COMMONWEALTH OF AUSTRALIA

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Surface and interfacial tension

Lecture 31

Chemical Kinetics of Liquids



Lecture 33

Surface wetting

Outline

This block of lectures will introduce you to surface forces and capillarity.

The next five lectures will include the following topics:

1) Introduction to surfaces; surface free energy, surface tension
2) Surfaces: wetting
3) Surfaces: adhesion and friction
4) Surface adsorption, Langmuir/BET analysis
5) Surface adsorption, Gibbs adsorption isotherm

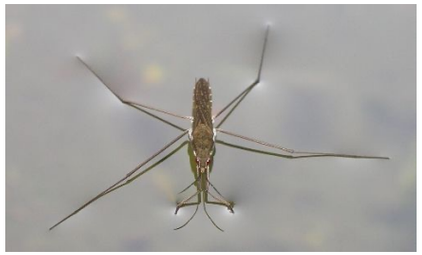
Textbooks

- **Applied Colloid and Surface Chemistry** **Electronic book in the library**
  Richard M. Pashley and Marilyn E. Karaman
  Wiley, 2004
- **Physics and chemistry of interfaces** **Electronic book in the library**
  Hans-Jürgen Butt, Karlheinz Graf and Michael Kappl
- **Interfacial Science: an introduction** **A copy of Chapter 2 available on ereserve**
  G. T. Barnes and I. R. Gentle
  Oxford University Press, 2011
- **Capillarity and Wetting Phenomena** (available at Scitech)
  P.-G. deGennes, F. Brochard-Wyart and D. Quéré
  Springer, 2004
- **Principles of Colloid and Surface Chemistry** (available at Scitech)
  P. C. Hiemenz and R. Rajagopalan
  Marcel Dekker Inc.: New York, 1997.
- **Physical Chemistry** (available at Scitech)
  P. W. Atkins
  Oxford University Press

Nature: functional wettability



'lotus effect'



water strider



desert beetle

© Hans Hillewaert.



http://www.abc.net.au/catalyst/stories/3257884.htm

USyd's own Prof Chiara Neto stars in this video!

Surface Coatings



decorative coatings



Thin polymer coatings

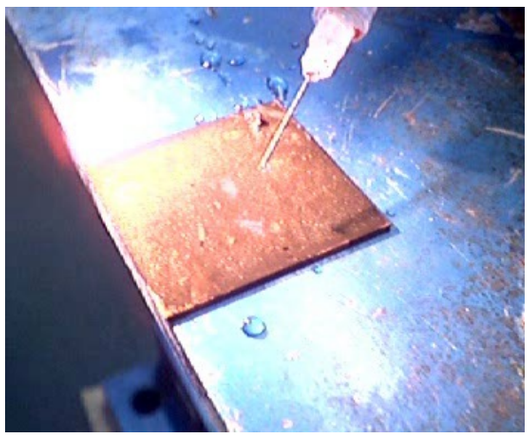


Protective coatings

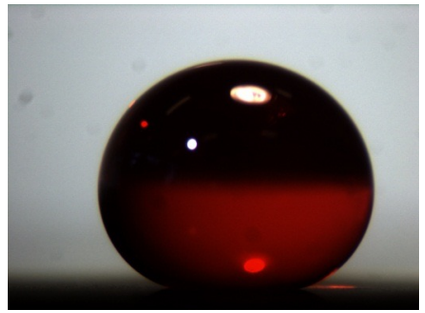
Functional materials



goretex, teflon...



© Joseph, Neto, 2009



self-cleaning surfaces



http://www.neverwet.com/index.php

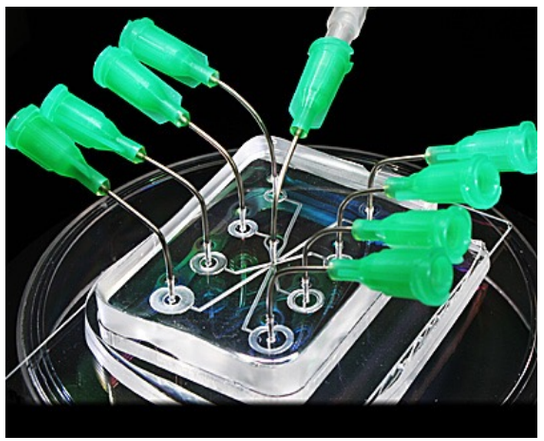
Hi-tech: printing and microfluidics

We need to understand, and to be able to control, both the breakup of liquid jets into small droplets, and the subsequent interaction of the droplets with the target.



inkjet

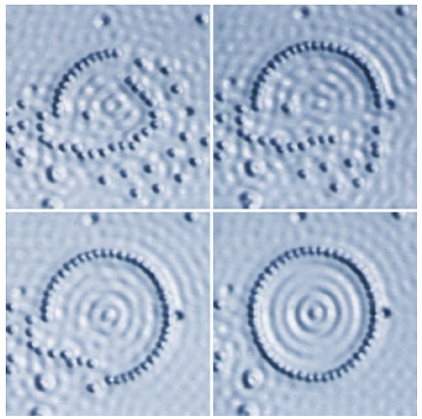
Reactions, separations, sensing can be done on a micro- or nano-liter scale in microfluidic devices.



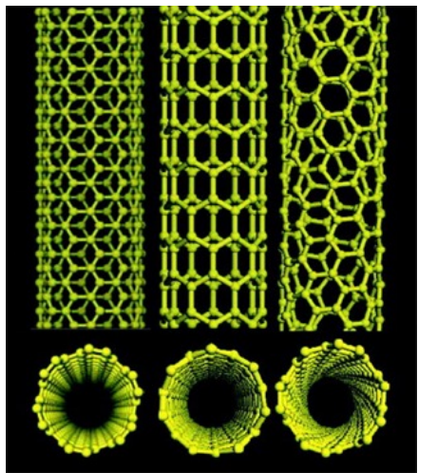
www.nist.gov

'lab-on-a-chip'

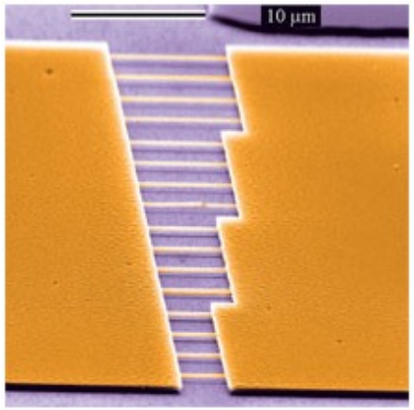
Nanoscience



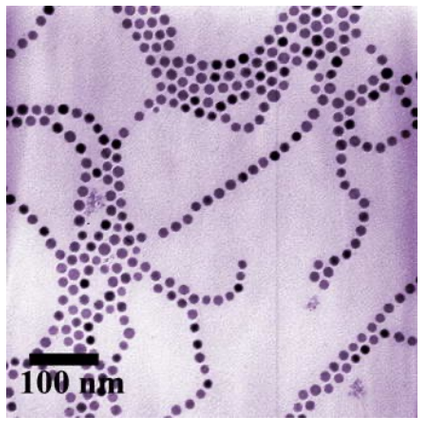
IBM Research, Almaden Research Center



Baughman *et al.*, *Science* **297**, 787 (2002)



http://cnst.nist.gov/nanofab_res/Projects/nanofluidics/nanofluidics.html



NIST

- Nanoscience is the study of materials in which one or more dimensions is **in the nanometer range.**
- Surfaces are especially relevant in nanoscience.
- Spans a wide range of traditional fields such as chemistry, materials science, energy sources, biology, medicine.
- Needs appropriate tools of investigation and theoretical frameworks.
- Forces that dominate are **intermolecular** in nature.

Surface Effect

A cube with side d =1 cm;

Its total surface area

$A = 6 \times d^2 = 6\ cm^2 = 6 \cdot 10^{-4}\ m^2$

Now divide the cube into 10^{18} cubes; sides 10^6 times smaller, i.e. d = 10 nm

The total surface area is now

$A = 10^{18} \times 600\ nm^2 = 600\ m^2$ (!)

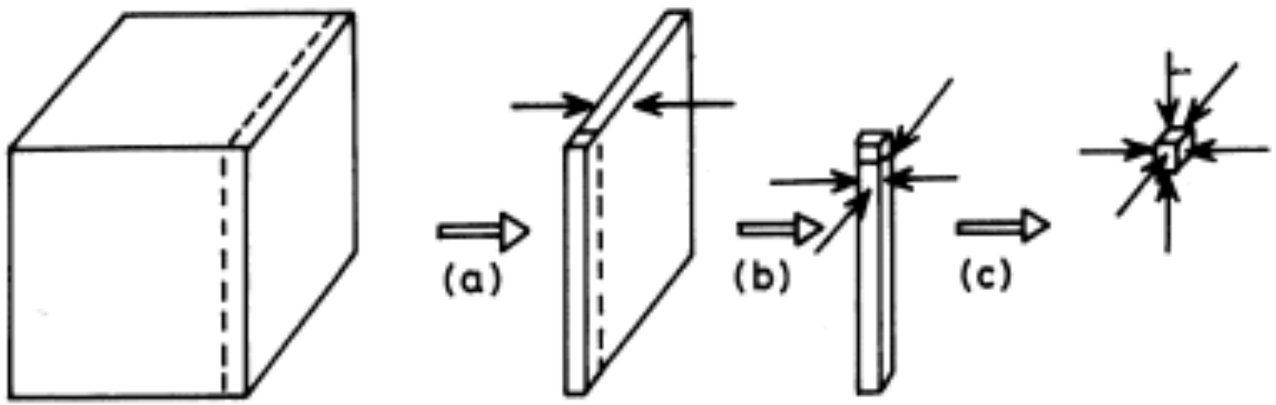


Figure taken from "Basic Principles of Colloid Science" D.H. Everett, RSC paperbacks

The volume is unchanged, but the surface area has increased by **1 million times**. This means most of the substance is now on the surface.

Surface tension: Physical origin

Q1

'Cohesion': water molecules attract each other

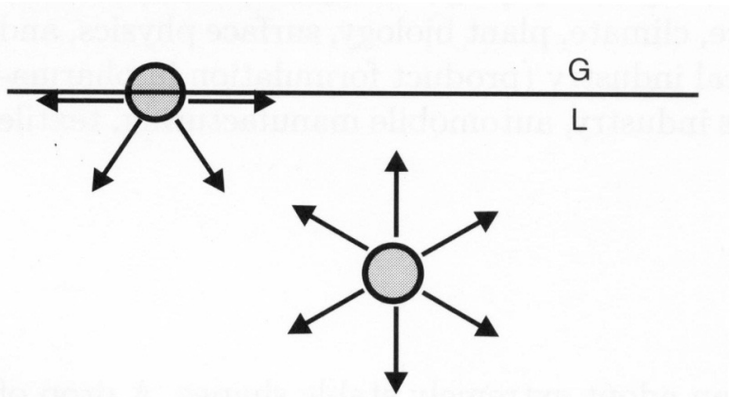


Fig 1.2 Capillarity and Wetting Phenomena
P.-G. deGennes et al., 2004



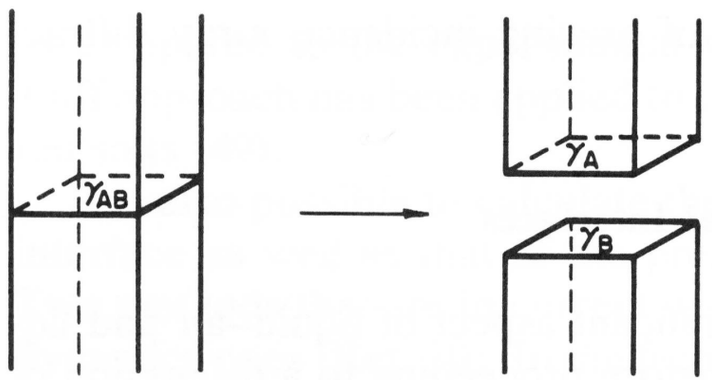
- Surface tension γ is the excess energy of a system due to the presence of a surface, per unit of area.
- The magnitude of the surface tension depends on the strength of intermolecular forces.
- It's expressed as an energy per surface area (J/m^2) or a force per unit length (N/m)

$$\frac{J}{m^2} = \frac{Nm}{m^2} = \frac{N}{m}$$

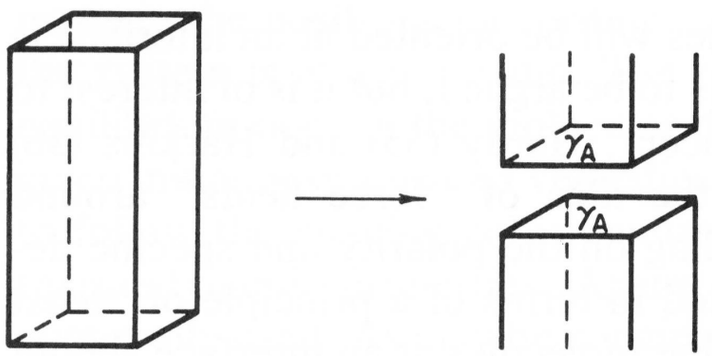
Surface tension at 20 °C and boiling point:

Liquid	γ (mN/m)	T_B (°C)
ethyl ether	17	34.5
acetone	24	56
ethanol	23	78
cyclohexane	25	81
water	73	100
mercury	485	357

Work of cohesion



(a)



(b)

Another way to think about surface tension (energy):

Consider the work W, per unit area, required to separate a material into two parts, creating two new surfaces and separating the parts beyond the range of their forces of interaction.

For a block made of two materials A and B

$$W_{AB} = \gamma_{AV} + \gamma_{BV} - \gamma_{AB}$$

For a block made of one material A:

$$W_{AA} = 2\gamma_{AV}$$

Free energy of a surface

Q2

Surface tension γ is the free energy required to create a unit of surface area, at constant temperature and volume

$$\gamma = \left(\frac{\partial G}{\partial A}\right)_{T,V}$$

Surface tension γ can be used in *equilibrium calculations*, in which G is minimised.
So the work required to create new surface area ΔA is

$$work = \gamma \cdot \Delta A$$

For liquids, γ is called the **surface tension** and has units of N m^{-1}.
For solids, γ is called the **surface energy** and has units of J m^{-2}.
N.B. These two units are equivalent, but this usage is the common convention.

Surface tension forces

For liquids, γ can also be described as a force per unit length acting on a line at an interface. Consider a liquid film suspended in a U-frame which can be stretched by means of a movable rod attached to the frame:

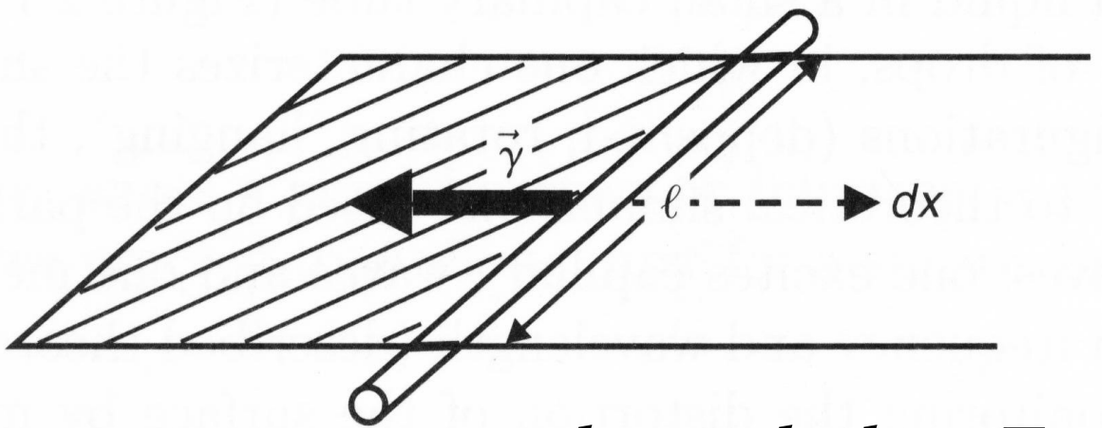
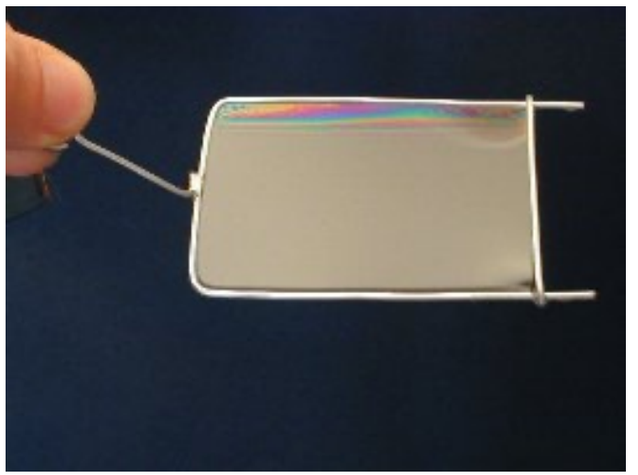


Fig 1.4 Capillarity and Wetting Phenomena
P.-G. deGennes et al., 2004



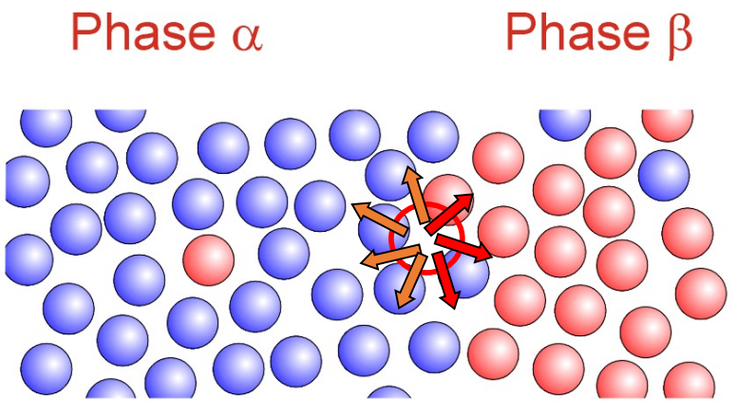
$$work = \gamma \cdot l \cdot dx = F \cdot dx$$

$$\Rightarrow \gamma = F/l$$

- γ is the force (per unit length) normal to the rod, in the plane of the surface, and directed toward the liquid. Clearly, this surface tension has units of N m^{-1}

Interfacial tension

- When two immiscible liquid phases are in contact, the free energy change to expand their "interfacial area" is known as interfacial tension, $\gamma_{\alpha\beta}$



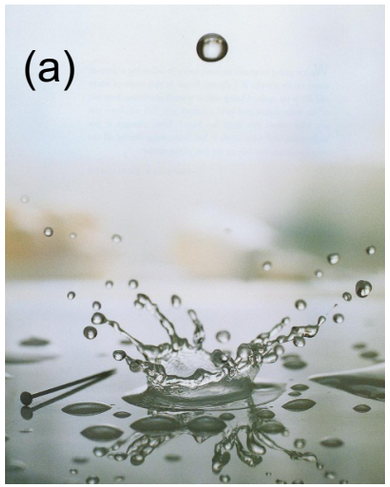
Interfacial tensions are typically much lower that surface tensions:
e.g. for water/chloroform $\gamma_{\alpha\beta}$ = 28 mN m^{-1}

- Surface tension of a liquid or solid is typically denoted as
  - γ_{LV} *for liquid/vapour*
  - γ_{SV} *for solid/vapour*

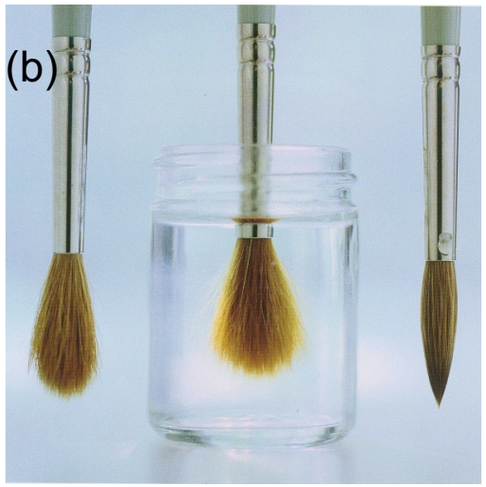
Surface tension

How do these images illustrate the effects of surface tension?

Wick, W. *A drop of Water, A book of science and wonder; Scholastic Press: Singapore, 1997.*



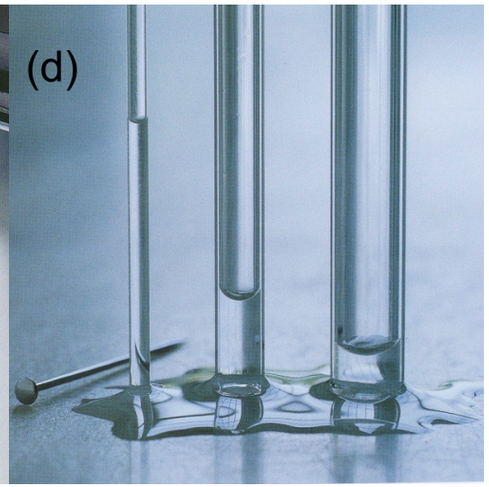
Partial film spreading and contact angle due to interfacial tensions; Spherical droplet shape due to surface tension; Break-up of liquid cylinders into droplets due to surface tension



Capillary bridges stick fibres together (Laplace pressure); But water wets the fibres so immersed fibres are separated



The shape of a droplet is spherical unless gravity deforms it; High water surface tension produces a long neck connecting the droplet to the faucet

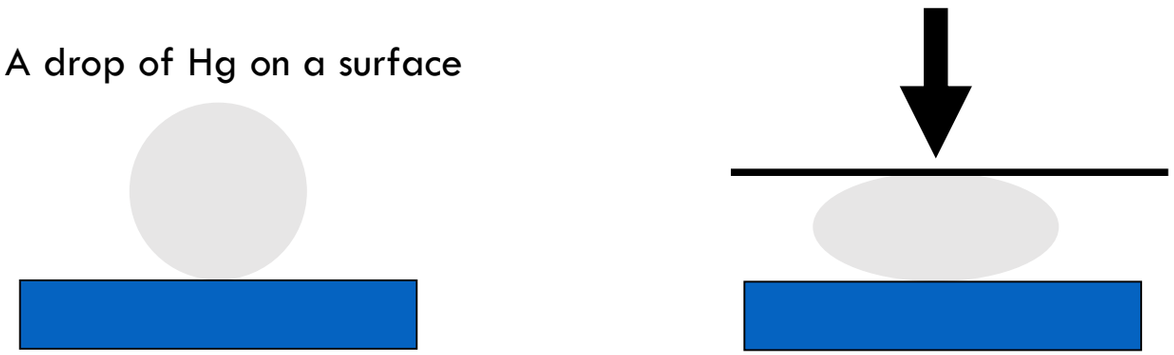


Capillary rise occurs for wetting liquids; The thinner the capillary the higher the liquid; Partial spreading on the surface

The shape of droplets & bubbles

- Why are bubbles and droplets spherical?

A drop of Hg on a surface



- For a given volume, a sphere has the least possible surface area.
  Hence γA, and therefore the free energy, is a minimum.

- In its oblate shape, Hg has a larger surface area
  i.e. atoms have been moved from the interior of the drop to the surface

$$work = \gamma \cdot \Delta A$$

Learning Outcomes

After this lecture you should be able to

- Explain why surface chemistry is important
- Define nanoscience
- Define types of surfaces and interfaces, and recognise where they occur
- Define *surface tension*, both by a thermodynamic derivative and using a physical explanation, and in terms of an energy per unit area and a force per unit length
- Define *interfacial tension*, how it determines spreading

Today's reading

- Pages 146-150 of *Physical Chemistry* (Atkins)
  on surface tension and capillary rise

- Pages 1-11 and 49-53 of *Capillarity & Wetting Phenomena (de Gennes)*
  on surface tension, spreading, contact angle, Laplace pressure

- Pages 209-241 of *Principles of Colloid & Surface Chemistry* (Hiemenz)
  on surface tension, spreading, contact angle, Laplace pressure