Surface tension, wetting, and capillarity

(de Gennes: Chs. 1-2)

- Surface tension
- Conventional surface tension measurement techniques
- Free-standing film tensiometer
- Wetting
- Capillary pressure/force

The Nobel Prize in Physics 1991

SOFT MATTER

Nobel Lecture, December 9, 1991

by

PIERRE-GILLES DE GENNES

College de France, Paris, France

for discovering that methods developed for studying order phenomena in simple systems can be generalized to more complex forms of matter, in particular to liquid crystals and polymers.

What do we mean by soft matter? Americans prefer to call it "complex fluids". This is a rather ugly name, which tends to discourage the young students. But it does indeed bring in two of the major features:

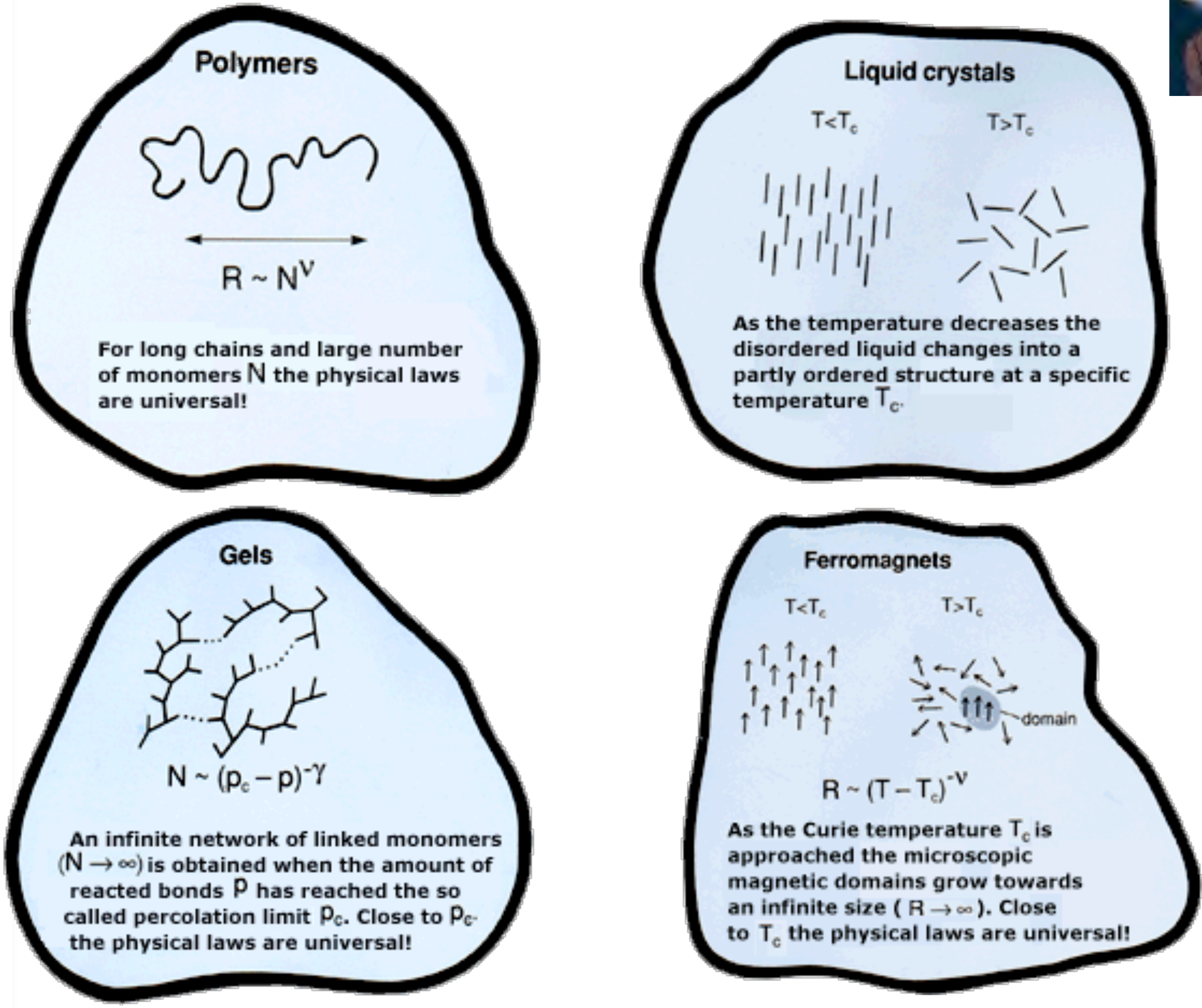
I) Complexity. We may, in a certain primitive sense, say that modern biology has proceeded from studies on simple model systems (bacterias) to complex multicellular organisms (plants, invertebrates, vertebrates...). Similarly, from the explosion of atomic physics in the first half of this century, one of the outgrowths is soft matter, based on polymers, surfactants, liquid crystals, and also on colloidal grains.

2) Flexibility. I like to explain this through one early polymer experiment, which has been initiated by the Indians of the Amazon basin: they collected the sap from the hevea tree, put it on their foot, let it "dry" for a short time. And, behold, they have a *boot*. From a microscopic point of view, the starting point is a set of independent, flexible polymer chains. The oxygen from the air builds in a few bridges between the chains, and this brings in a spectacular change: we shift from a liquid to a network structure which can resist tension - what we now call a *rubber* (in French: caoutchouc, a direct transcription of the Indian word). What is striking in this experiment, is the fact that a very mild chemical action has induced a drastic change in mechanical properties: a typical feature of soft matter.

“Have fun on sea and land
Unhappy it is to become famous
Riches, honors, false glitters of this world
All is but soap bubbles”

Nobel Lecture, December 9, 1991
by PIERRE-GILLES DE GENNES

The master of analogies



http://nobelprize.org/nobel_prizes/physics/laureates/1991/illpres/master.html

Polymers

What do they look like? ....

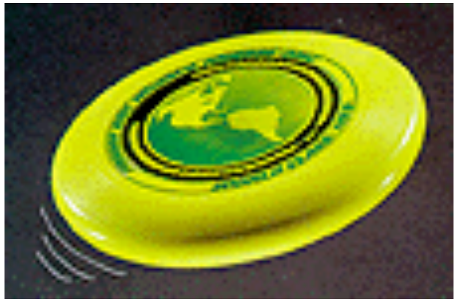
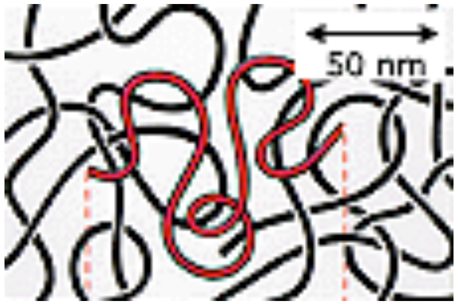
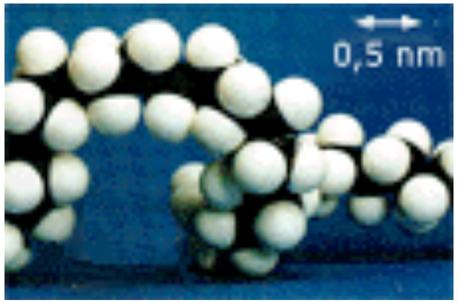


Photo: L. Falk





Surface tension (physical origin)

$\gamma \cong U/(2a^2)$

$U \cong kT \cong$ 25 meV for oils

$\cong$ 1 eV for Hg

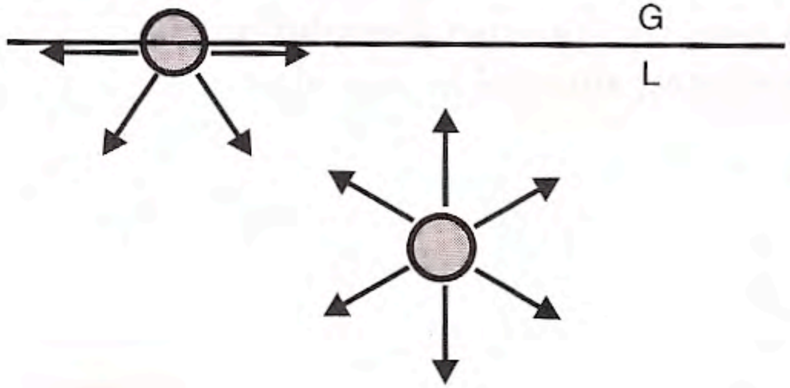


FIGURE 1.2. An "unhappy" molecule at the surface: It is missing half its attractive interactions.

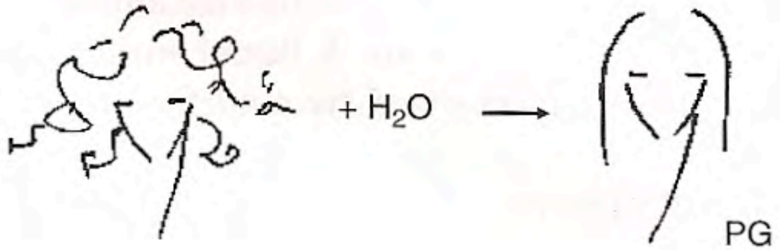


FIGURE 1.3. Full dry hair vs. sticky wet hair.

Physical origin of the surface tension

Fowkes: 1960

Surface tension resides in the surface monolayer, although in some systems it has been demonstrated to have contribution from second or third layers.

Langmuir : 1961
"Principle of Independent Surface Action"

Each part of a molecule possess a local surface free energy. (equivalent to surface tension)

Surface tension

Unit of Surface tension : force / length
= force * length / length * length
= energy / area
Surface energy density

In liquid, normally we use the term *surface tension* while in solid, *surface energy density*

Liquid/vapor interface: surface tension

Liquid/solid interface: surface tension or surface energy density

Surface tension of common liquids

TABLE 1.1. Surface tension of a few common liquids (at 20°C unless otherwise noted) and interfacial tension of the water/oil system.

Liquid	Helium (4K)	Ethanol	Acetone	Cyclohexane	Glycerol
γ(mN/m)	0.1	23	24	25	63
Liquid	Water	Water (100°C)	Molten glass	Mercury	Water/oil
γ(mN/m)	73	58	~300	485	~ 50

Surface tension at work

Dew droplet: water beading on a leaf

Surface tension at work

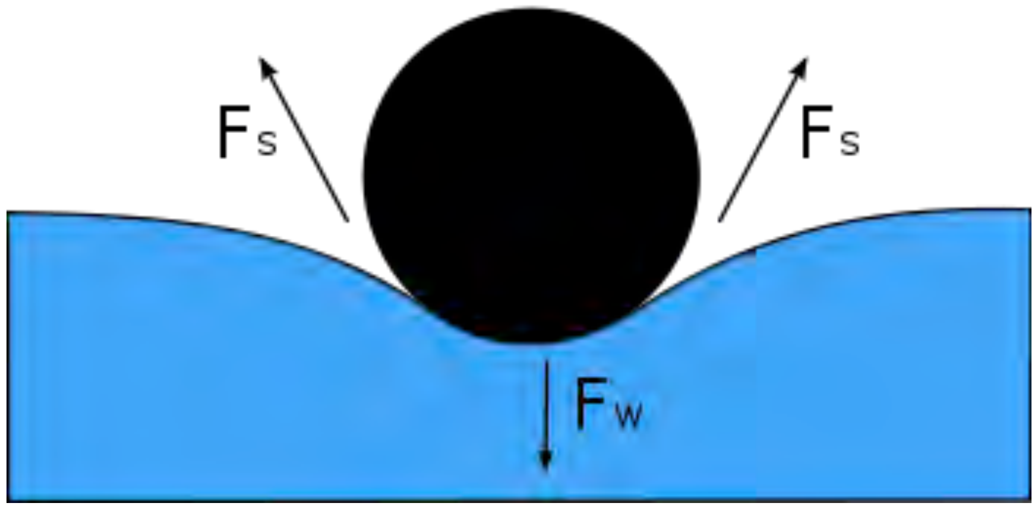
FIGURE 1.1. Drops and bubbles form perfect spheres.[2] (From *A Drop of Water: A Book of Science and Wonder*, by Walter Wick. Published by Scholastic Press, a division of Scholastic Inc. Photographs © 1997 by Walter Wick. Reproduced by permission.)

Surface tension at work

Water striders

Surface tension at work

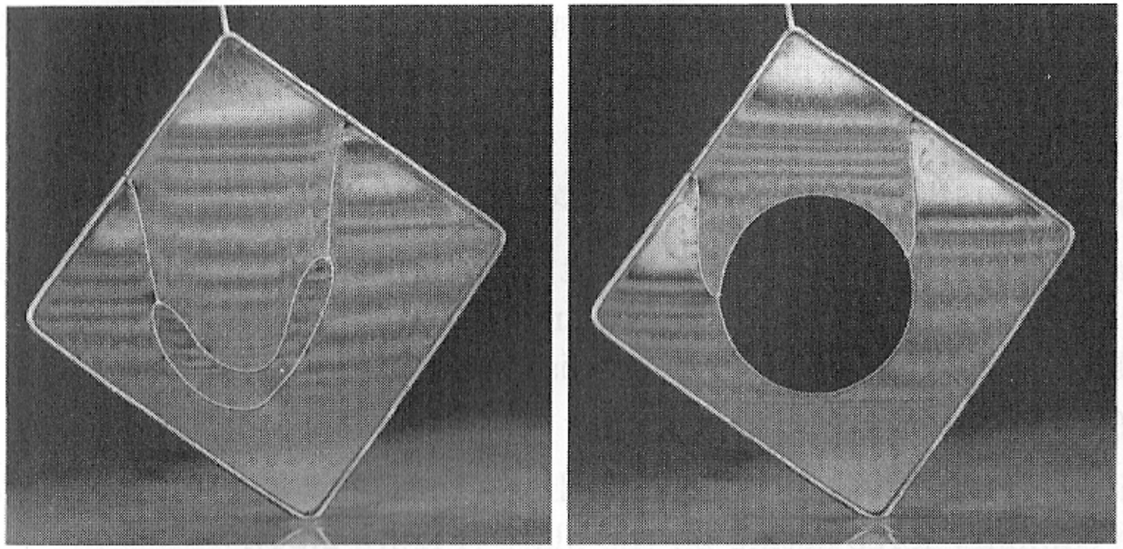
Why water strider floats?



Surface tension at work

Surface tension prevents a coin from sinking:
the coin is indisputably denser than water, so it cannot be floating due to [buoyancy](#) alone.

A soap bubble balances surface tension forces against internal pneumatic pressure



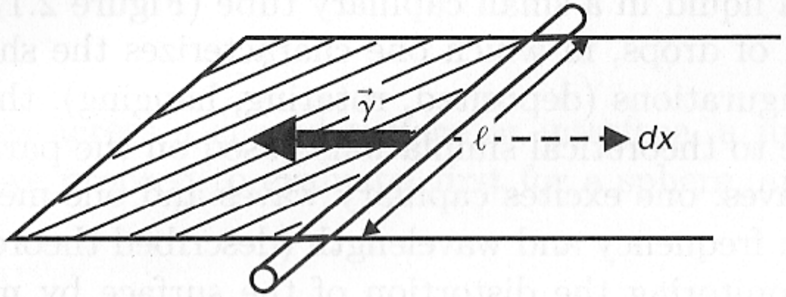


FIGURE 1.4. Manifestation of surface tension: force normal to the line (wire, rod). (From *A Drop of Water: A Book of Science and Wonder*, by Walter Wick. Published by Scholastic Press, a division of Scholastic Inc. Photographs © 1997 by Walter Wick. Reproduced by permission.)

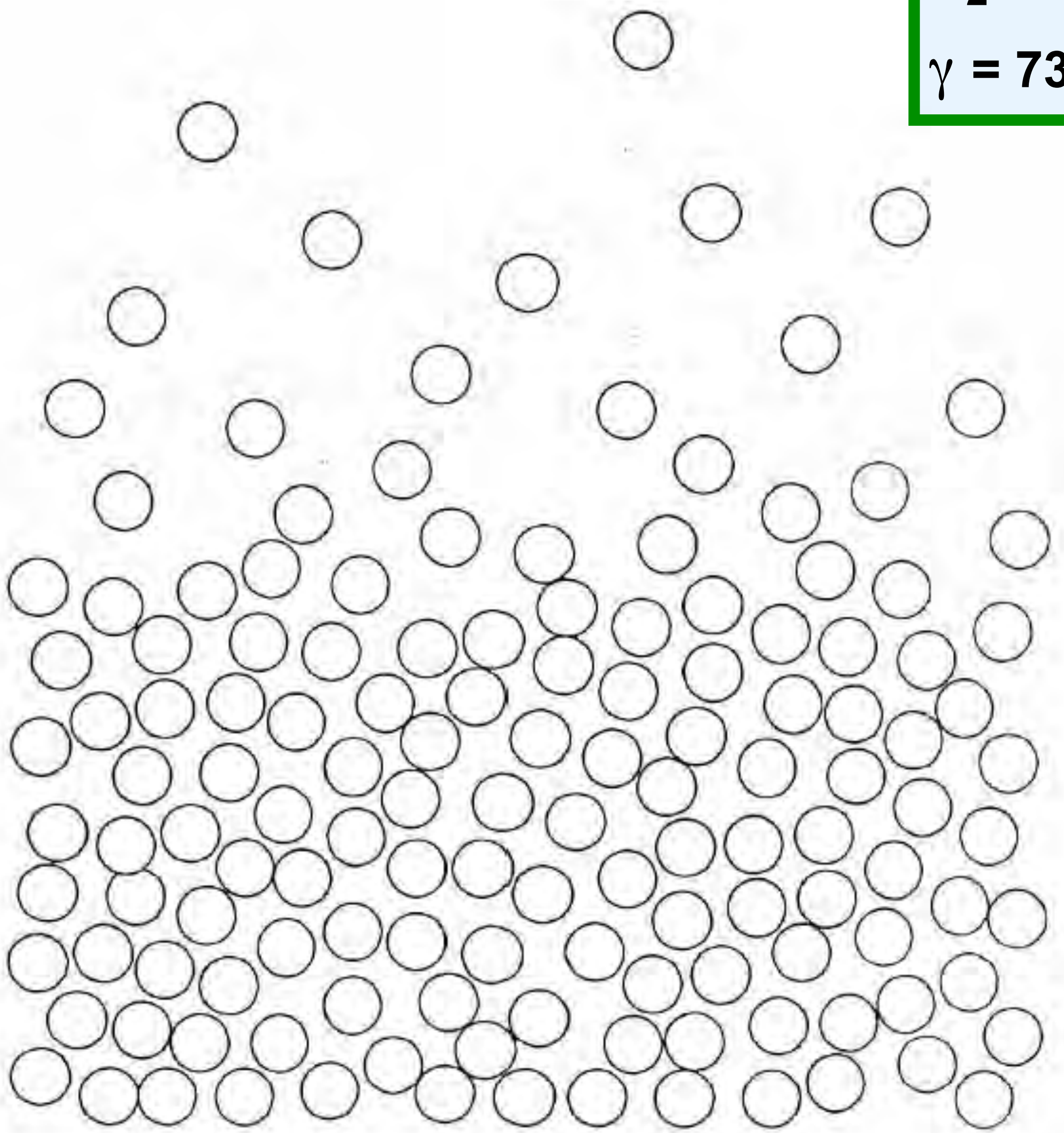
H_2O:

γ = 73 mN/m

Vapor

Interface?

Liquid

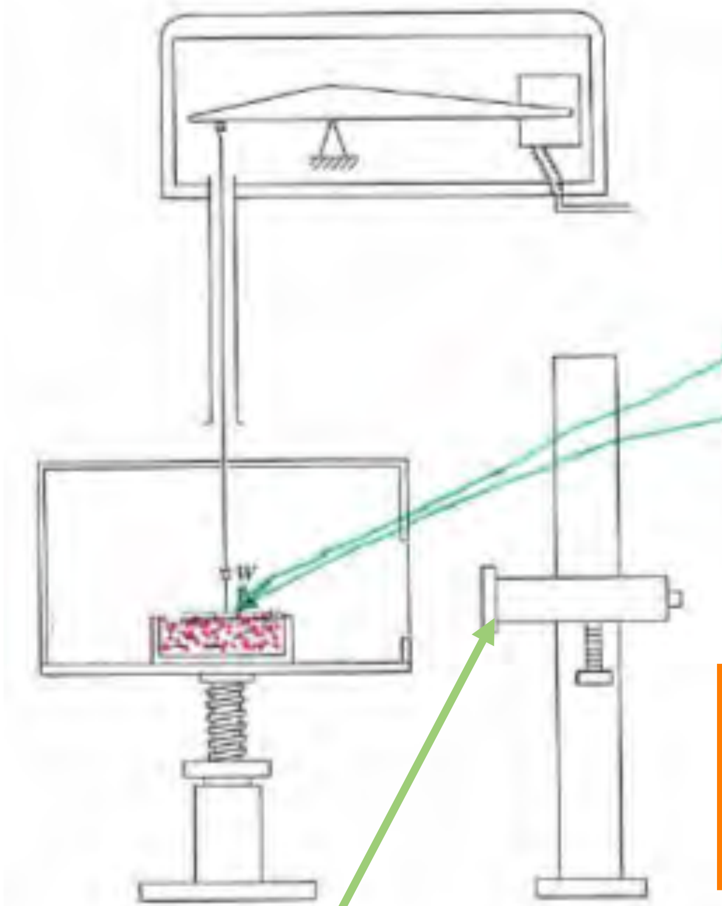


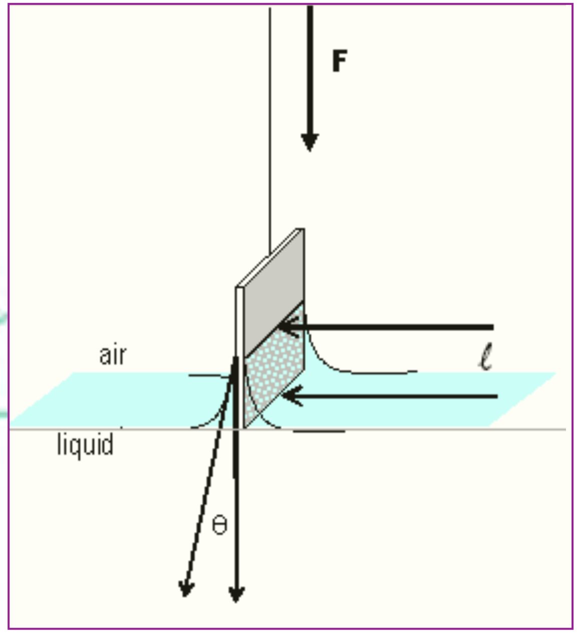
Courtesy of Prof. CC Huang @ U. Minnesota

How to measure surface tension?

Wilhelmy plate technique

Balance to measure *F*

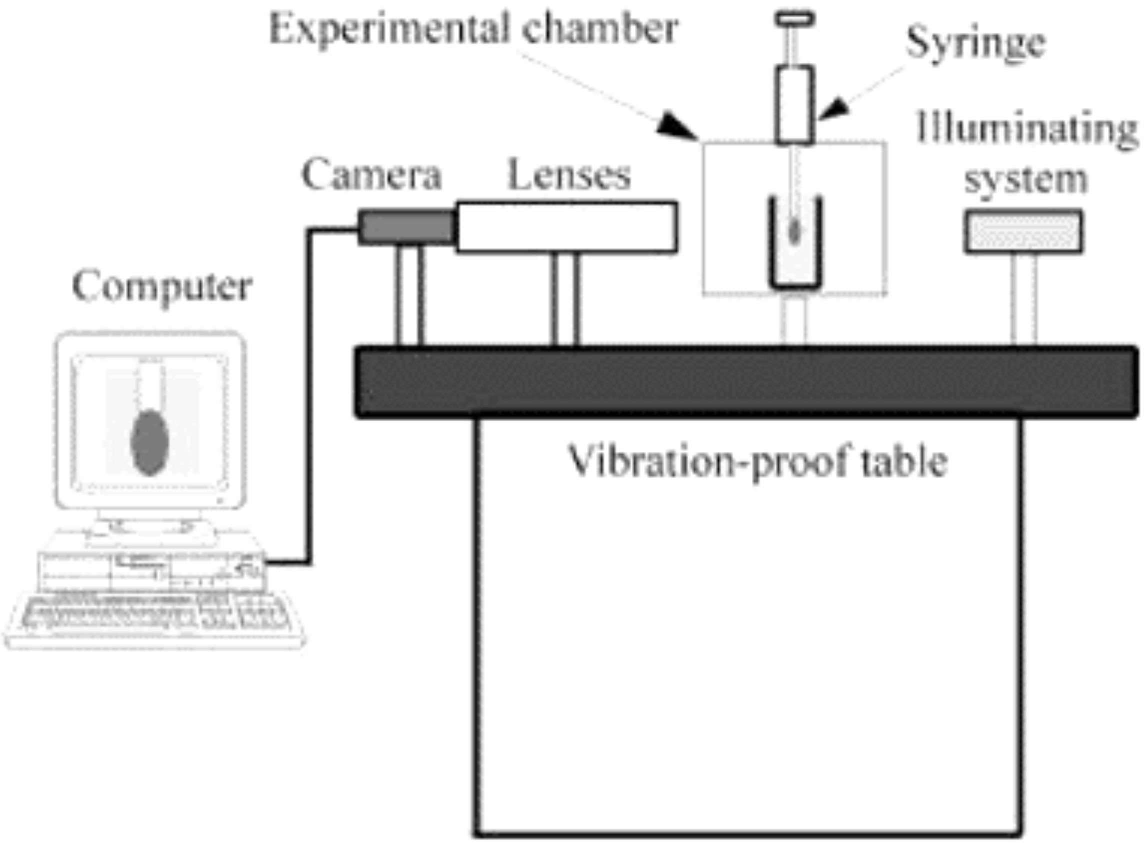


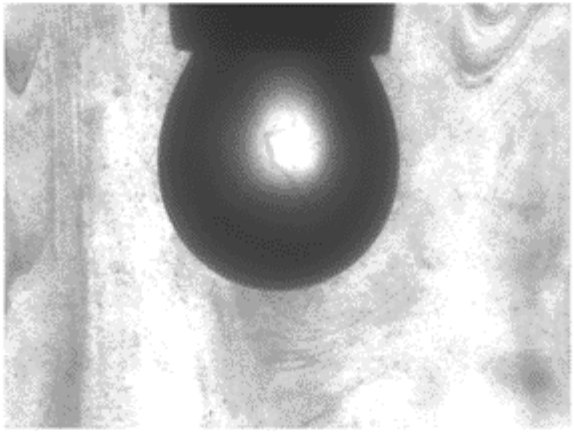


Telescope, measures height of the meniscus: *l* and angle of meniscus: θ

Surface tension: $\gamma = \dfrac{F}{2l \cdot \cos\theta}$

Pendant drop technique





Drop of polystyrene

Pedant drop apparatus

Shape of the drop → surface tension

Courtesy of Prof. CC Huang @ U. Minnesota

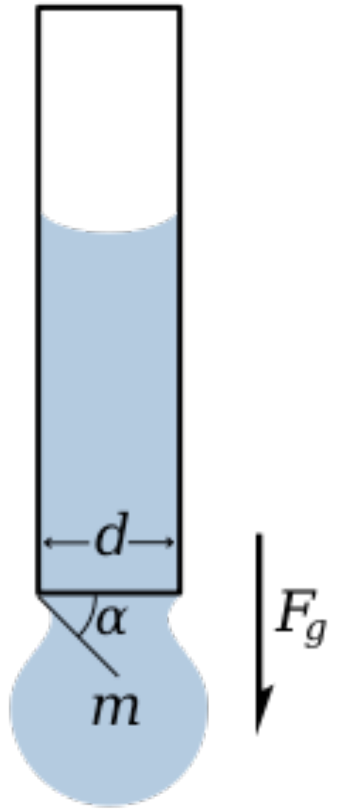
Pendant drop technique

The length of this boundary is the circumference of the tube

$$F_\gamma = \pi d \gamma$$

$$mg = \pi d \gamma \sin \alpha$$

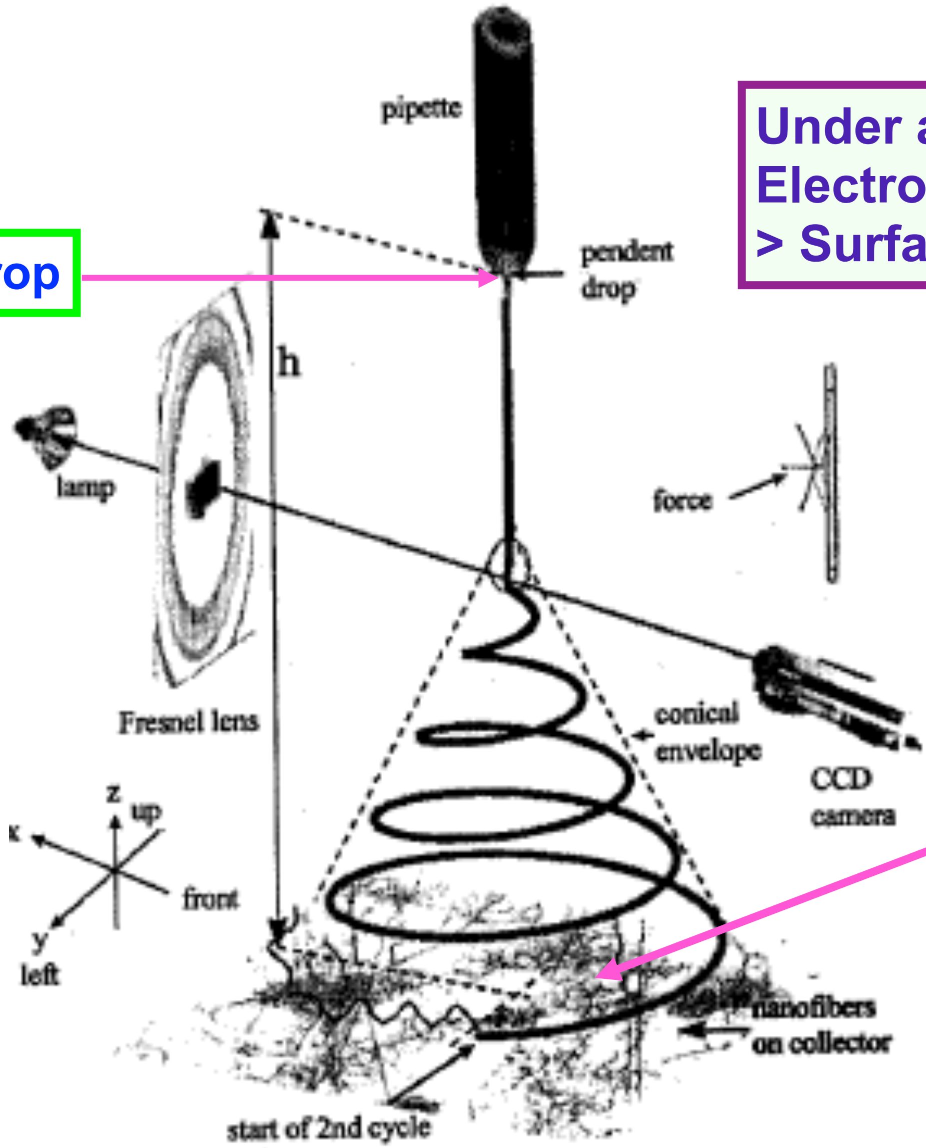
$$mg = \pi d \gamma$$



Electrospinning

Under a high electric field:
Electrostatic energy
> Surface tension

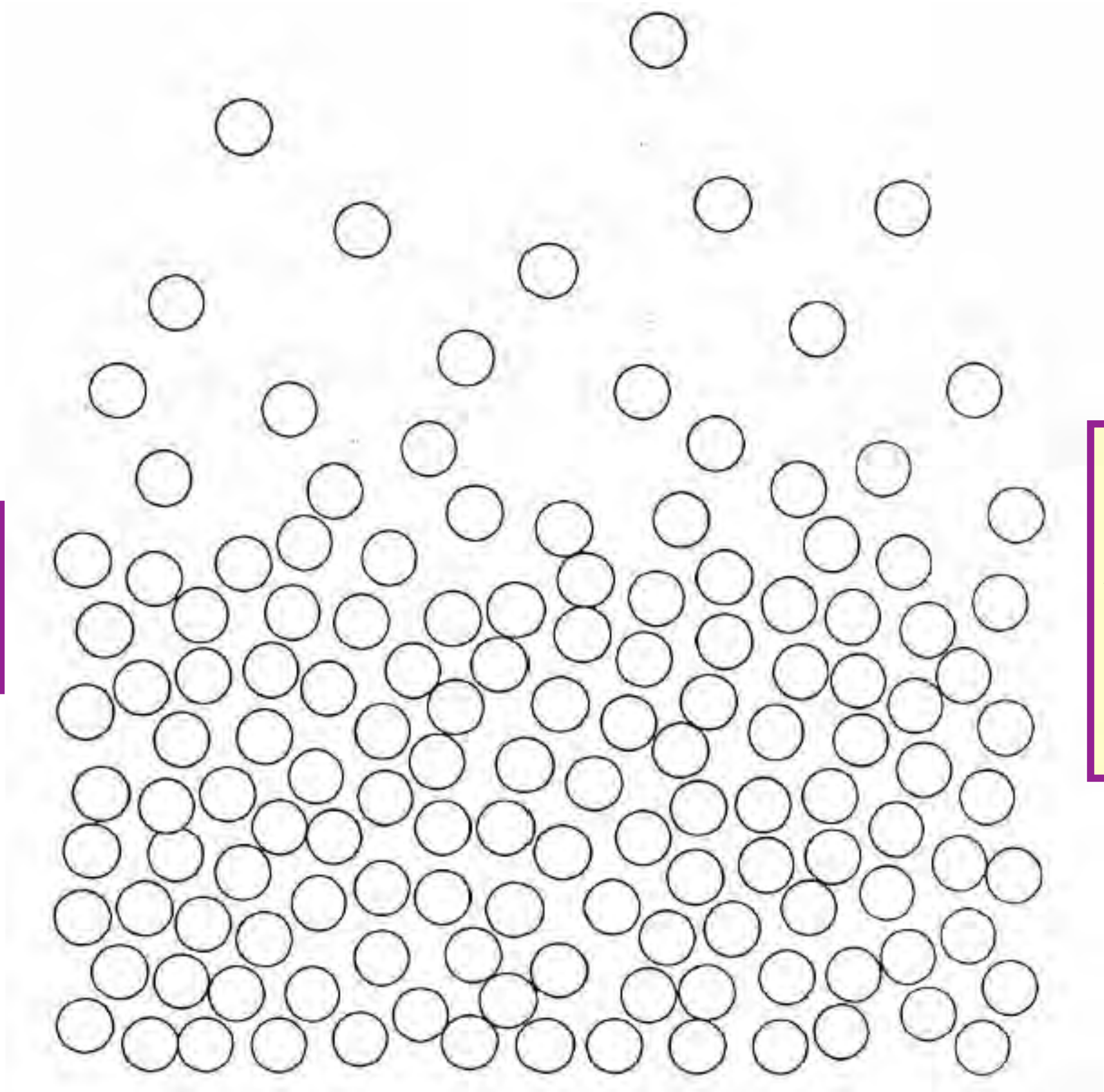
Pendant drop



Nano-fibers on collector

Vapor

Fowkes: Surface monolayer?



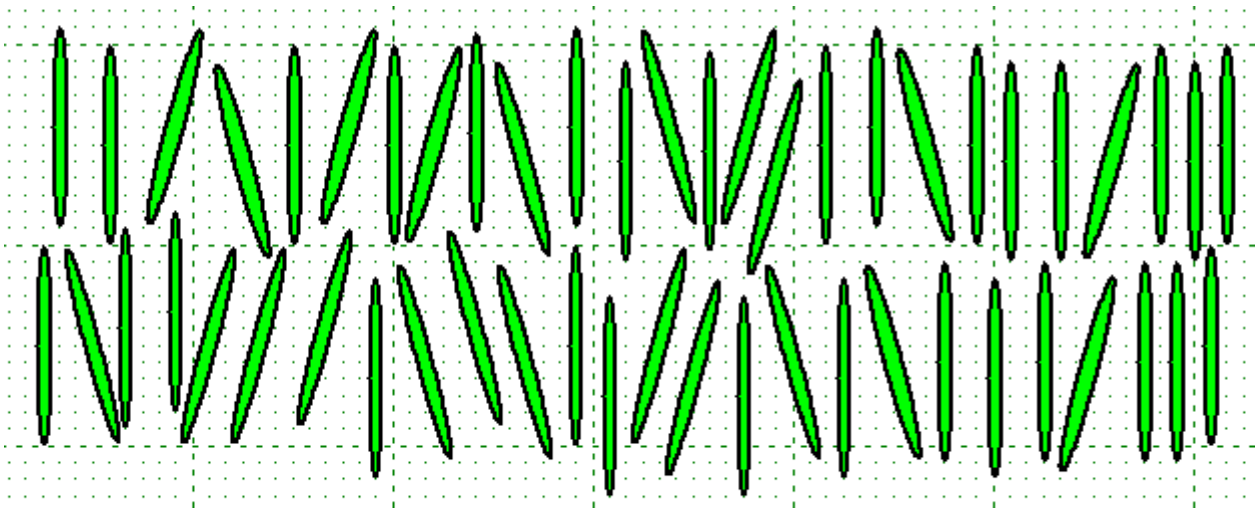
Langmuir: Local surface energy of each molecule

Liquid

The advantage of free-standing liquid crystal films for studying the molecular origin of surface tension

Fowkes:
Surface monolayer?

Langmuir:
Local surface energy of each molecule

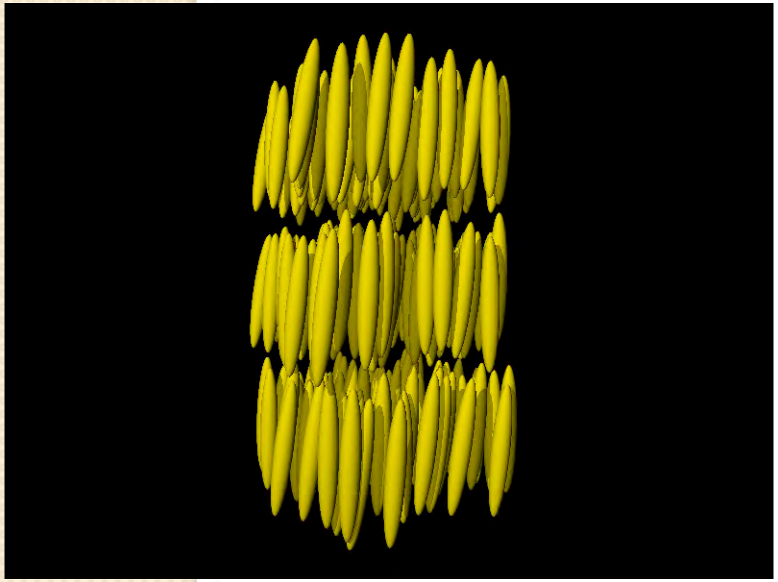


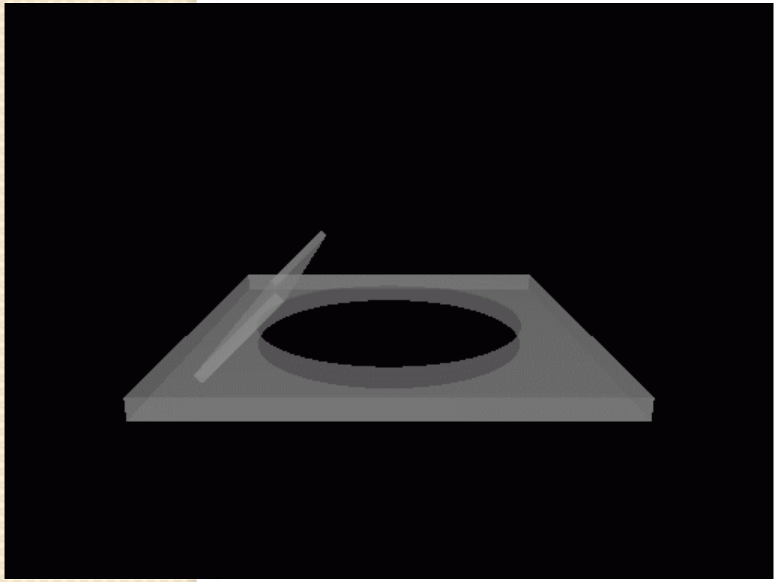
Schematic of the molecular arrangement in a two-layer liquid-crystal free-standing film in SmA phase

Molecular arrangement at the air/film interface is well defined

Courtesy of Prof. CC Huang @ U. Minnesota

Free-standing film: experimental geometry





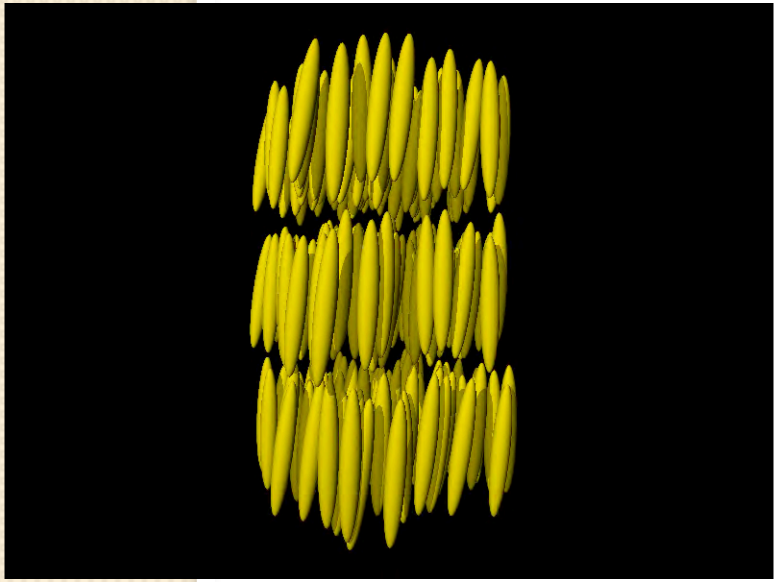
Smectic liquid crystals: layered structure

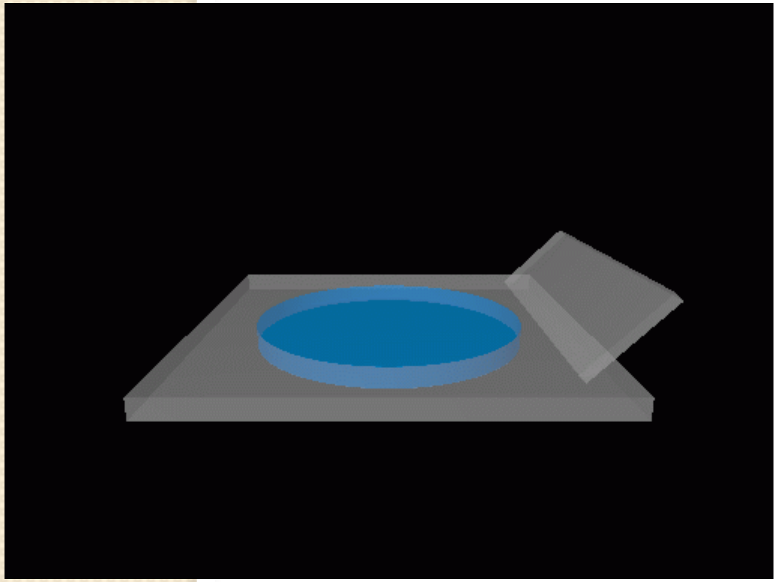
Free standing films:
- a) easy to get film of uniform thickness
- b) smectic layers parallel to film plate
- c) no substrate involved
- d) two air-liquid crystal interfaces
- e) controlled thickness

Fig. a) Schematic drawing of SmA phase;
b) preparation of a free standing film

Courtesy of Prof. CC Huang @ U. Minnesota

Free-standing film: experimental geometry





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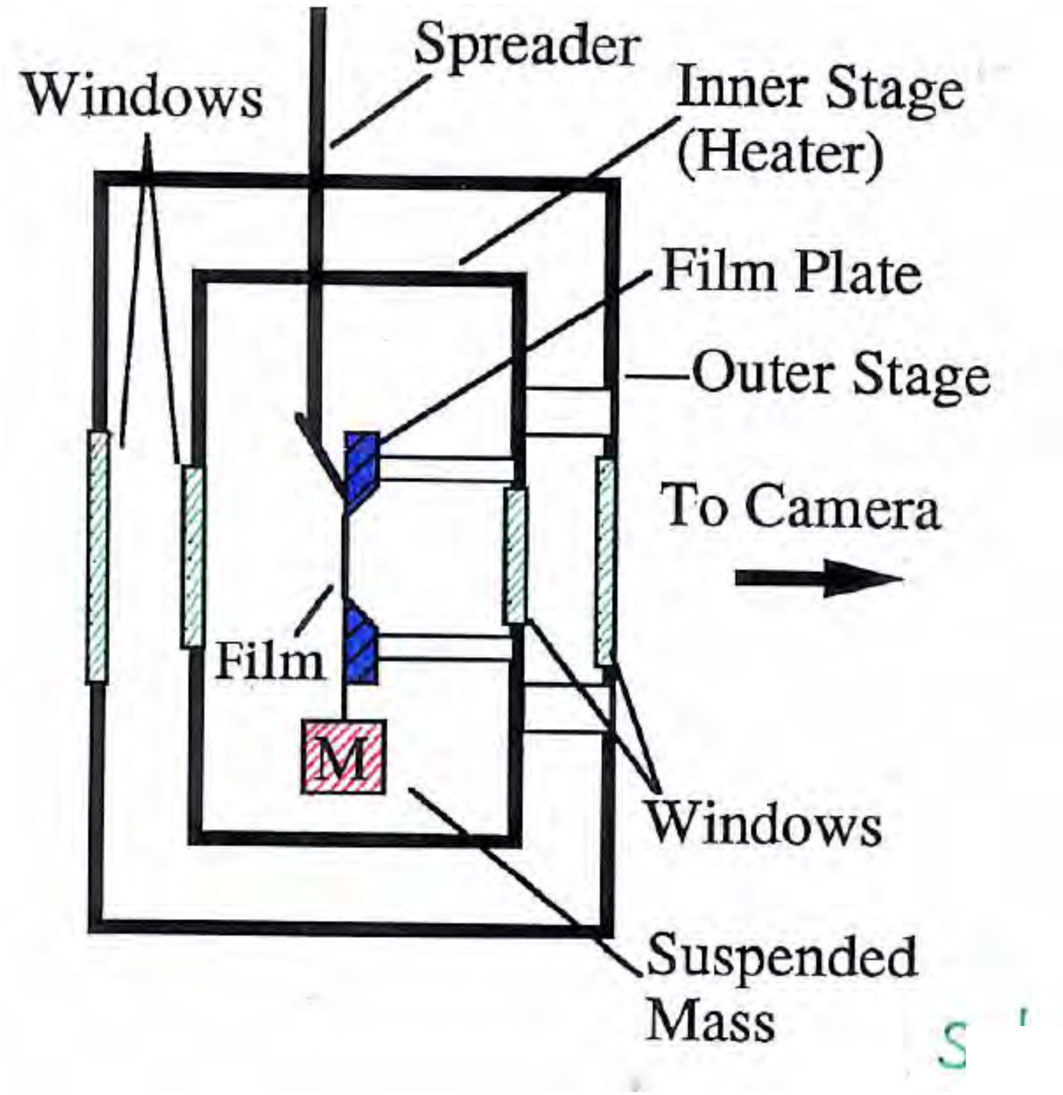
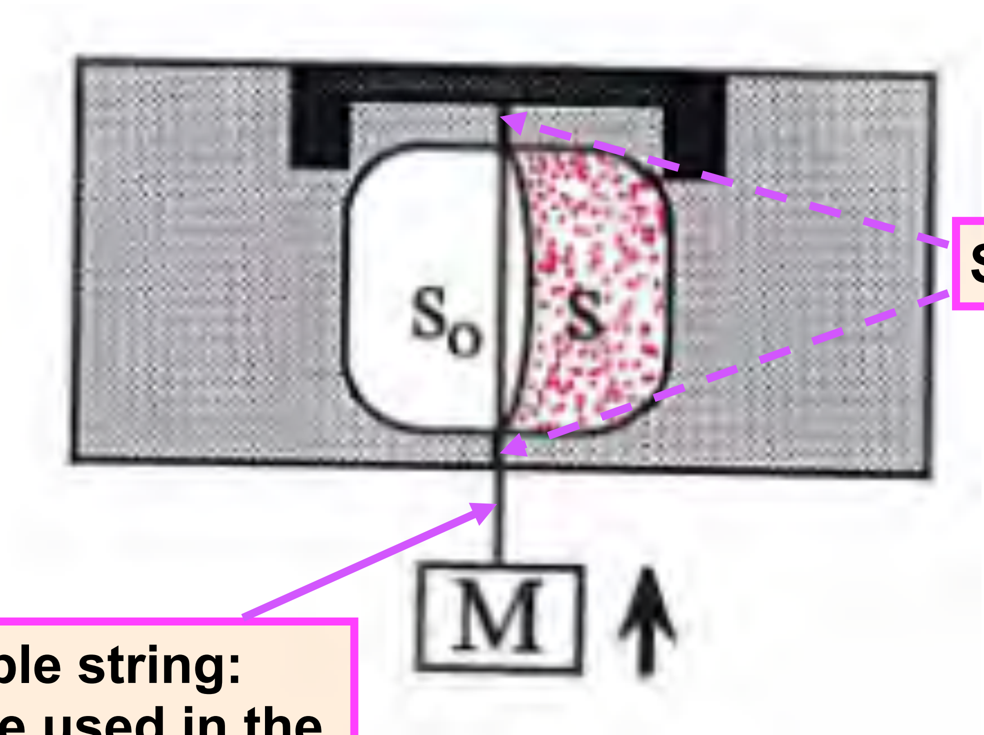
Courtesy of Prof. CC Huang @ U. Minnesota

Flexible–string tensiometer, side view



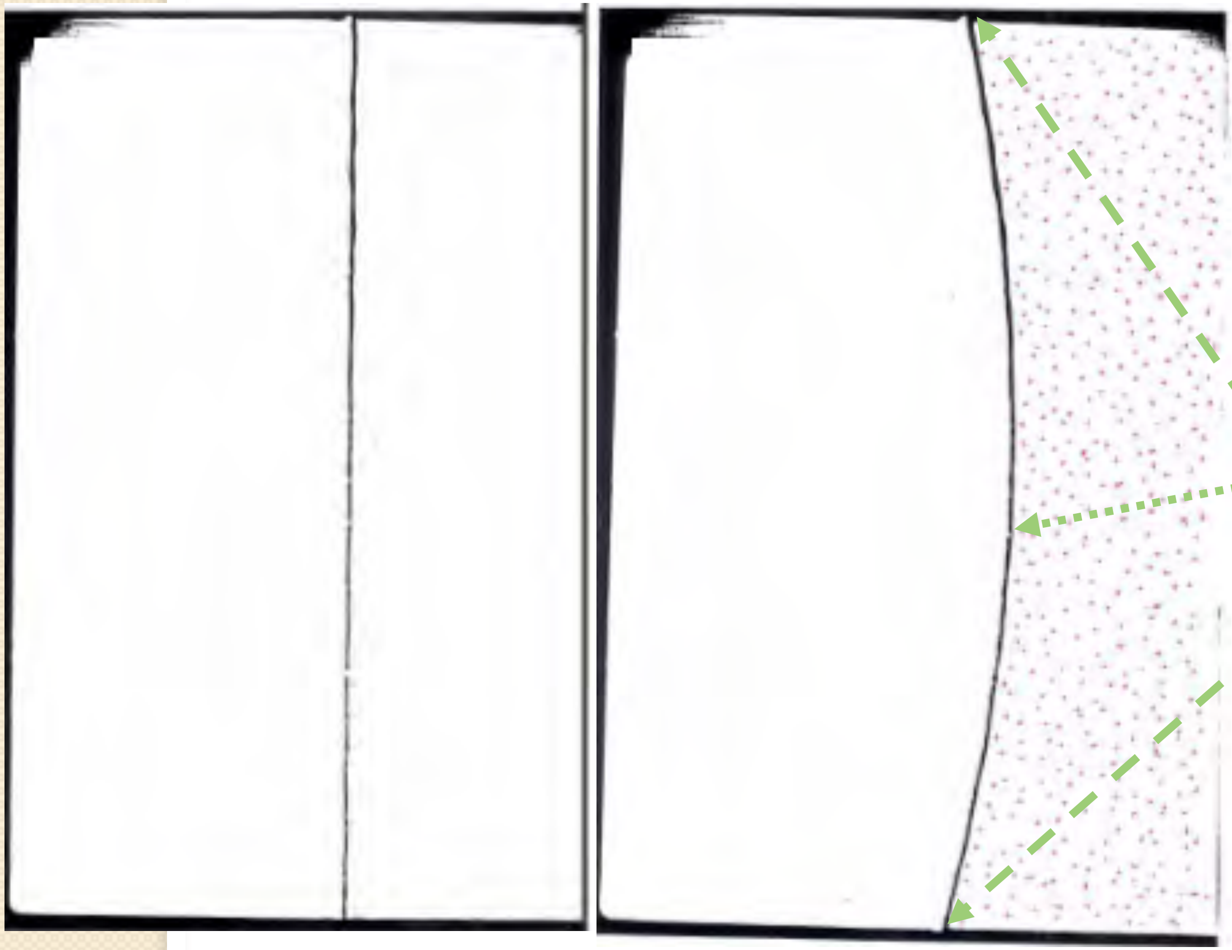
Flexible–string tensiometer, front view



Smooth V-groves

Flexible string: suture used in the eye surgery, about 40 μm in diameter

Photographic pictures of the flexible string



Without a film

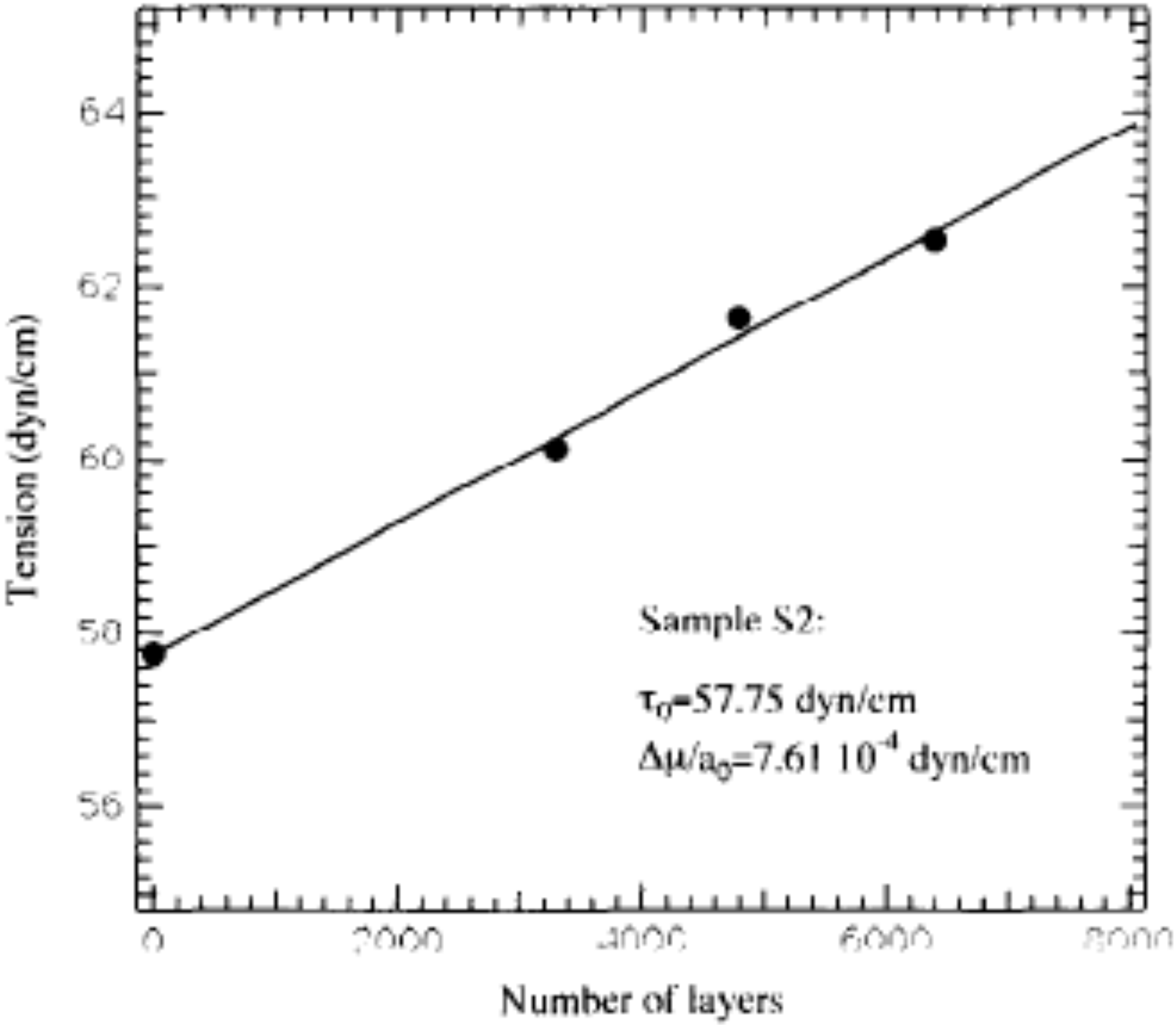
With a film on the right hand side

Great care requires to minimize the size of the meniscus, i.e., additional material on the string or the edges

$$2 * \gamma * R = M * g + f_f$$

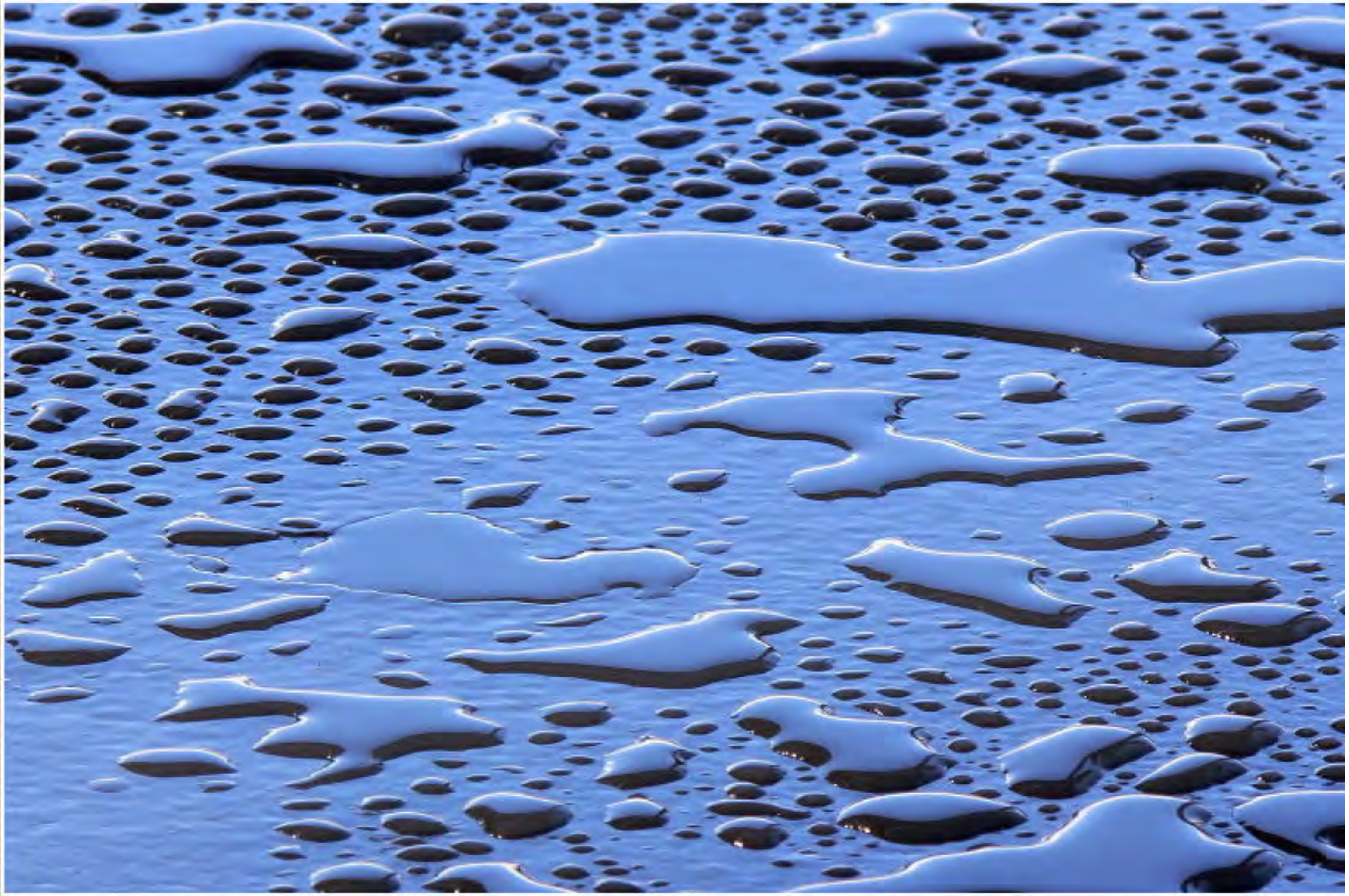
Courtesy of Prof. CC Huang @ U. Minnesota

Film tension as a function of film thickness



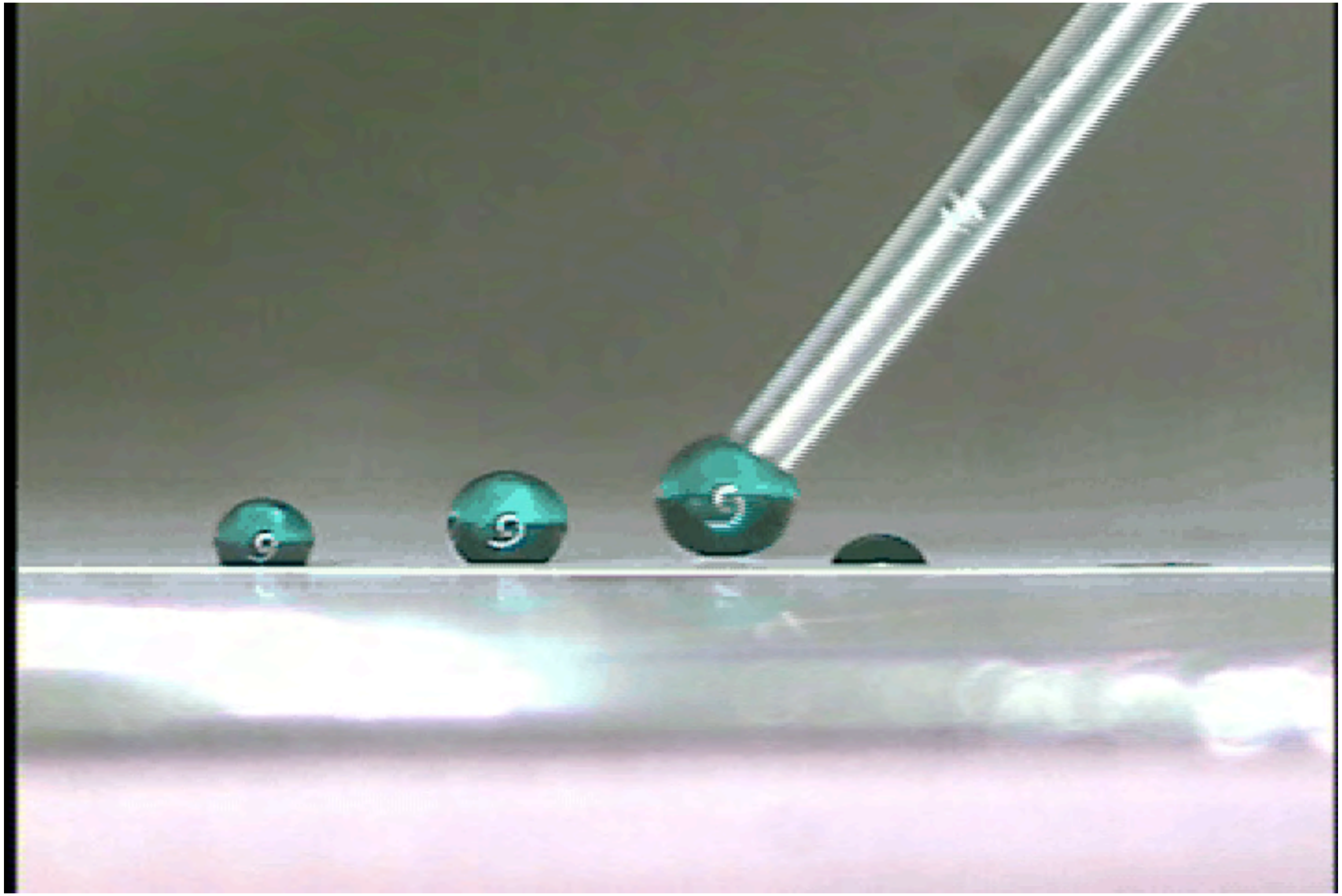
P. Pieranski *et al*. Physics A 194, 364 (1993)

To wet or not to wet?



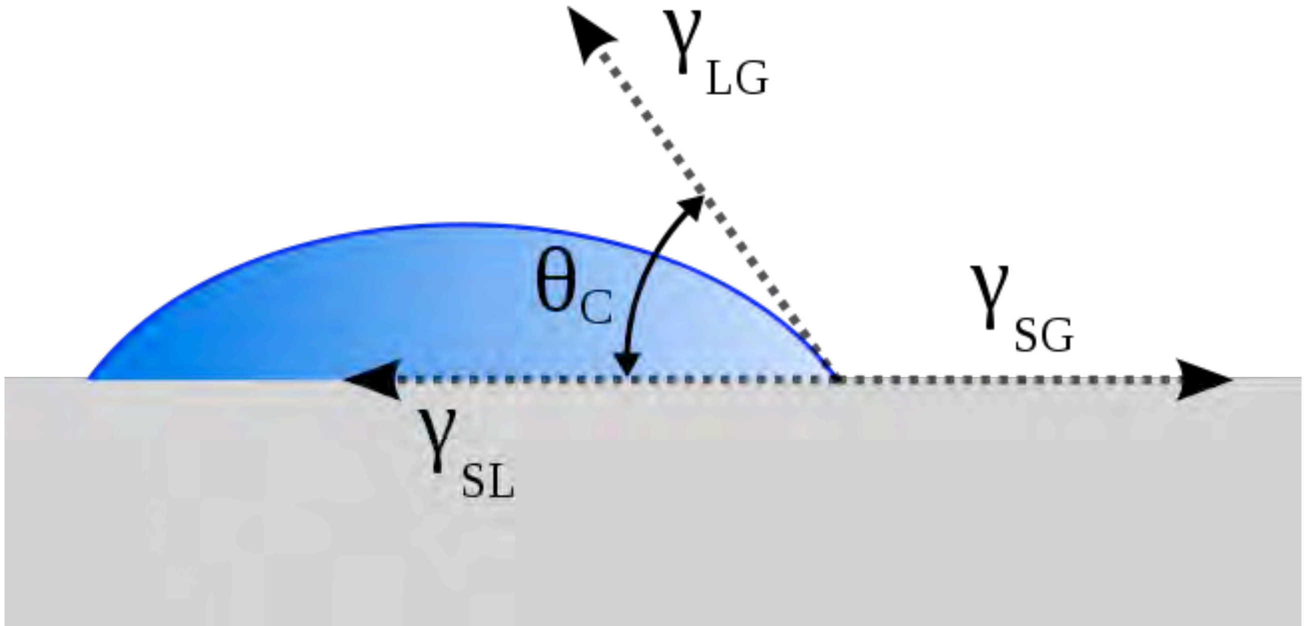
Small puddles of water on a smooth clean (hydrophilic) surface have perceptible thickness.

To wet or not to wet?



Hydrophobic surface-PDMS

Wetting



Young equation: $\gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cos\theta$

Spreading parameter

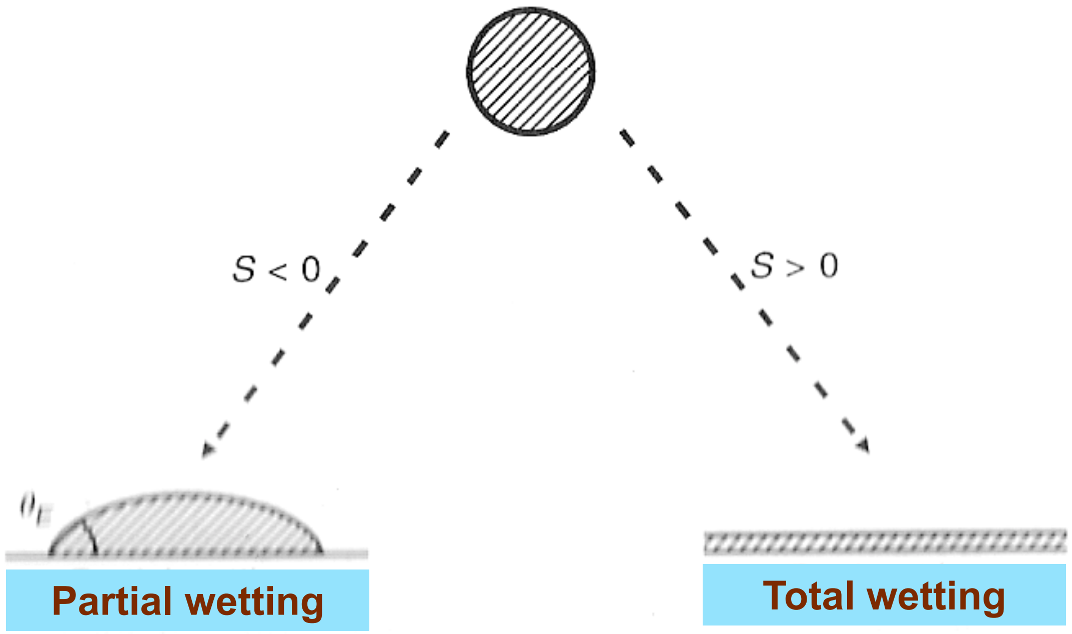
$$S = [E_{substrate}]_{dry} - [E_{substrate}]_{wet}$$

"Difference between surface energy/area"

or

$$S = \gamma_{SG} - (\gamma_{SL} + \gamma_{LG})$$

where the three coefficients γ are the surface tensions at the solid/air, solid/liquid, and liquid/air interfaces, respectively.



The two wetting regimes for sessile drops

Young equation:

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cos\theta$$

$$S = \gamma_{LG}(\cos\theta - 1)$$

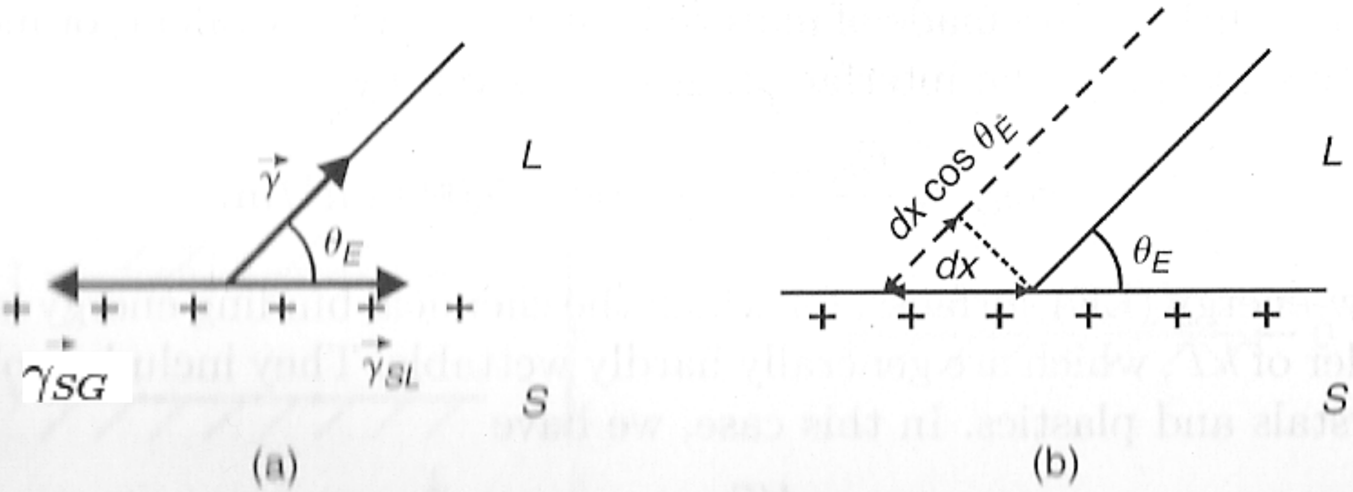


FIGURE 1.14. Determination of θ_E: (a) via forces or (b) via works.

Contact angle	Degree of wetting	Strength of: Sol./Liq. interactions	Strength of: Liq./Liq. interactions
Superhydrophilic $\theta = 0$	Perfect wetting	strong	weak
$0 < \theta < 90°$	high wettability	strong	strong
		weak	weak
$90° \leq \theta < 180°$	low wettability	weak	strong
$\theta = 180°$ Superhydrophobic	perfectly non-wetting	weak	strong

(>150°)

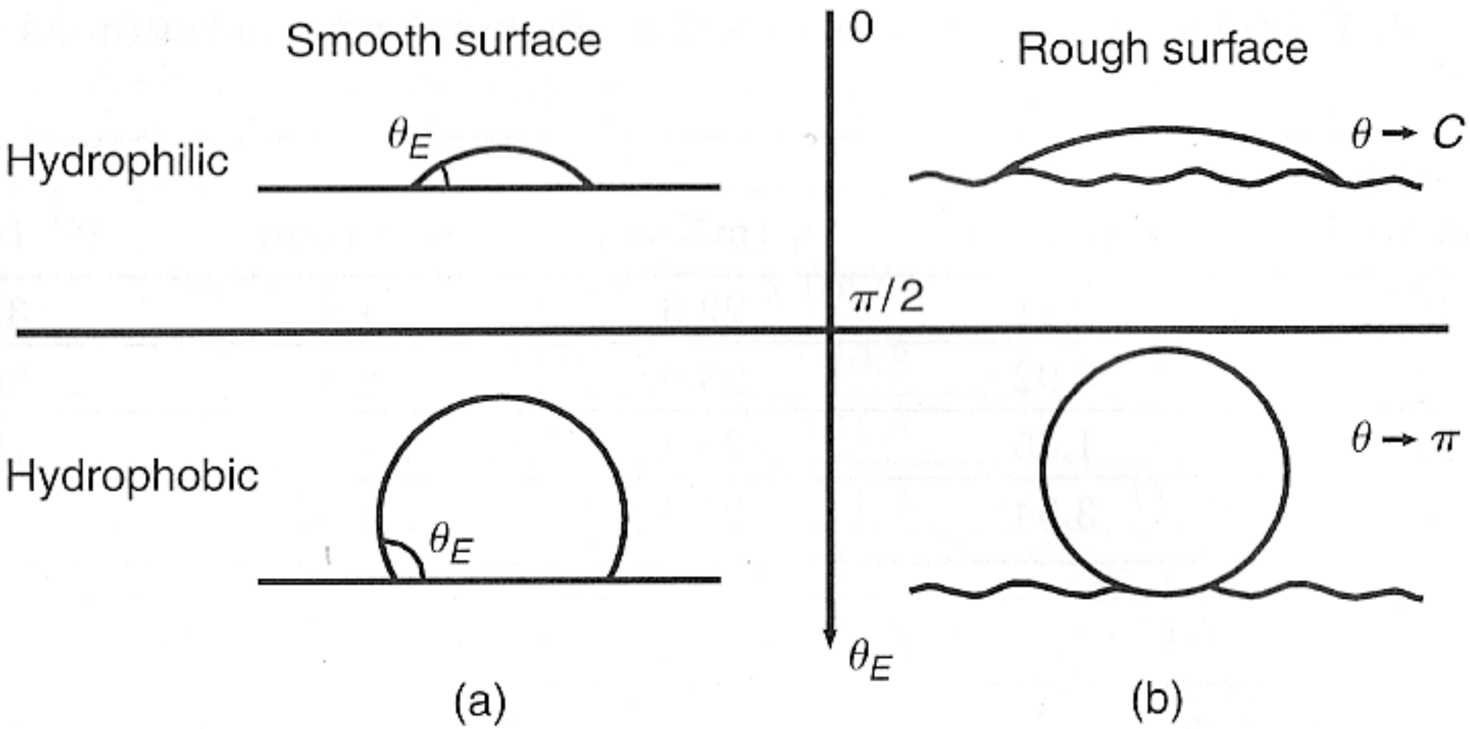
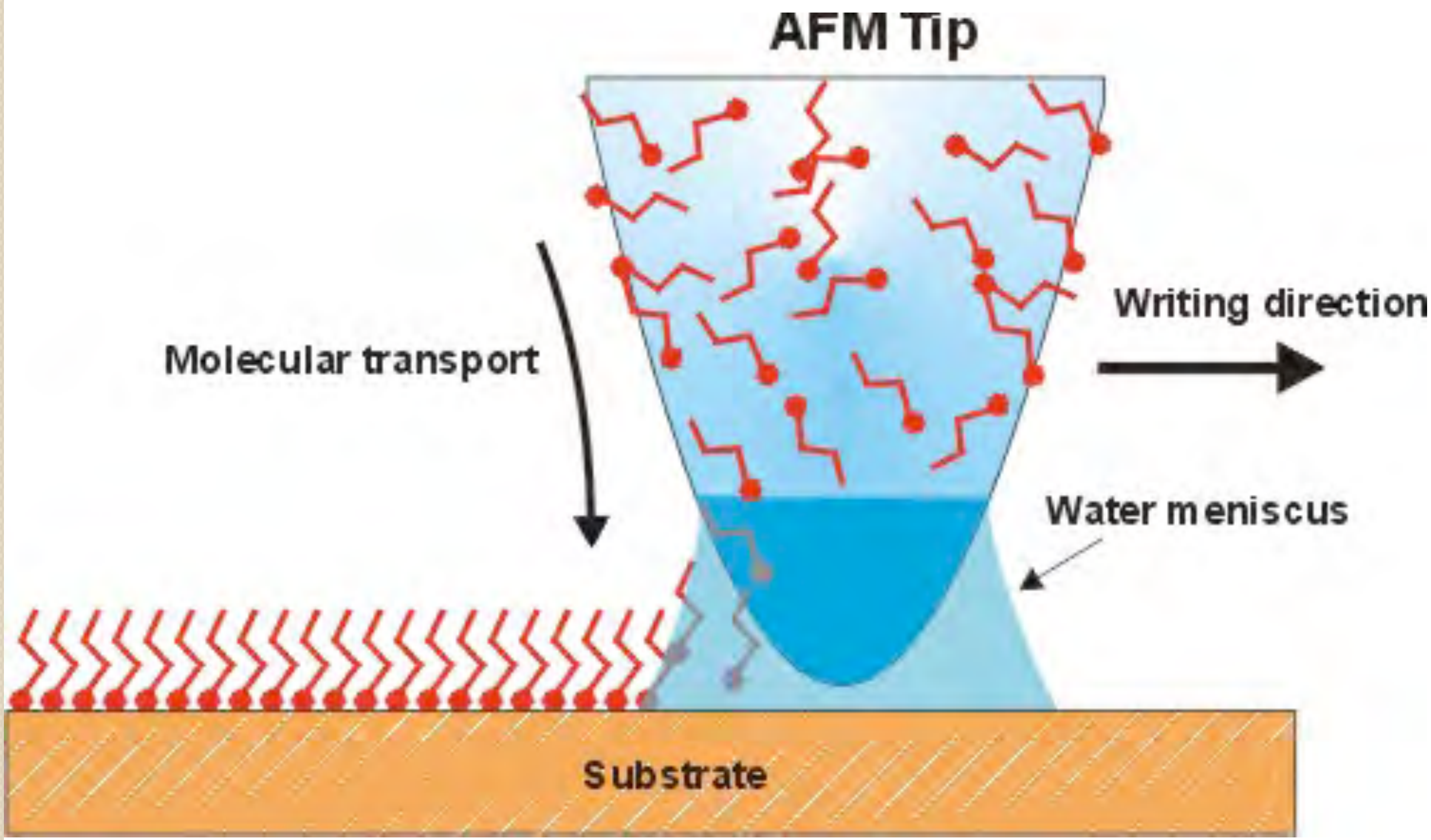


FIGURE 1.17. Controlling the wettability of a substrate through its roughness. Smooth surface (a); rough surface (b). Hydrophilic substrate becoming even more hydrophilic with a rough surface (top); hydrophobic substrate becoming "super-hydrophobic" (bottom).

Dip-Pen Nanolithography



Transport to a surface via a water meniscus

D. Piner,et al., *Science*, 1999, *283*, 661–63.

Dip-Pen Nanolithography

As soon as I mention this, people tell me about miniaturization, and how far it has progressed today. They tell me about electric motors that are the size of the nail on your small finger. And there is a device on the market, they tell me, by which you can write the Lord's Prayer on the head of a pin. But that's nothing; that's the most primitive, halting step in the direction I intend to discuss. It is a staggeringly small world that is below. In the year 2000, when they look back at this age, they will wonder why it was not until the year 1960 that anybody began seriously to move in this direction.

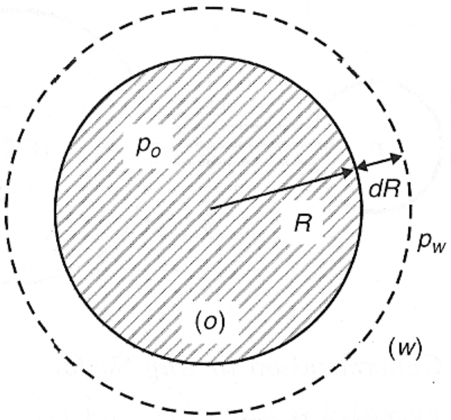
There's Plenty of Room at the Bottom
An Invitation to Enter a New Field of Physics
(Richard P. Feynman, 1960)

http://www.zyvex.com/nanotech/feynman.html

Mirkin group at NWU

Electrowetting
(How does it work?)

FIGURE 1.5. Overpressure inside a drop of oil "o" in water "w."



As one passes across a curved surface or interface, a jump in pressure occurs, which we proceed to evaluate, first for a sphere, and then for any curved surface.

Sphere

We take the example of a drop of oil (o) in water (w) (Figure 1.5). In order to lower its surface energy, the drop adopts a spherical shape of radius R. If the o/w interface is displaced by an amount dR, the work done by the pressure and capillary force can be written as

$$\delta W = -p_o\, dV_o - p_w\, dV_w + \gamma_{ow}\, dA \tag{1.4}$$

where $dV_o = 4\pi R^2\, dR = -dV_w$, and $dA = 8\pi R\, dR$ are the increase in volume and surface, respectively, of the drop, p_o and p_w are the pressures in the oil and water, and γ_{ow} is the interfacial tension between oil and water. The condition for mechanical equilibrium is $\delta W = 0$, which amounts to

$$\Delta p = p_o - p_w = \frac{2\gamma_{ow}}{R}. \tag{1.5}$$

For an aerosol drop of radius 1 µm, Δp is typically comparable to the atmospheric pressure. Note that equation (1.5) can be obtained just as well by minimizing the grand potential $\Omega = -p_o V_o - p_w V_w + \gamma_{ow} A$.

Laplace pressure

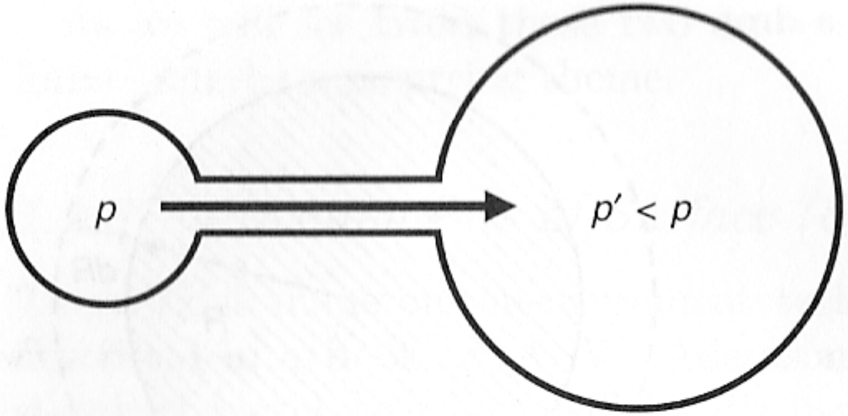


FIGURE 1.6. Small bubbles empty themselves into larger ones.

Generalization to Any Surface

Laplace's theorem:

The increase in hydrostatic pressure Δp that occurs upon traversing the boundary between two fluids is equal to the product of the surface tension γ and the curvature of the surface $C = \frac{1}{R} + \frac{1}{R'}$:

$$\Delta p = \gamma \left(\frac{1}{R} + \frac{1}{R'} \right) = \gamma C \qquad (1.6)$$

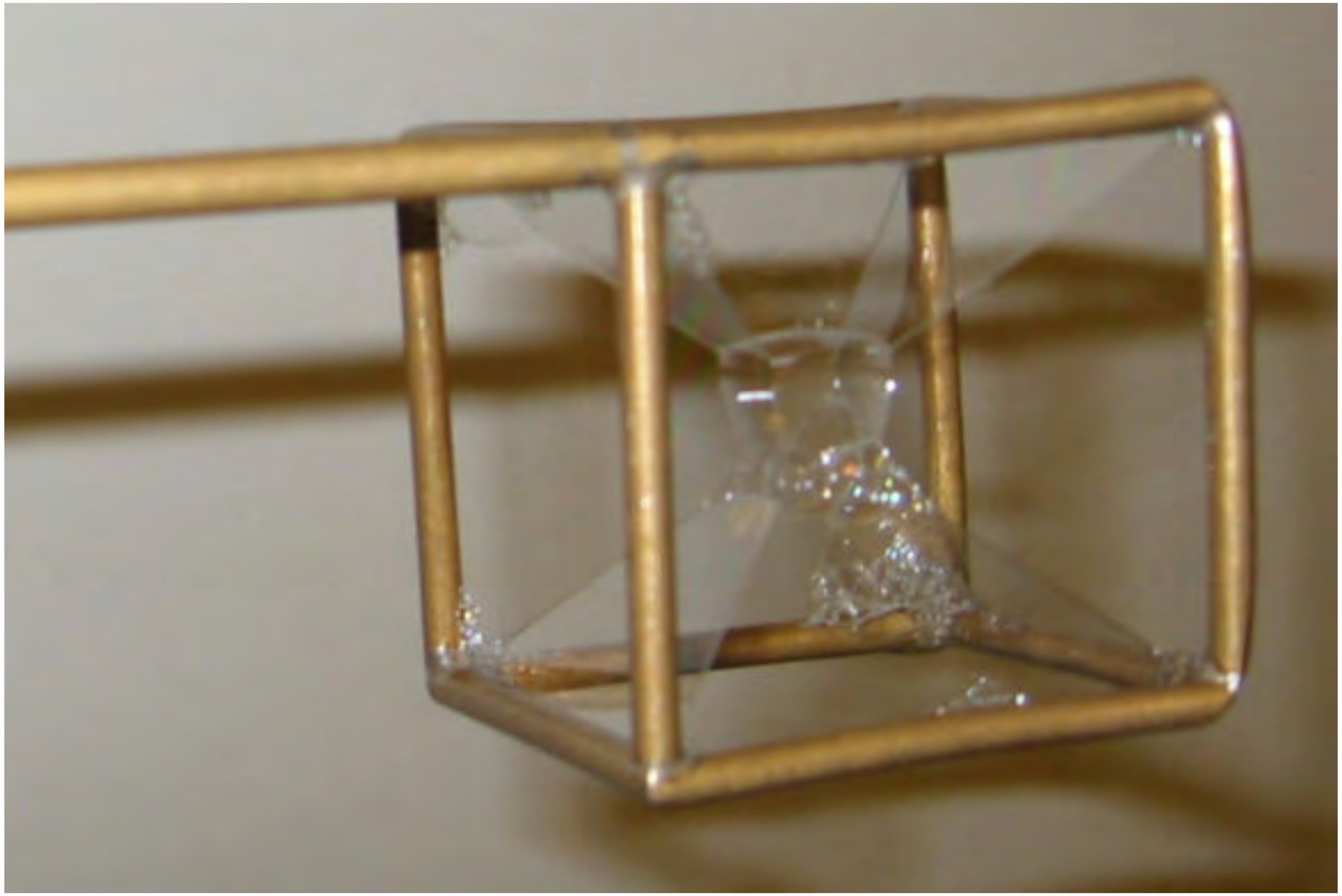
Laplace pressure

$$\Delta p = \gamma \left(\frac{1}{R_x} + \frac{1}{R_y} \right)$$

Is it easy to form a micro- or nano-droplet?

Δp for water drops of different radii at STP				
Droplet radius	1 mm	0.1 mm	1 μm	10 nm
Δp (atm)	0.0014	0.0144	1.436	143.6

Minimal Surface



The reason for this is that the pressure difference across a fluid interface is proportional to the mean curvature, as seen in the Young-Laplace equation. For an open soap film, the pressure difference is zero, hence the mean curvature is zero, and minimal surfaces have the property of **zero mean curvature**.

Capillary adhesion

Two wetted surfaces can stick together with great strength if the liquid wets them with an angle $\theta_E < \pi/2$. The angle θ_E is defined in Figure 1.8. (It will be discussed in more detail in Section 1.2.) Imagine that we mash a large drop between two plates separated by a distance H. The drop forms what is called a *capillary bridge* characterized by a radius R and a surface area $A = \pi R^2$. The Laplace pressure within the drop reads

$$\Delta p = \gamma \cdot \left(\frac{1}{R} - \frac{\cos\theta_E}{H/2} \right) \approx - \frac{2\gamma\cos\theta_E}{H}. \tag{1.7}$$

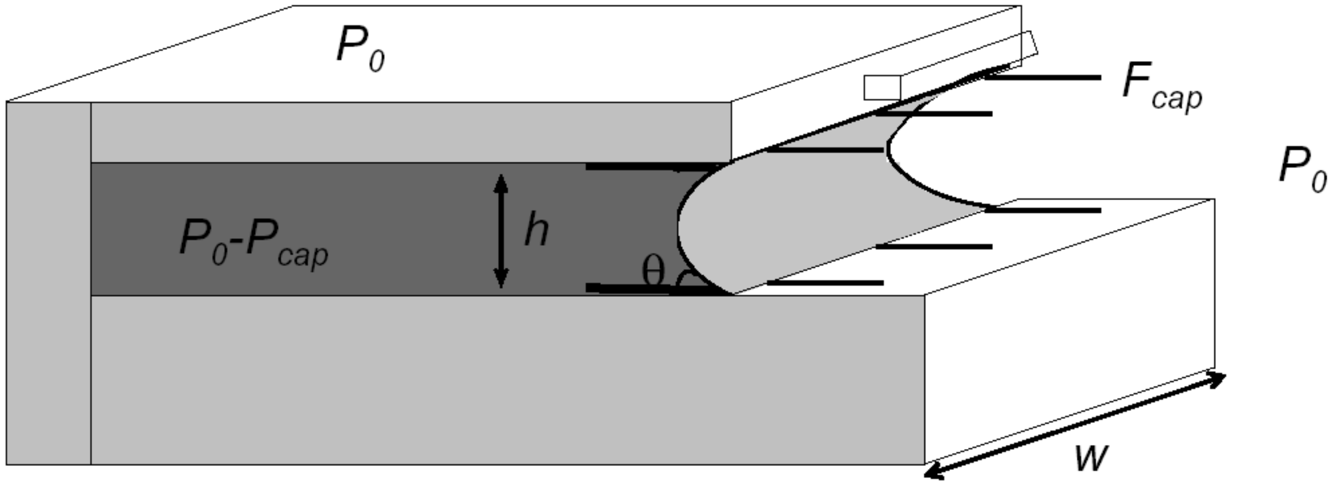
The force that glues the two plates together is attractive as long as $\theta_E < \pi/2$. If $H \ll R$, it is equal to

$$F = \pi R^2 \frac{2\gamma\cos\theta_E}{H}.$$

For water, using $R = 1$ cm, $H = 5$ μm, and $\theta_E = 0$ (best case), one calculates a pressure drop $\Delta p \sim 1/3$ atm and an adhesive force $F \sim 10$ N, which is enough to support the weight of one liter of water!

Capillary Force

Capillary pressure



$$F_{cap} = 2w\gamma\cos\theta$$

$$P_{cap} = \frac{2\gamma\cos\theta}{h}$$

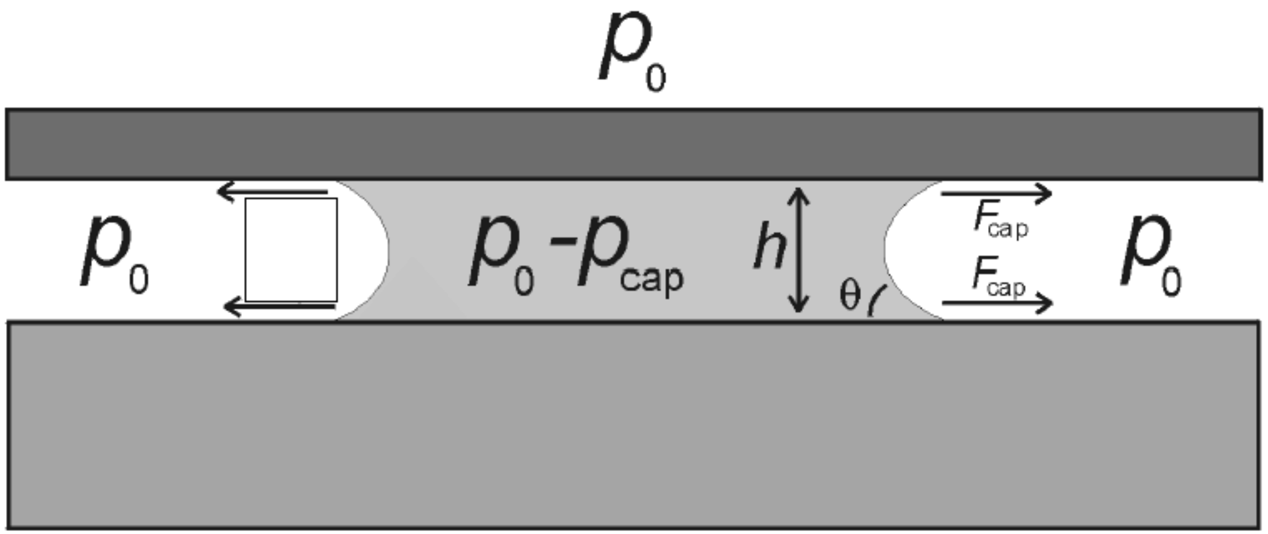
Pressure increases with *1/h* !!

γ : surface tension (Nm^{-1})

θ : contact angle

Force/length or Energy/area

Capillarity induced negative pressure

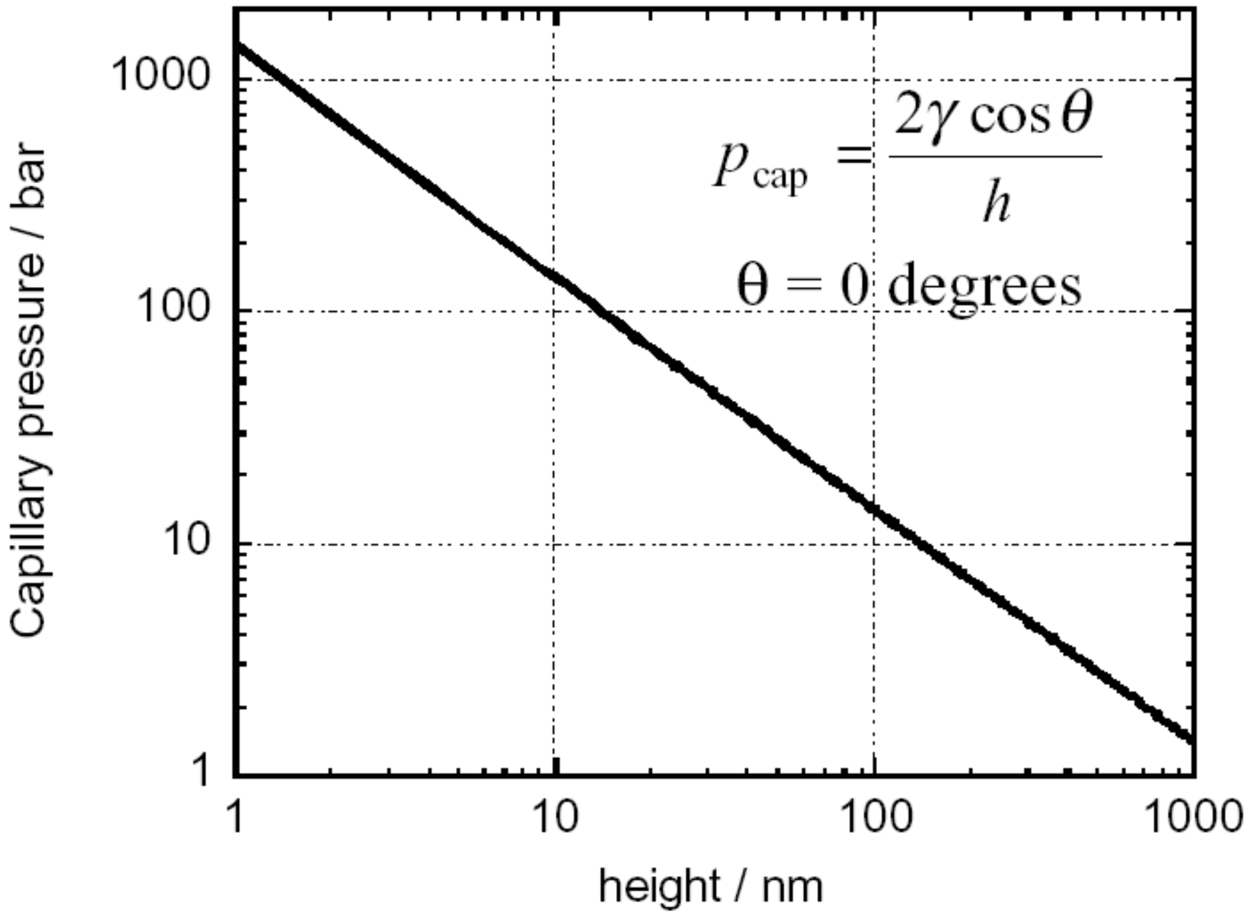


$$p_{\text{cap}} = \frac{2\gamma \cos\theta}{h}$$

h = 108 nm, γ = 0.07 Nm^{-1} θ = 18°

$\rightarrow p_0 - p_{\text{cap}}$= -12 bar

Scaling



Capillary pressure / bar
1000
100
10
1
1
10
100
1000
height / nm
$p_{cap} = \frac{2\gamma \cos\theta}{h}$
θ = 0 degrees

Capillary action

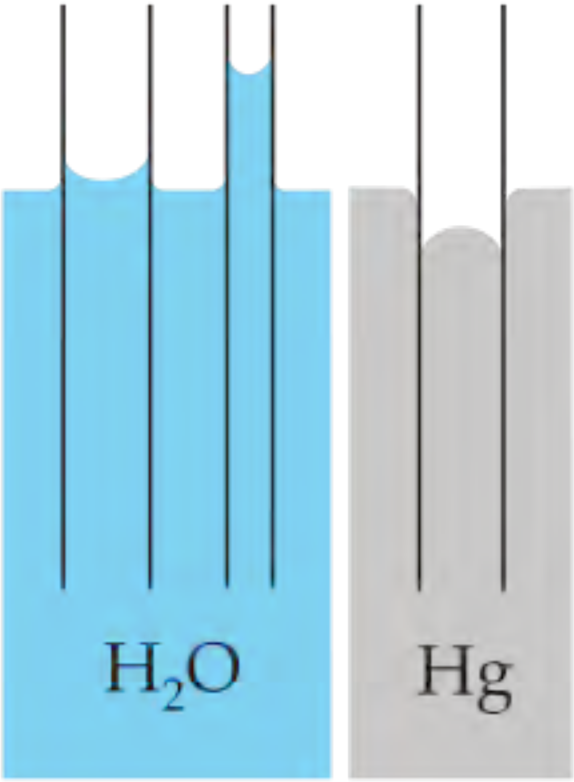
$$h = \frac{2\gamma \cos\theta}{\rho g r}$$ (H.W.)

- γ is the liquid-air surface tension (force/unit length)
- θ is the contact angle
- ρ is the density of liquid (mass/volume)
- g is local gravitational field strength (force/unit mass)
- r is radius of tube (length).

For a water-filled glass tube in air at standard laboratory conditions, using SI units:

γ is 0.0728 J/m² at 20 °C
θ is 20° (0.35 rad)
ρ is 1000 kg/m³
g is 9.8 N/kg

$$h \approx \frac{1.4 \times 10^{-5}}{r} \text{ m}$$



Polymer Drop Breakup in Microfluidic Devices

Water drop

Exercise 3

- What is the capillary pressure inside a nanotube with a diameter of 5 nm and a 30° of contact angle? (i.e. the inner surface of nanotube is hydrophilic.)