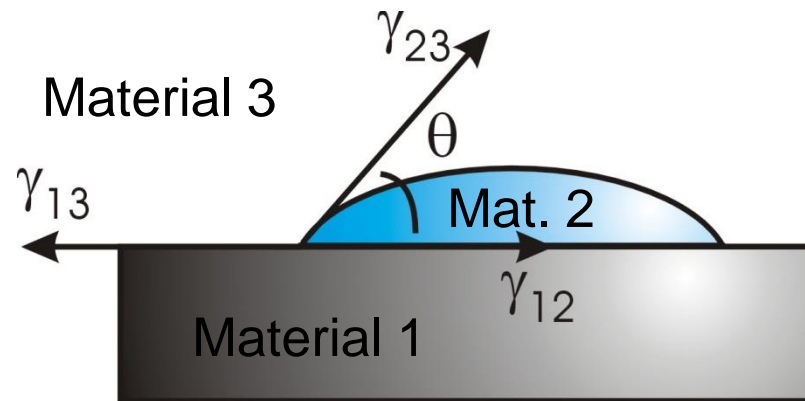
Completely Wetting film ($S > 0$)



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 $\gamma_{12} = 5\text{mJm}^{-2}$, $\gamma_{13} = 15\text{mJm}^{-2}$, $\gamma_{23} = 20\text{mJm}^{-2}$,

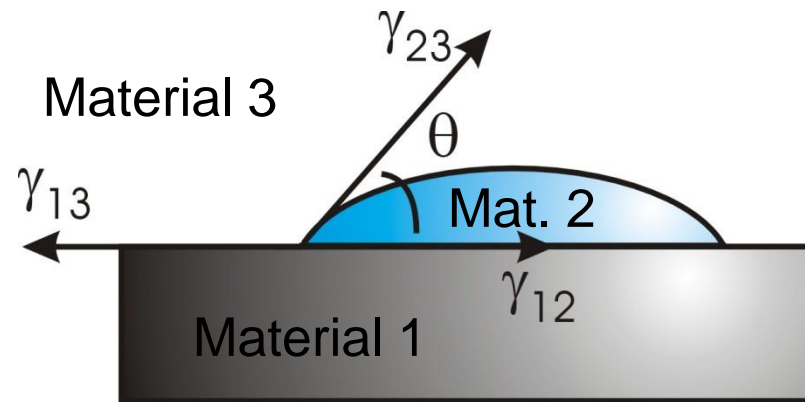


“Young-Laplace Equation”

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

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

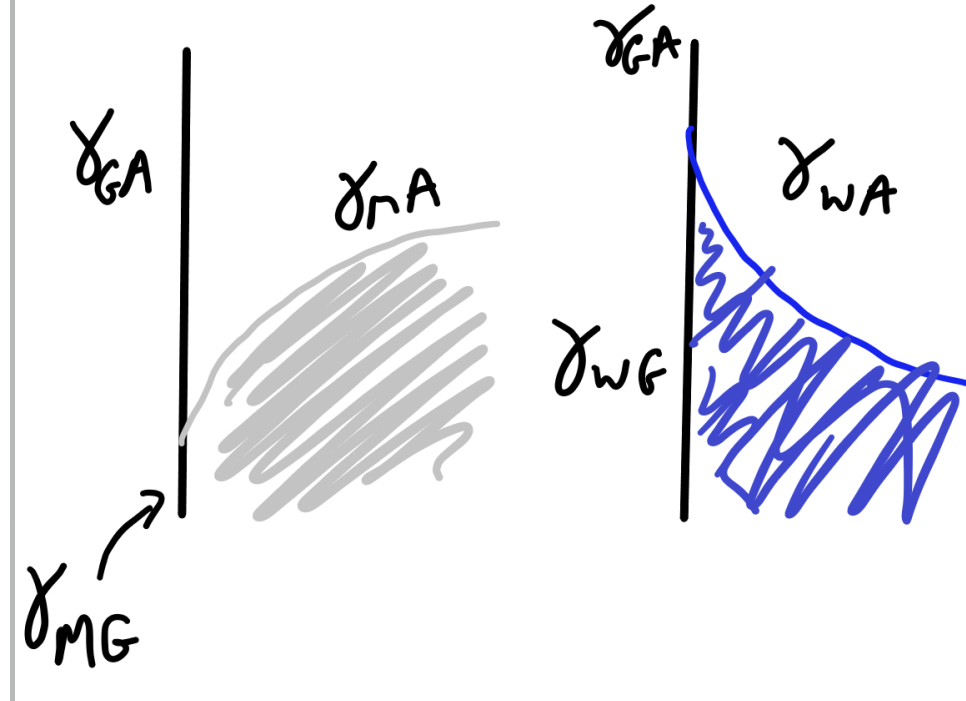


Mercury and water in a glass tube

Thinking through interfacial energies

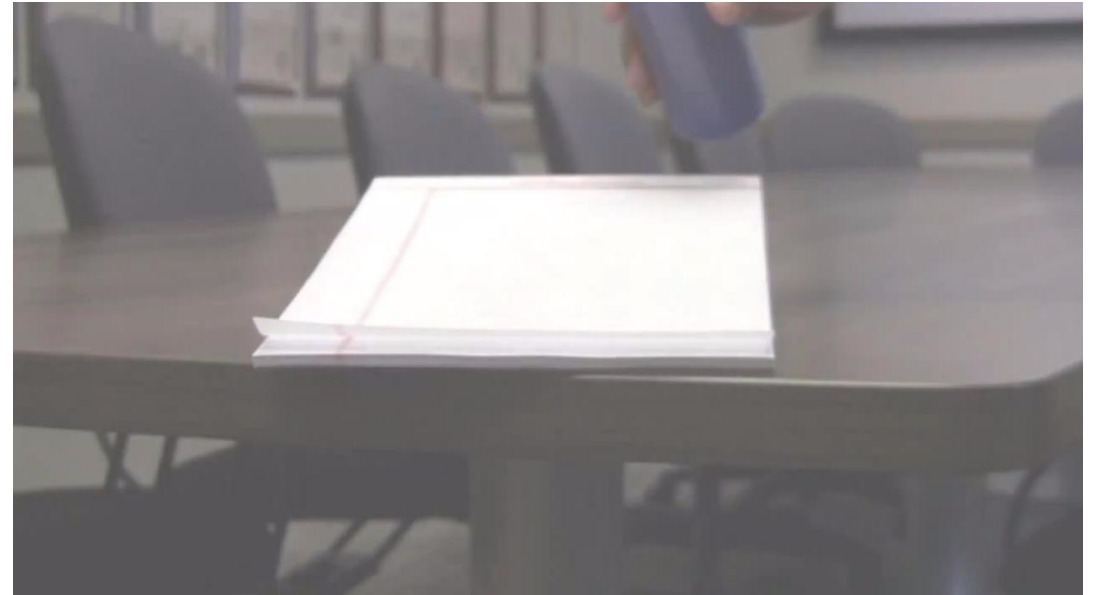
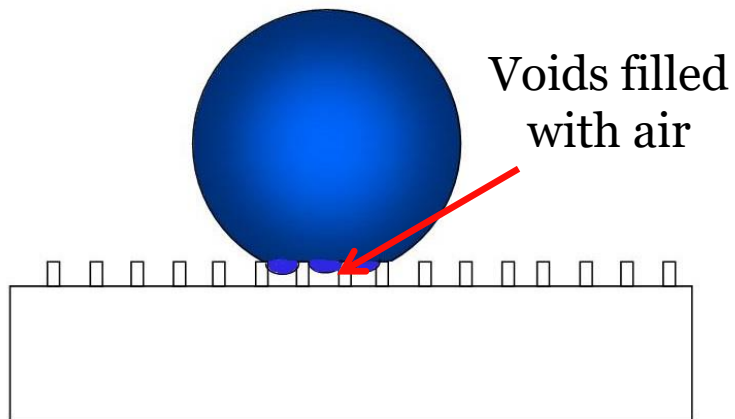


Mercury and water in a glass tube



Why does water spread upwards and mercury curve downwards?

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.

