



# Surface tension, wetting, and capillarity

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



# SOFT MATTER

Nobel Lecture, December 9, 1991

by

PIERRE - GILLES DE GENNES

College de France, Paris, France



## The Nobel Prize in Physics 1991

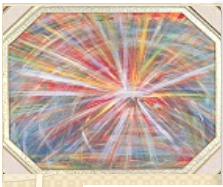


for discovering that methods developed for studying order phenomena in simple systems can be generalized to more complex forms of matter, in particular to liquid crystals and polymers.

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:

1) 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.



*La Souffleuse de Savon.*  
*Amusez-vous sur la terre et sur l'eau* | *Richesse, honneur, plaisir et tout de ce monde*  
*Médisances, qui se font un nom ?* | *Tout n'est que bulles de savon.*  
*A Paris chez le Citoyen de la Vérité*

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

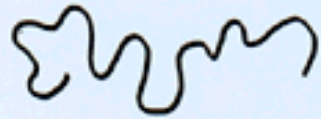
Nobel Lecture, December 9, 1991  
by  
PIERRE-GILLES DE GENNES



# The master of analogies



## Polymers



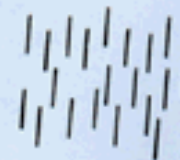
$$R \sim N^{\nu}$$

For long chains and large number of monomers  $N$  the physical laws are universal!

## Liquid crystals

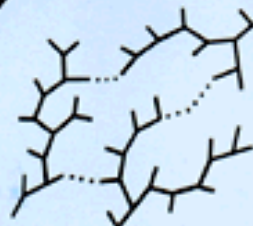
$$T < T_c$$

$$T > T_c$$



As the temperature decreases the disordered liquid changes into a partly ordered structure at a specific temperature  $T_c$ .

## Gels



$$N \sim (p_c - p)^{-\gamma}$$

An infinite network of linked monomers ( $N \rightarrow \infty$ ) is obtained when the amount of reacted bonds  $p$  has reached the so called percolation limit  $p_c$ . Close to  $p_c$  the physical laws are universal!

## Ferromagnets

$$T < T_c$$

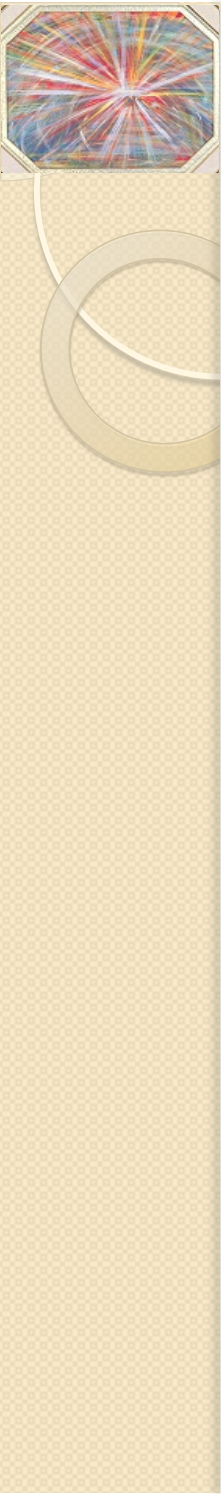
$$T > T_c$$



$$R \sim (T - T_c)^{-\nu}$$

As the Curie temperature  $T_c$  is approached the microscopic magnetic domains grow towards an infinite size ( $R \rightarrow \infty$ ). Close to  $T_c$  the physical laws are universal!



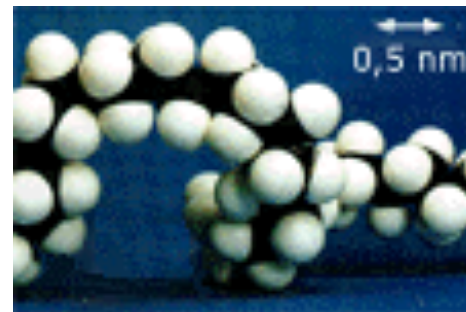
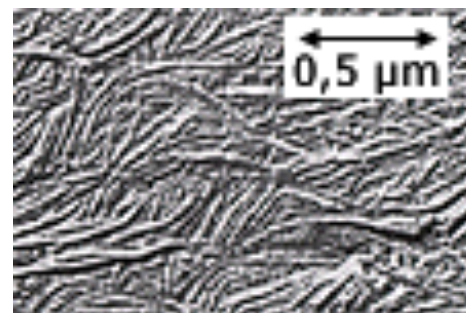


# Polymers

**What do they look like? .....**



Photo: L. Falk



# Surface tension (physical origin)

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

$$U \approx kT \approx 25 \text{ meV for oils} \\ \approx 1 \text{ eV for Hg}$$

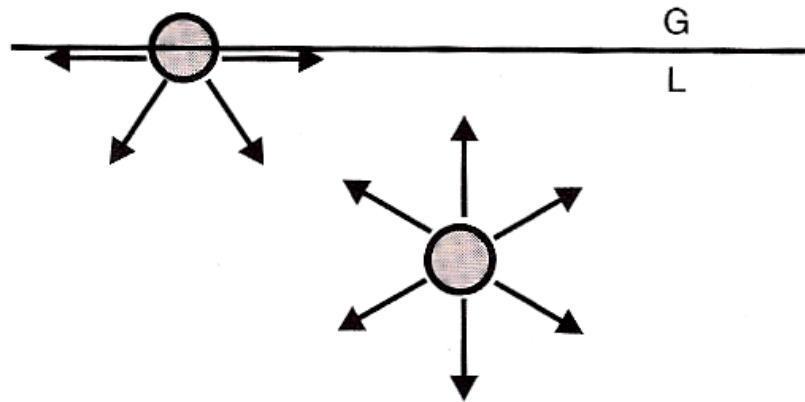


FIGURE 1.2. An “unhappy” molecule at the surface: It is missing half its attractive interactions.

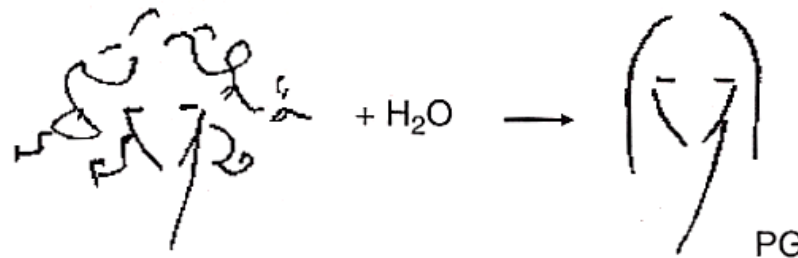


FIGURE 1.3. Full dry hair vs. sticky wet hair.

# Physical origin of the surface tension

**Langmuir : 1961**

**“Principle of Independent Surface Action”**

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



# 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
$\gamma(\text{mN/m})$	0.1	23	24	25	63
Liquid	Water	Water (100°C)	Molten glass	Mercury	Water/oil
$\gamma(\text{mN/m})$	73	58	~300	485	~ 50



**Water beading on a leaf**



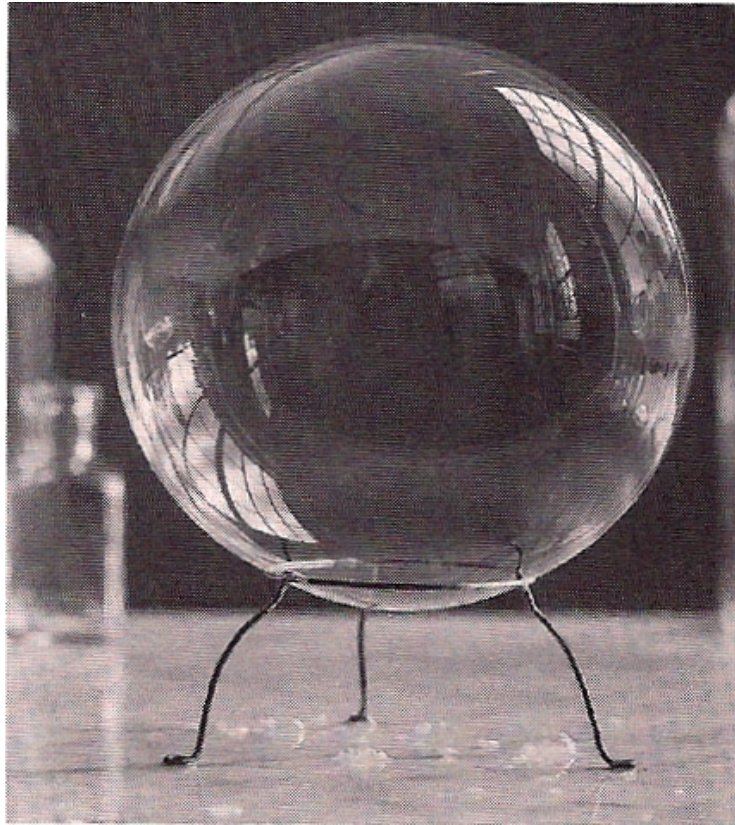


FIGURE 1.1. Drops and bubbles form perfect spheres.<sup>2</sup> (From *A Drop of Water: A Book of Science and Wonder*, by Walter Wick. Published by Scholastic Press, a division of Scholastic Inc. Photographs © 1997 by Walter Wick. Reproduced by permission.)



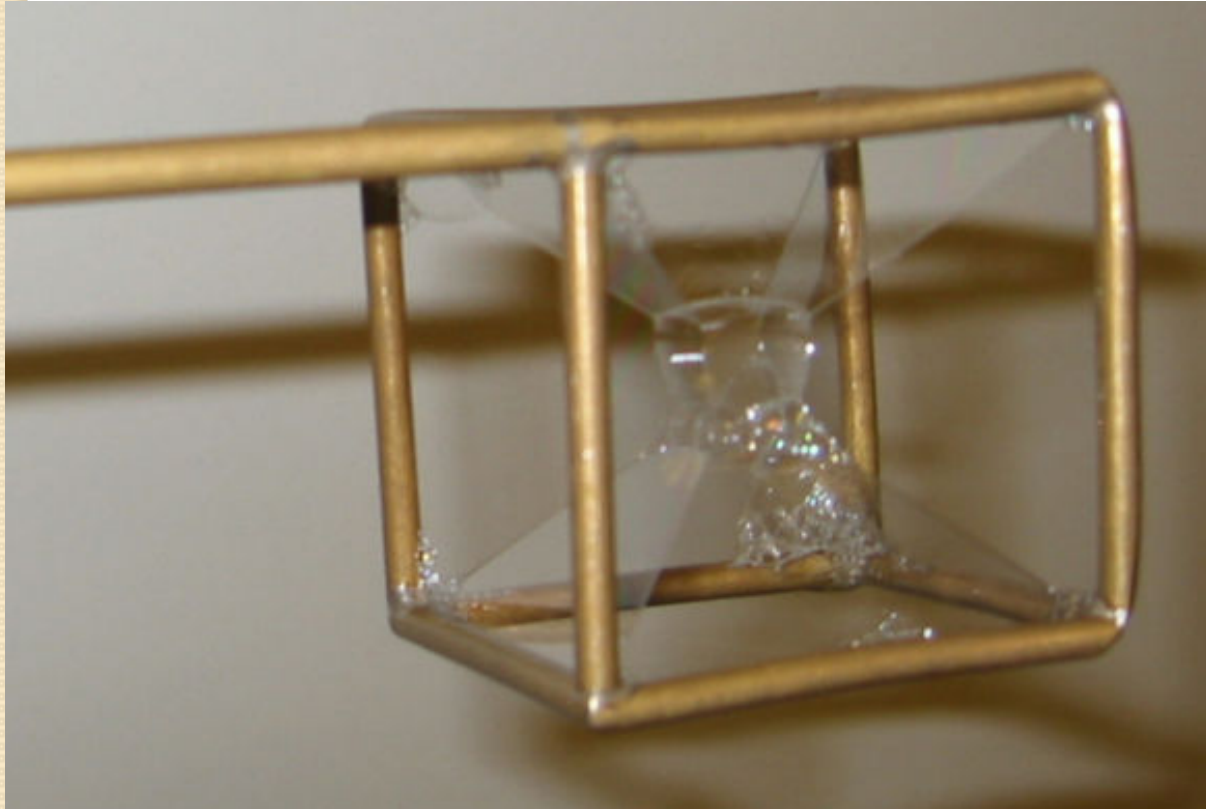


**Surface tension** prevents a coin from sinking: the coin is indisputably denser than water, so it cannot be floating due to **buoyancy** alone.





PTFE is often used to coat non-stick frying pans as it is not water-wettable and possesses fairly high heat resistance.



**Minimal surface**



A soap bubble balances surface tension forces against internal pneumatic pressure



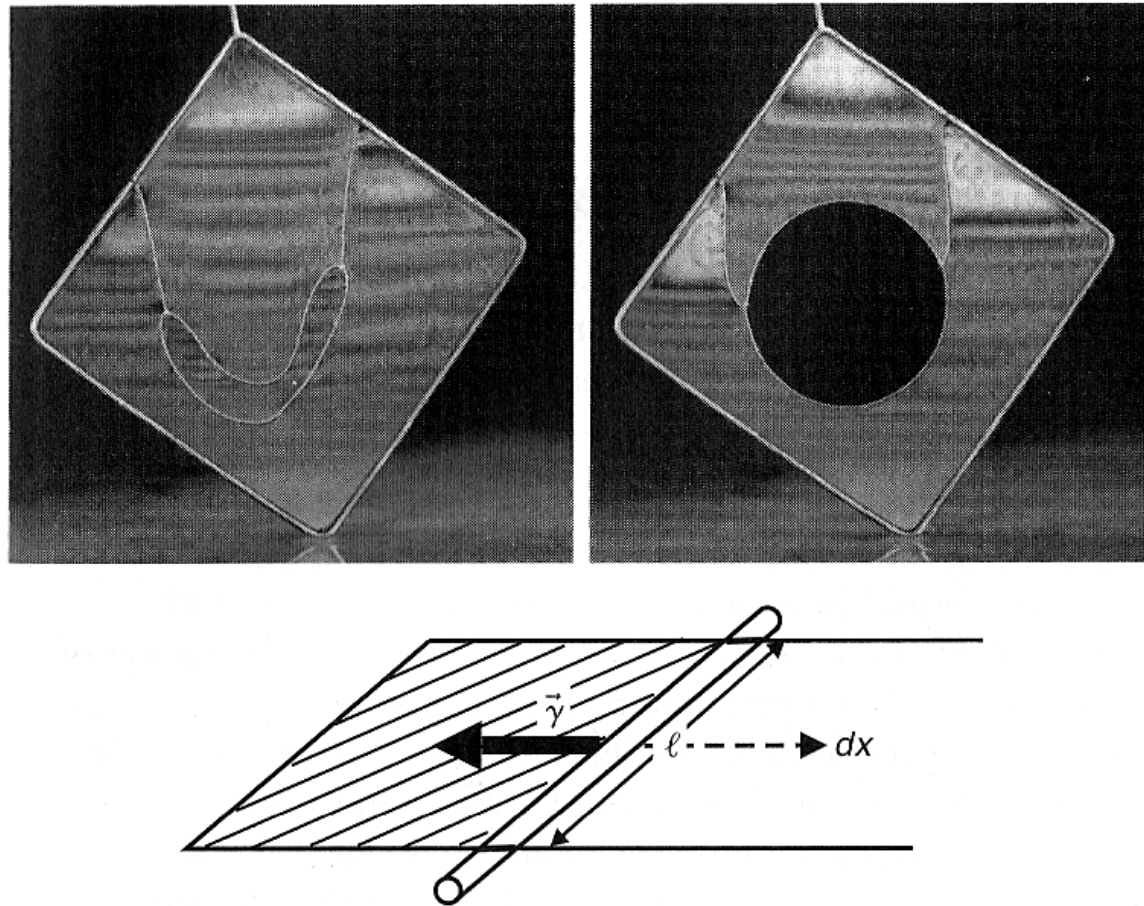


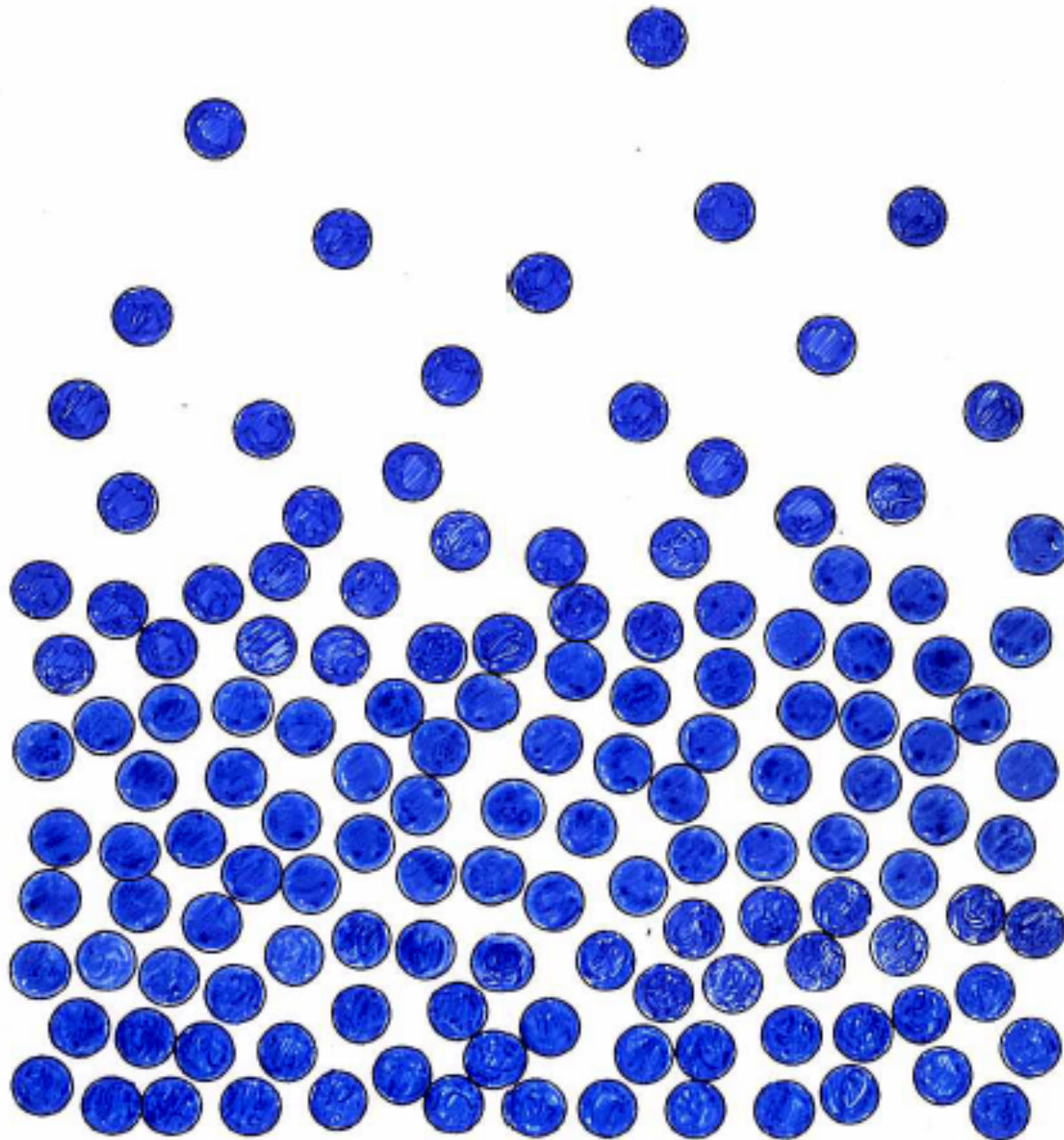
FIGURE 1.4. Manifestation of surface tension: force normal to the line (wire, rod). (From *A Drop of Water: A Book of Science and Wonder*, by Walter Wick. Published by Scholastic Press, a division of Scholastic Inc. Photographs © 1997 by Walter Wick. Reproduced by permission.)



**Vapor**

**Interface?**

**Liquid**



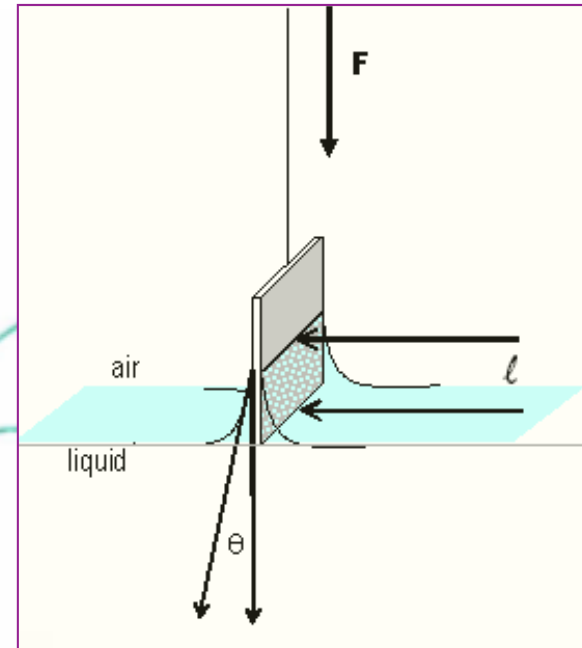
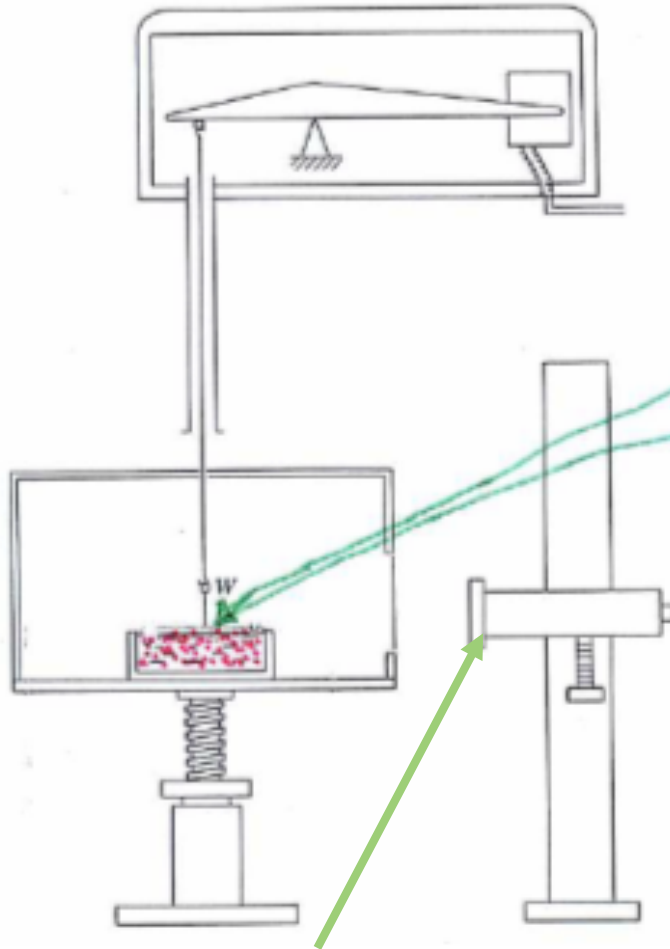
**H<sub>2</sub>O:**

$$\gamma = 73 \text{ mN/m}$$



# Wilhelmy plate technique

Balance to measure  $F$

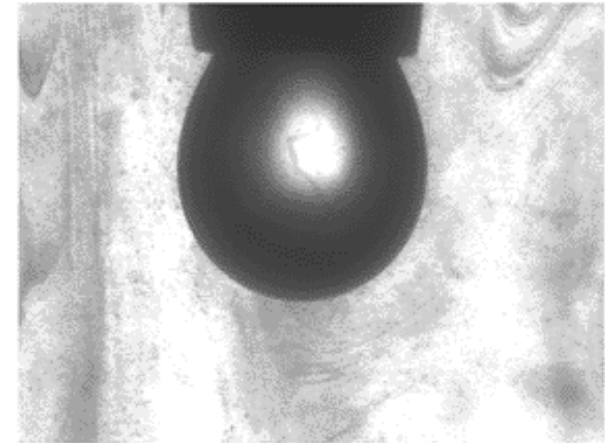
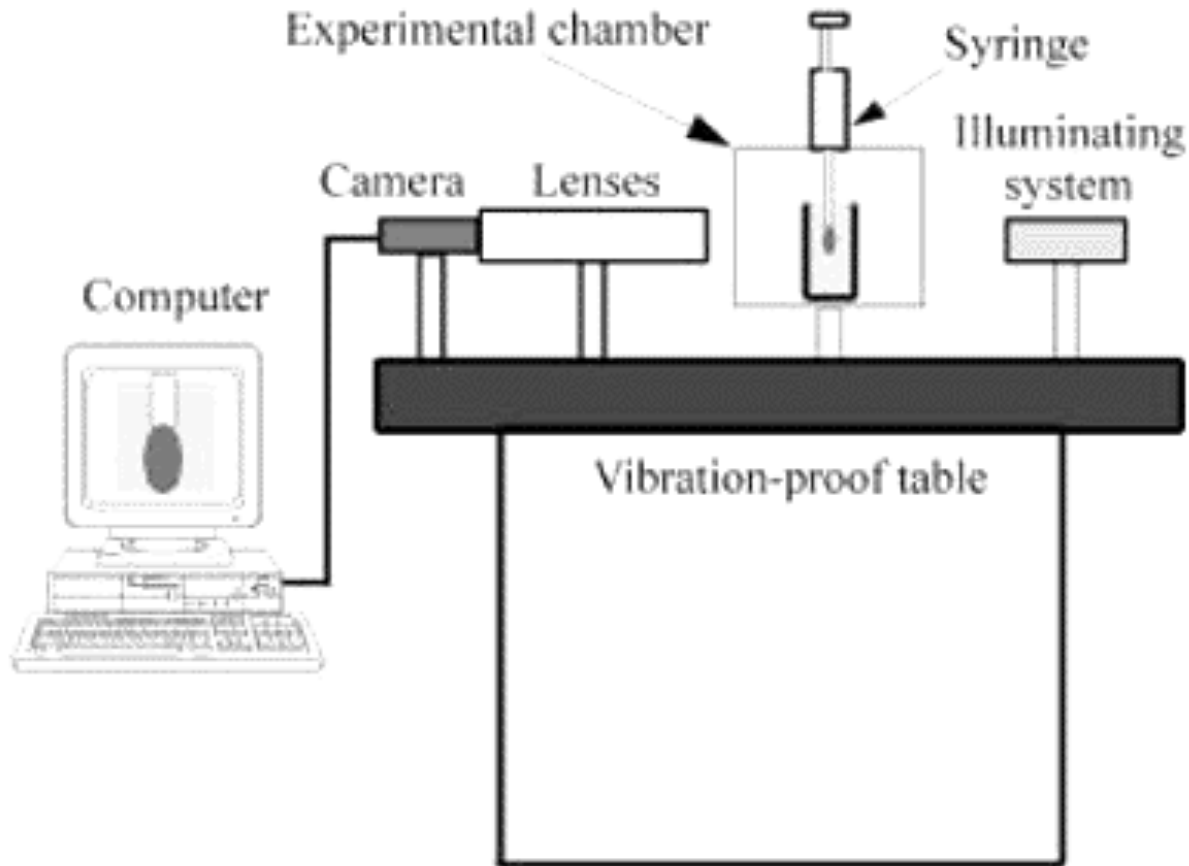


$$\text{Surface tension: } \gamma = \frac{F}{2l \cdot \cos \theta}$$

Telescope, measure  
height of the meniscus:  $l$   
and angle of meniscus:  $\theta$



# Pendant drop technique

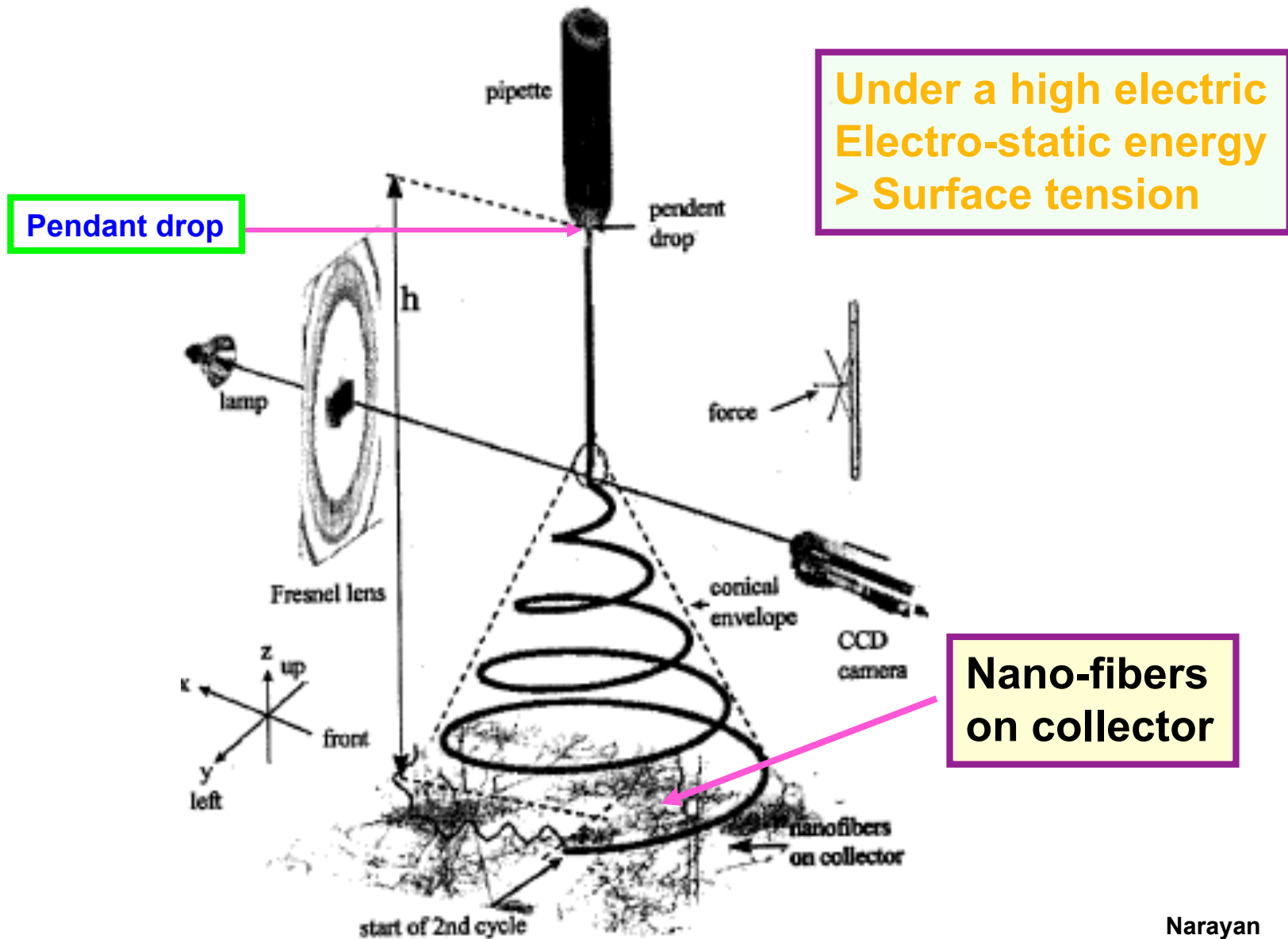


Drop of polystyrene

Pendant drop apparatus

Shape of the drop → surface tension

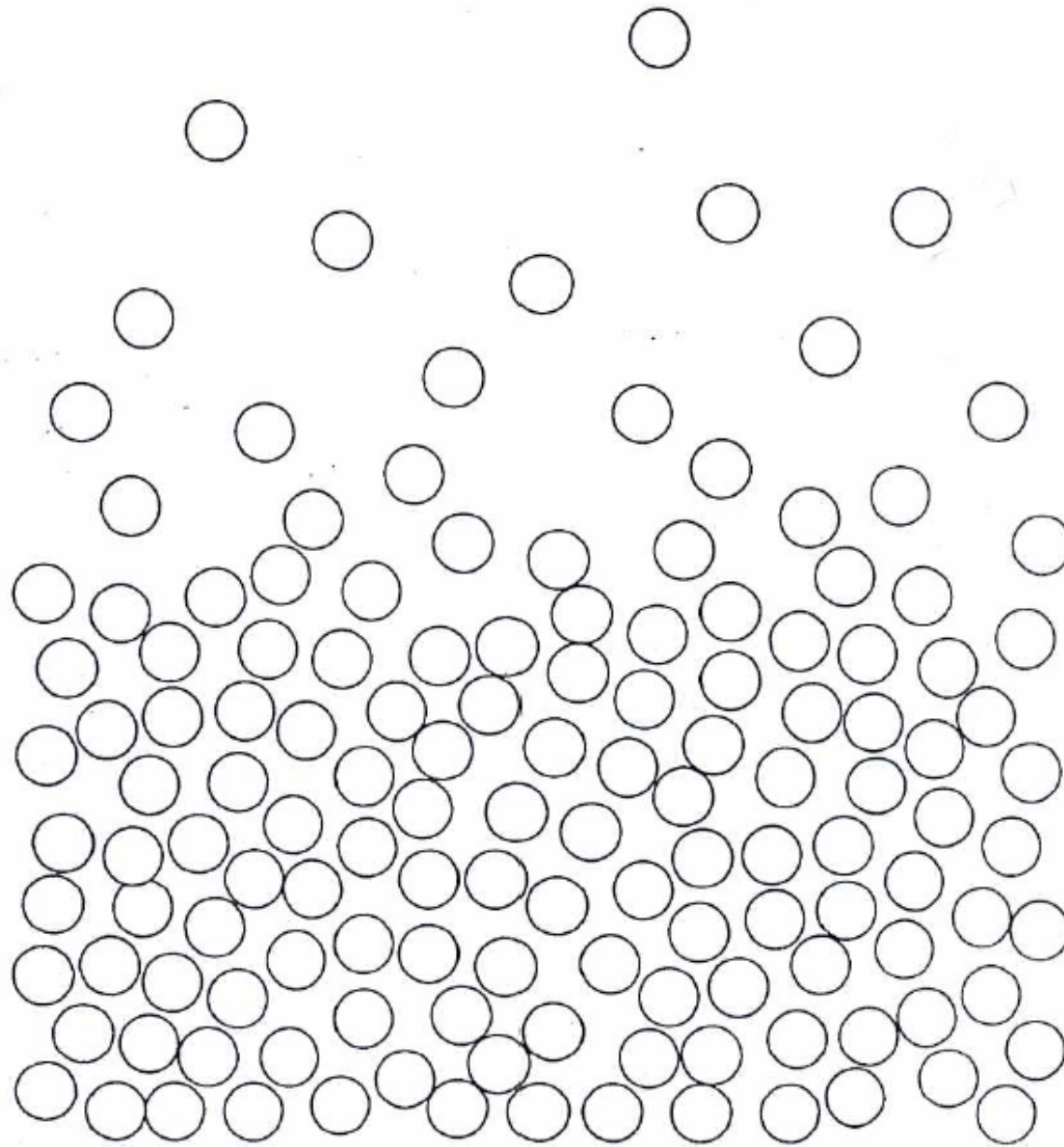
# Electrospinning



**Vapor**

**Fowkes:  
Surface  
monolayer?**

**Liquid**

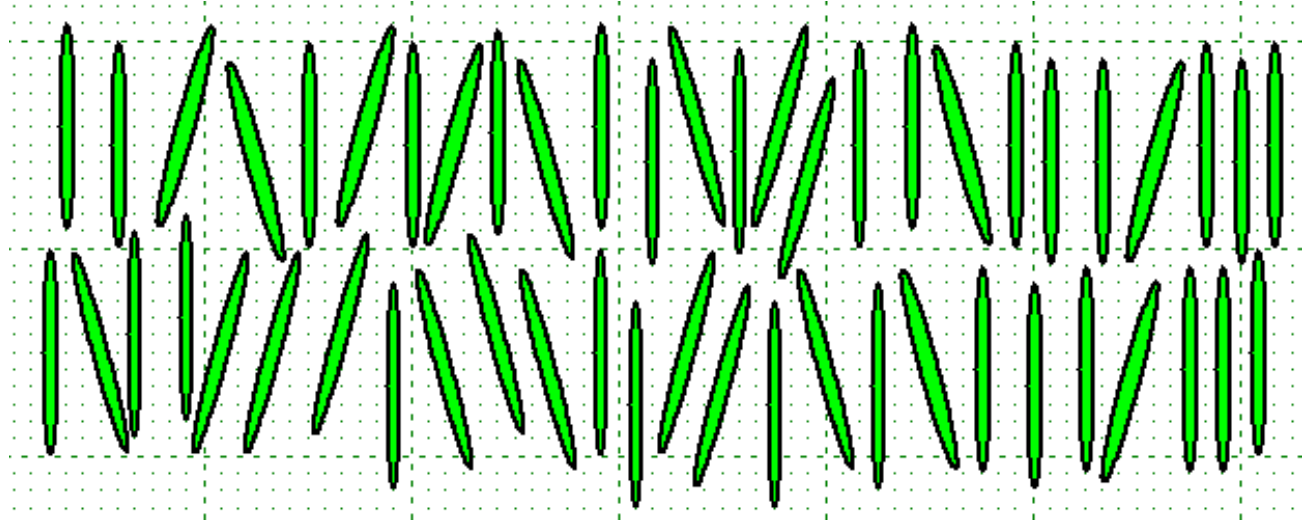


**Langmuir:  
Local  
surface  
energy of  
each  
molecule**

**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**

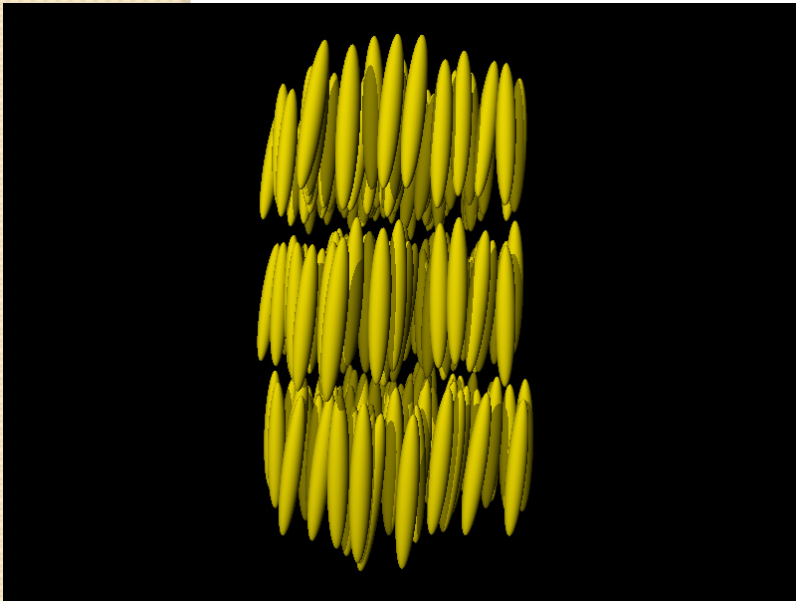


**Schematic of the molecular arrangement in  
a two-layer liquid-crystal free-standing film in SmA phase**

**Molecular arrangement at the air/film interface is well defined**



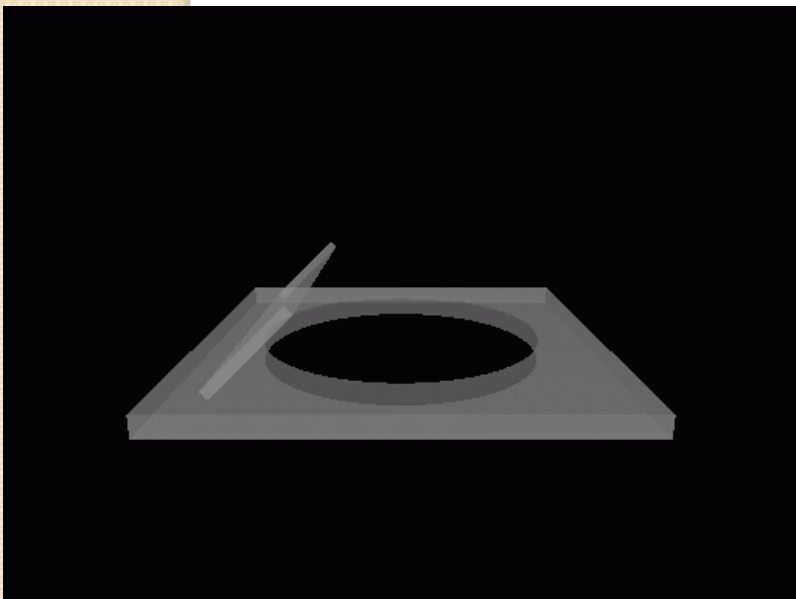
## Free-standing film: experimental geometry



**Smectic liquid crystals: layered structure**

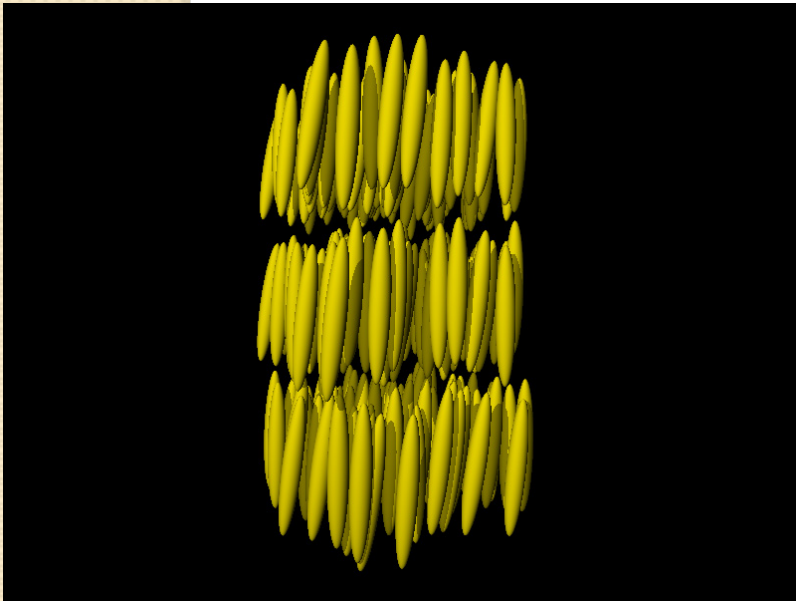
**Free standing films:**

- 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**

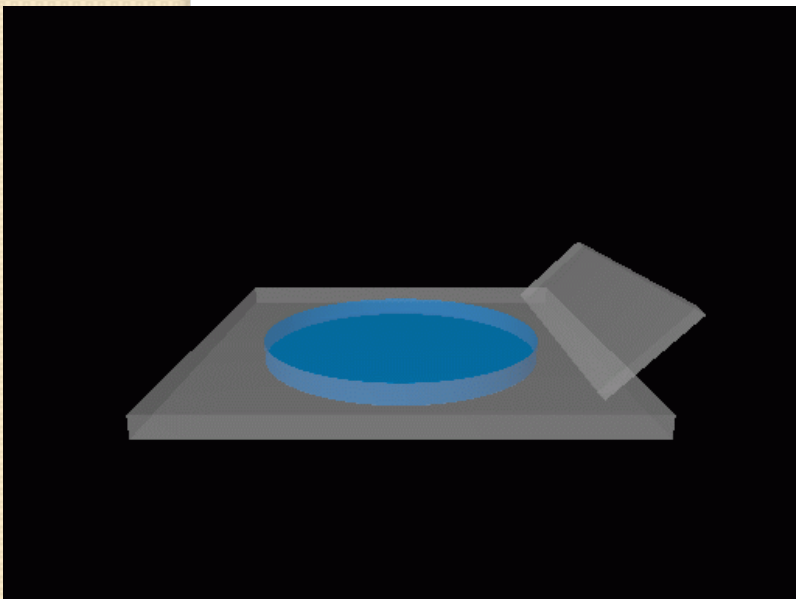
## Free-standing film: experimental geometry



**Smectic liquid crystals: layered structure**

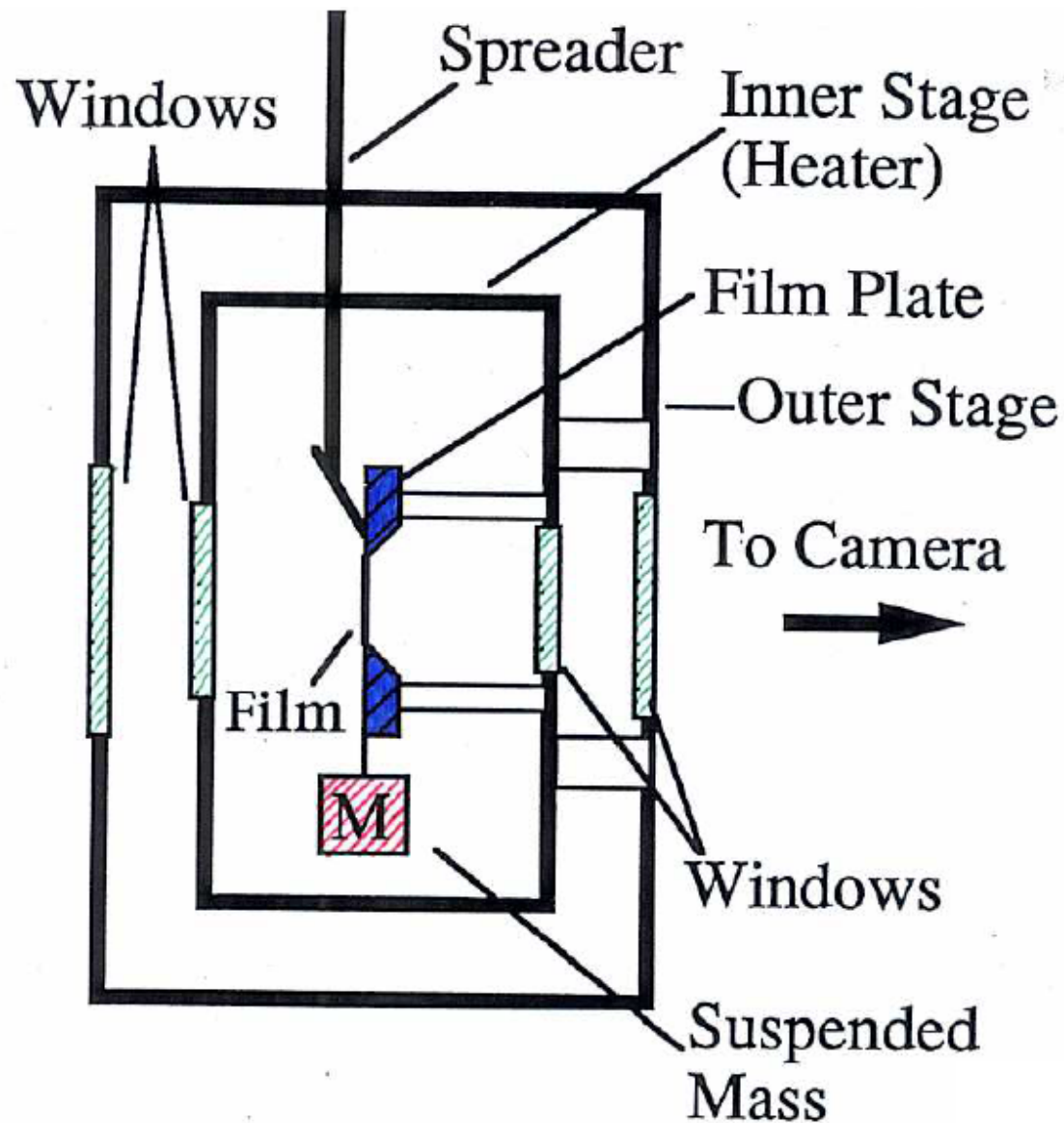
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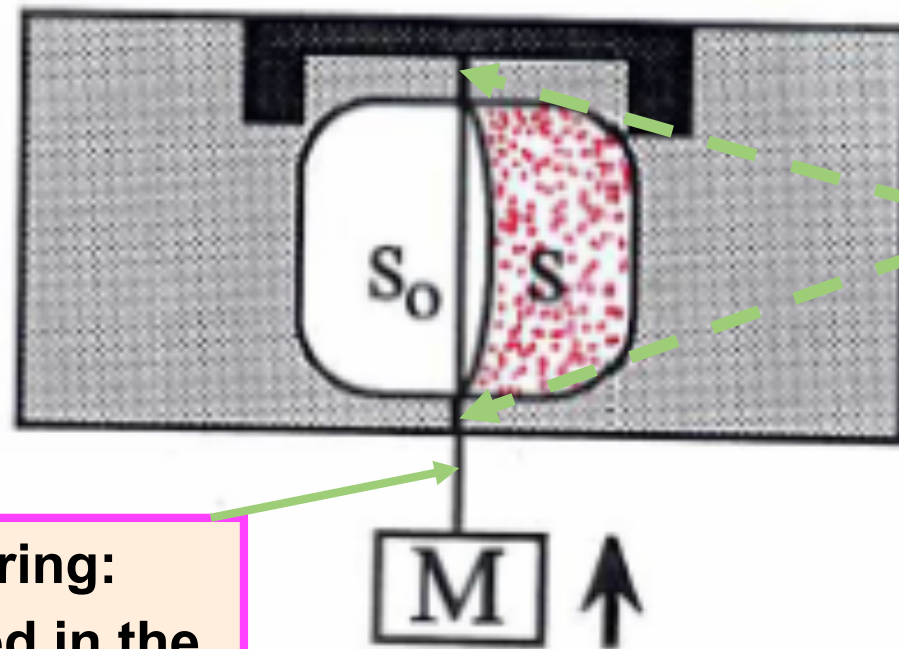


**Fig. a) Schematic drawing of SmA phase;  
b) preparation of a free standing film**

## Flexible-string tensiometer, side view



## Flexible-string tensiometer, front view

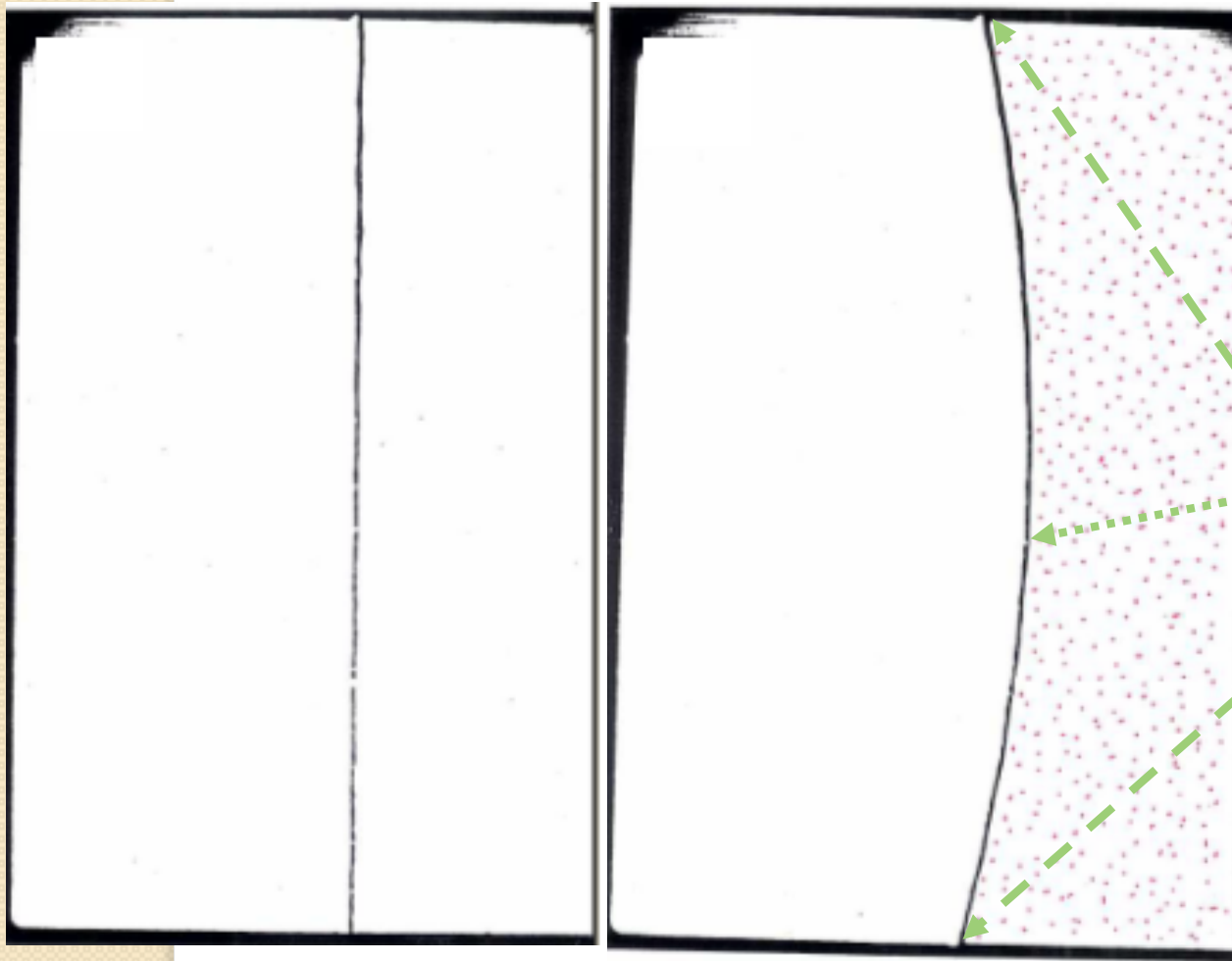


Smooth V-grooves

Flexible string:  
suture used in the  
eye surgery, about  
40  $\mu\text{m}$  in diameter



## Photographic pictures of the flexible string



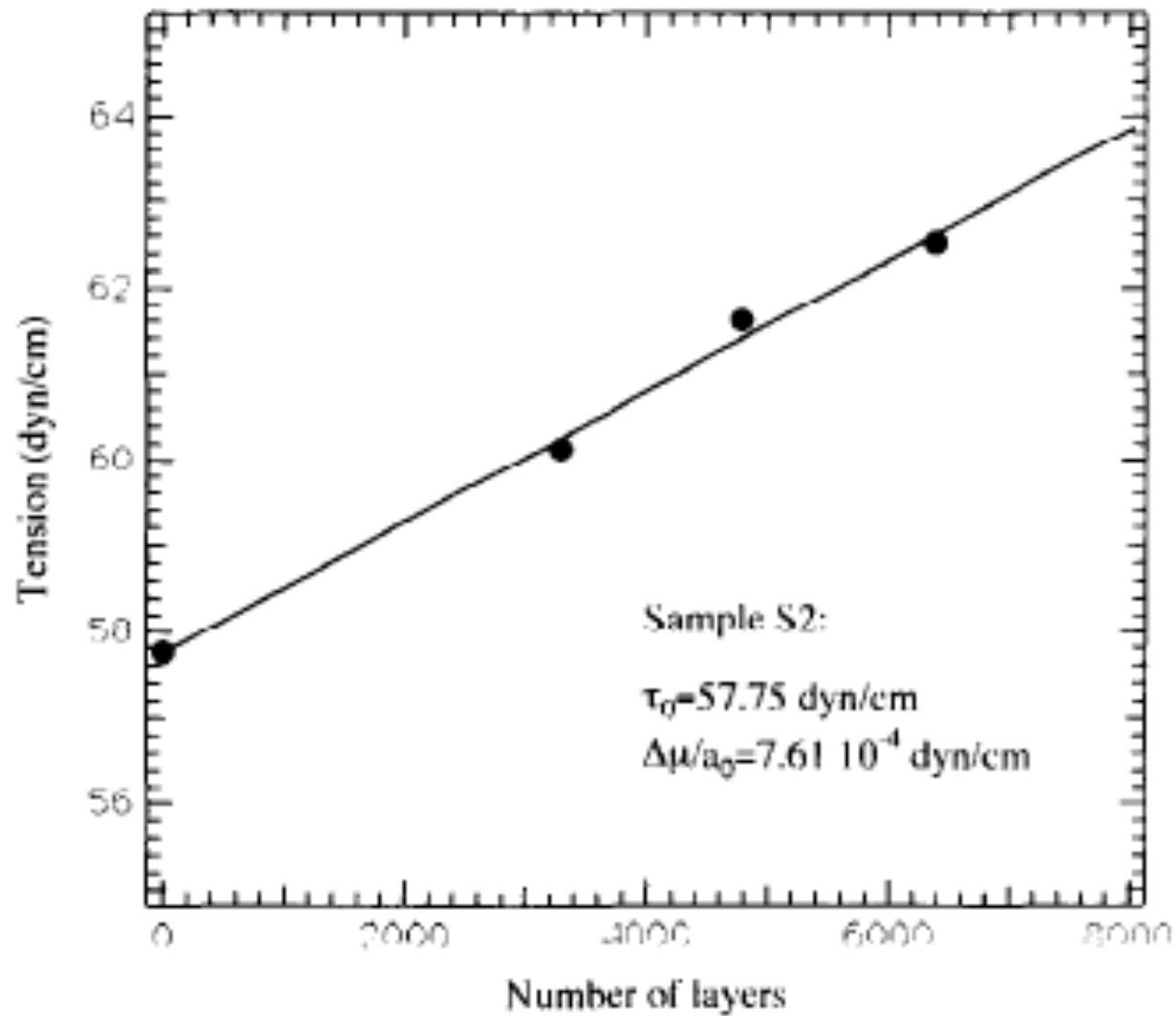
Great care requires  
to minimize the  
size of the meniscus,  
i.e., additional  
material on  
the string  
or the edges

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

Without a film

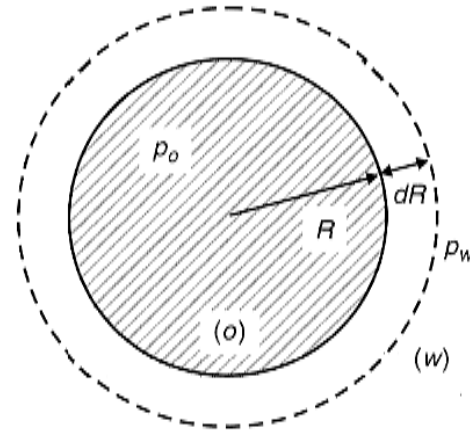
With a film on the right hand side

## Film tension as a function of film thickness



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

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

$$\delta W = -p_o dV_o - p_w dV_w + \gamma_{ow} dA \quad (1.4)$$

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  $\gamma_{ow}$  is the interfacial tension between oil and water.

The condition for mechanical equilibrium is  $\delta W = 0$ , which amounts to

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

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

The smaller the drop, therefore, the greater its internal pressure. This means

# Laplace pressure

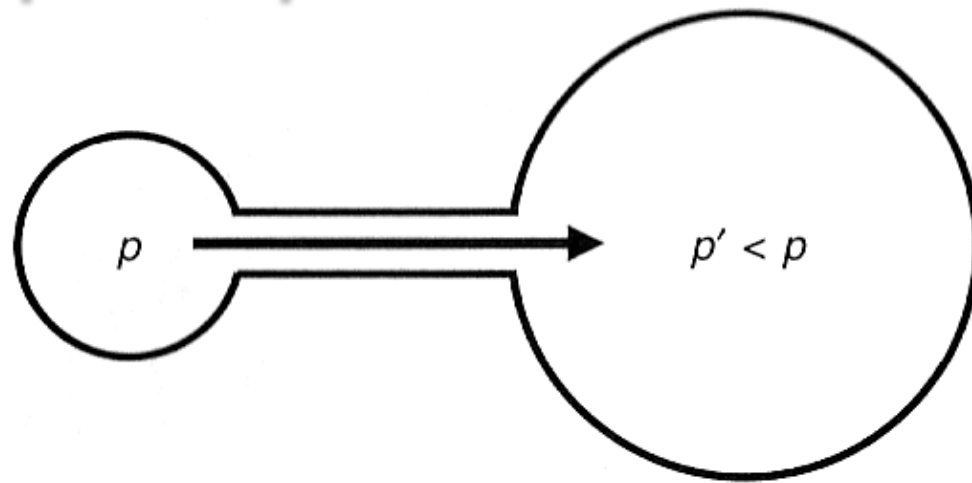


FIGURE 1.6. Small bubbles empty themselves into larger ones.

*Generalization to Any Surface*

*Laplace's theorem:*

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

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



# 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  $\theta_E$  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

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

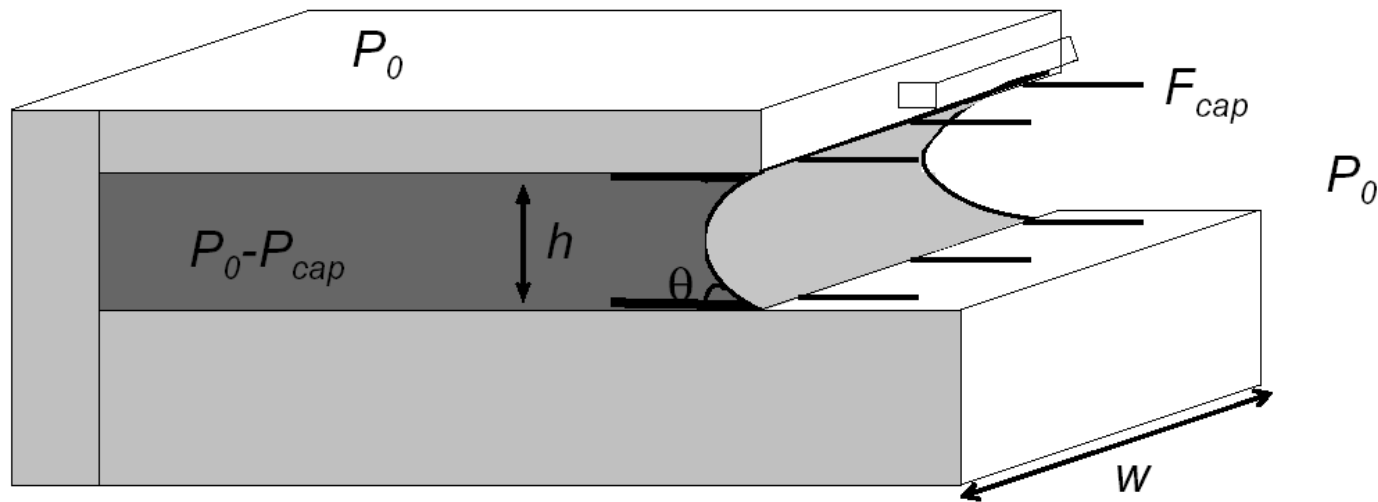
The force that glues the two plates together is attractive as long as  $\theta_E < \pi/2$ . If  $H \ll R$ , it is equal to

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

For water, using  $R = 1$  cm,  $H = 5$   $\mu\text{m}$ , 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



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

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

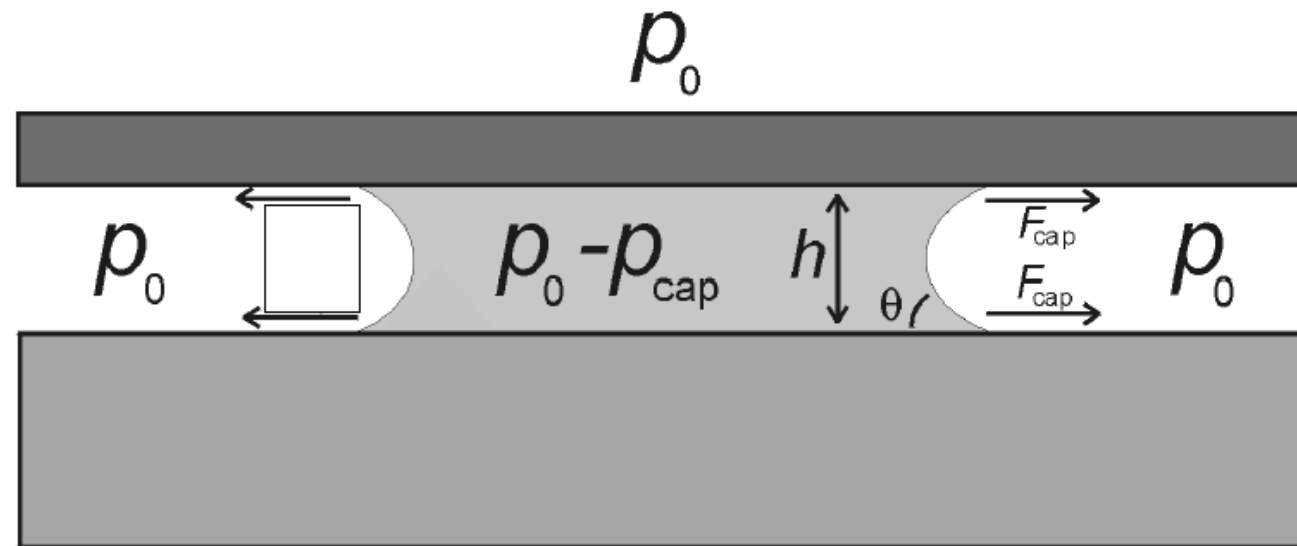
Pressure increases with  $1/h$  !!

$\gamma$  : surface tension ( $\text{Nm}^{-1}$ )

$\theta$  : contact angle

Force/length or  
Energy/area

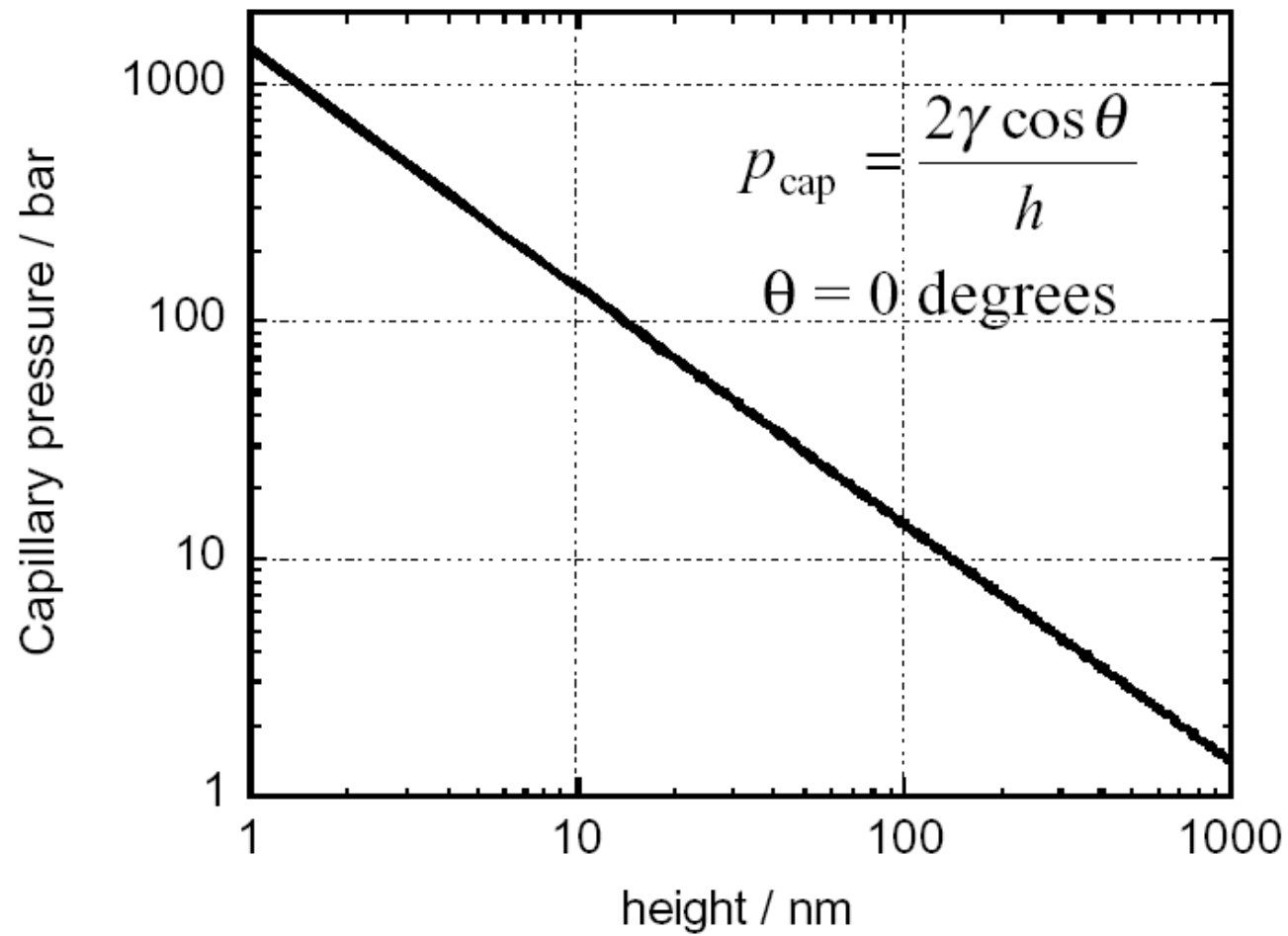
# Capillarity induced negative pressure



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

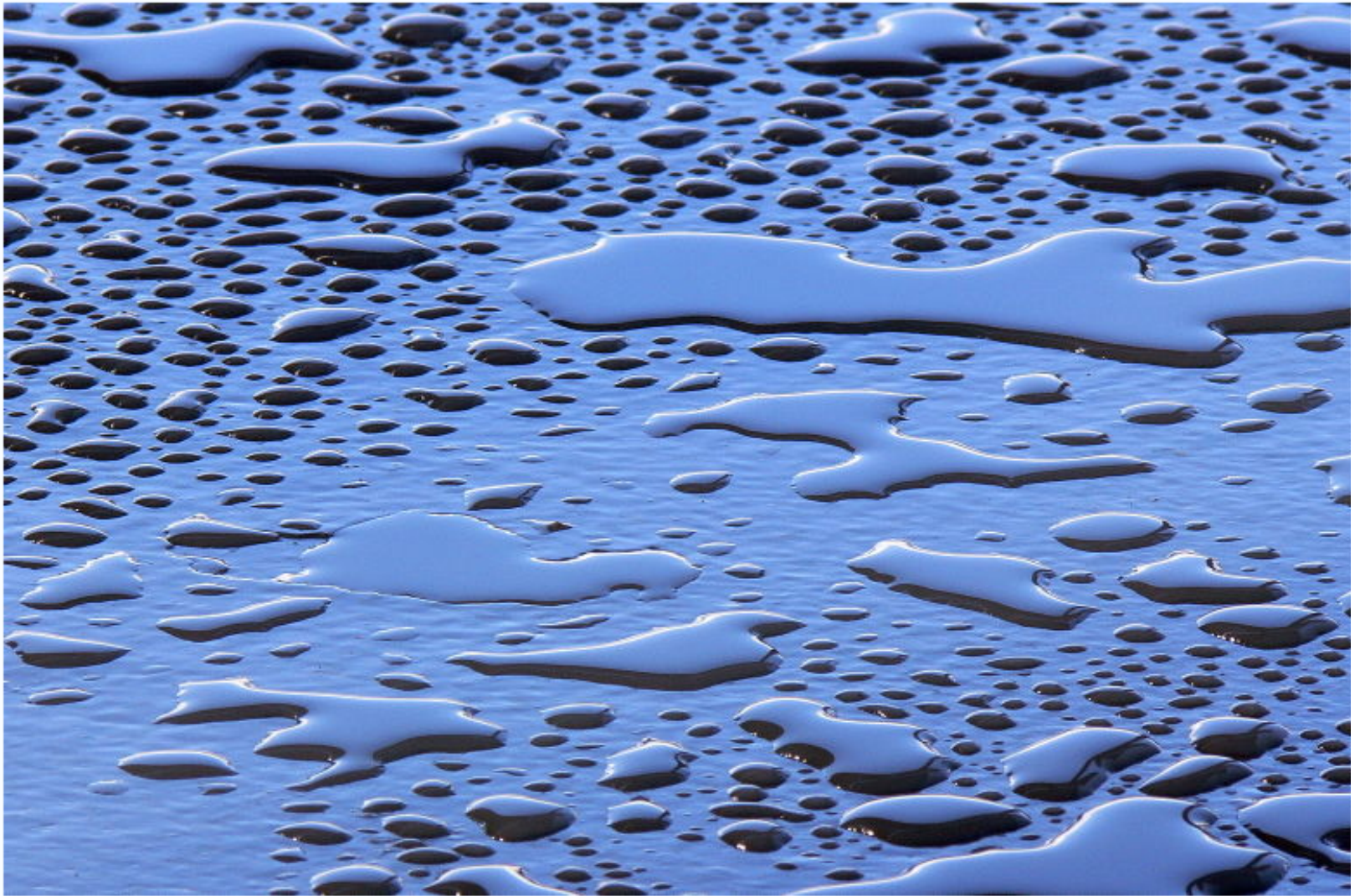
$$h = 108 \text{ nm}, \gamma = 0.07 \text{ Nm}^{-1} \theta = 18^\circ$$
$$\rightarrow p_0 - p_{\text{cap}} = -12 \text{ bar}$$

# Scaling



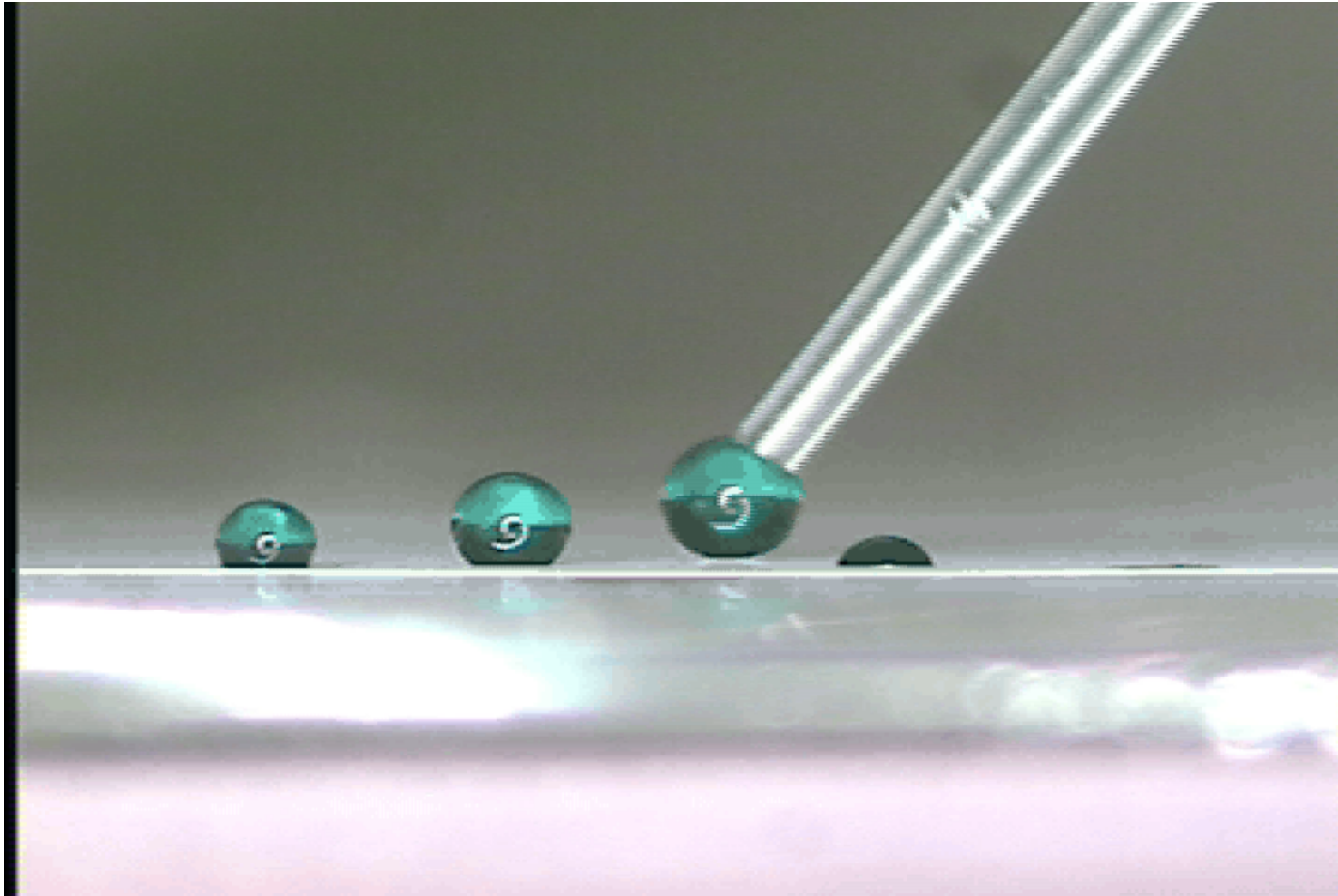


## To wet or not to wet?



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

**To wet or not to wet?**



Hydrophobic surface-PDMS

# Wetting

$$S = [E_{\text{substrate}}]_{\text{dry}} - [E_{\text{substrate}}]_{\text{wet}} \quad (1.21)$$

or

$$S = \gamma_{SO} - (\gamma_{SL} + \gamma), \quad (1.22)$$

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

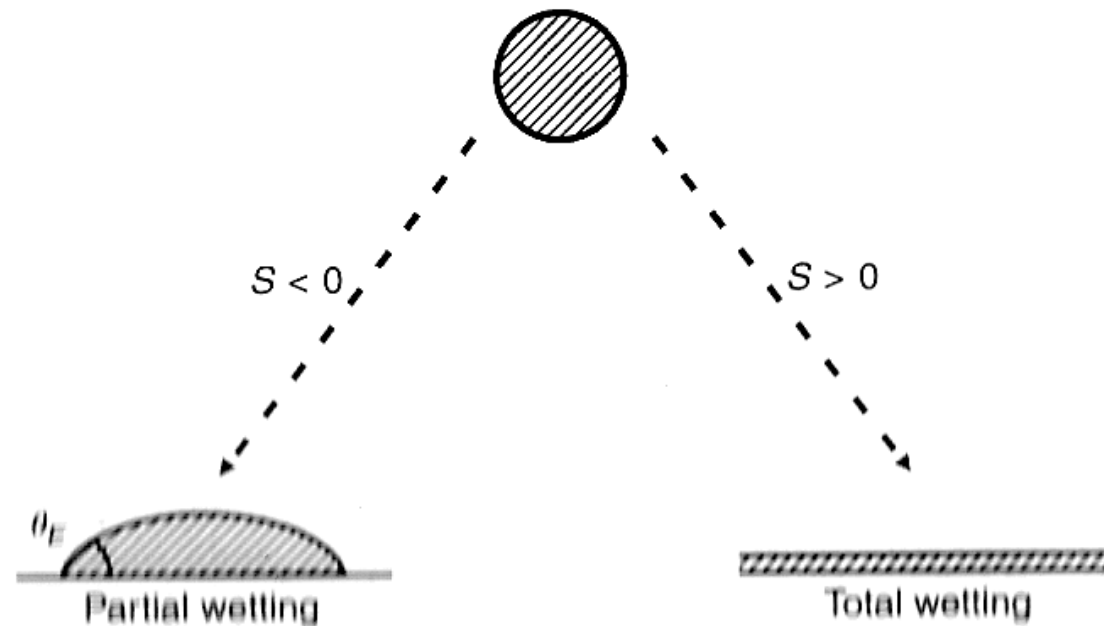


FIGURE 1.13. The two wetting regimes for sessile drops.



$$\gamma \cos \theta_E = \gamma_{SO} - \gamma_{SL}$$

(1.23)

Substituting (1.22) into (1.23) yields:

$$S = \gamma(\cos \theta_E - 1)$$

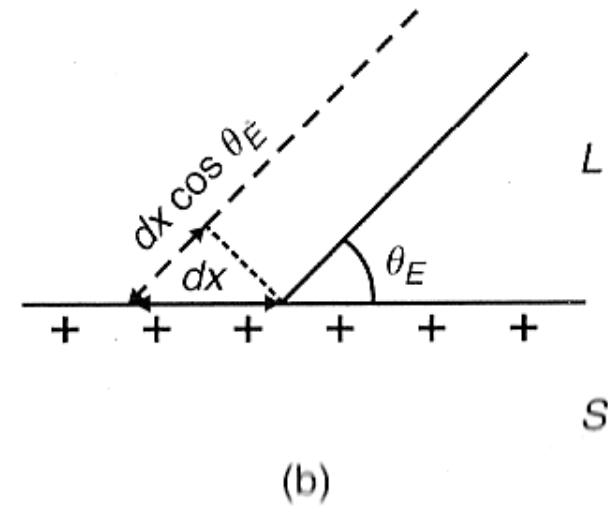
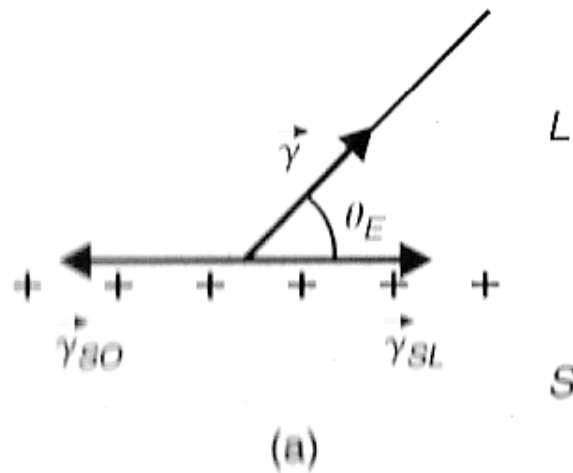


FIGURE 1.14. Determination of  $\theta_E$ : (a) via forces or (b) via works.



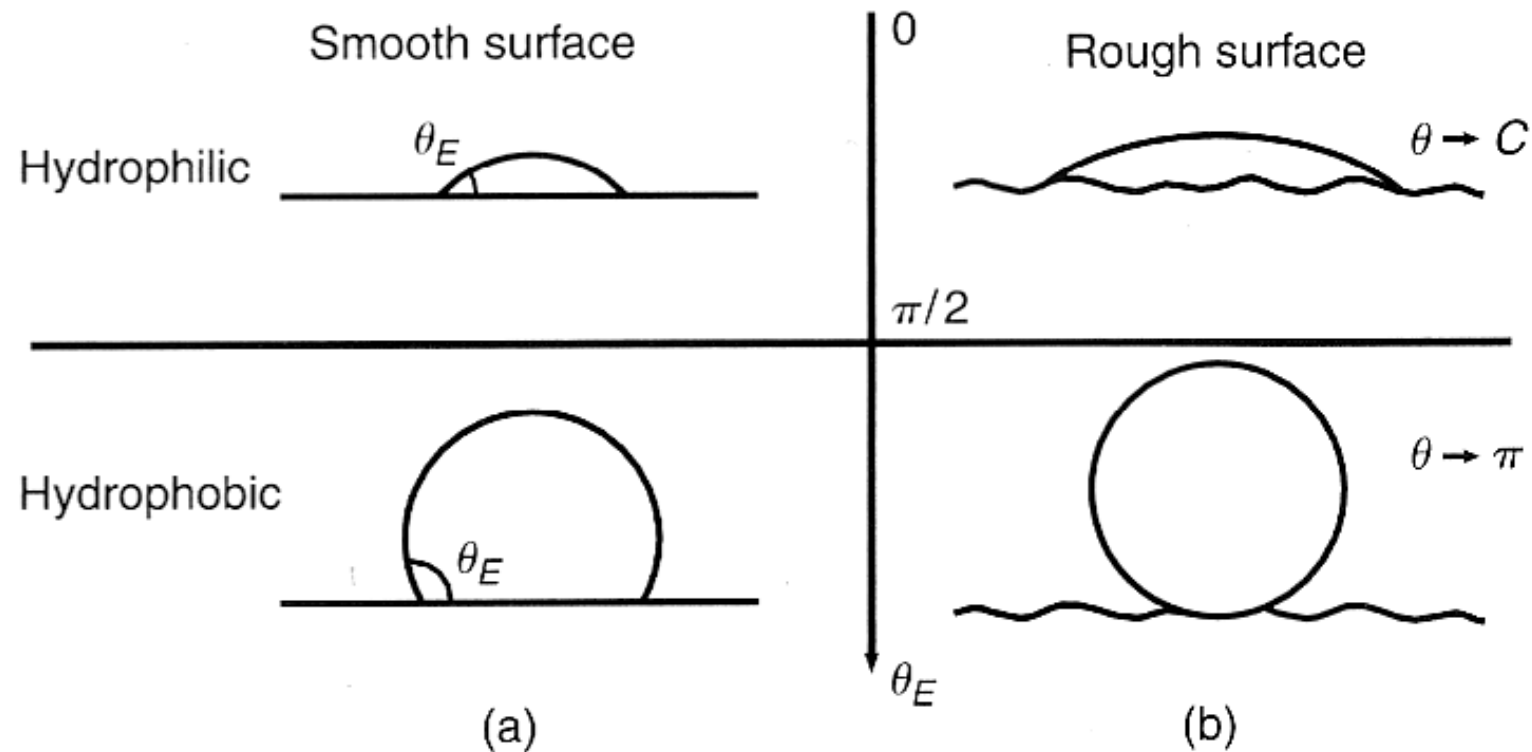
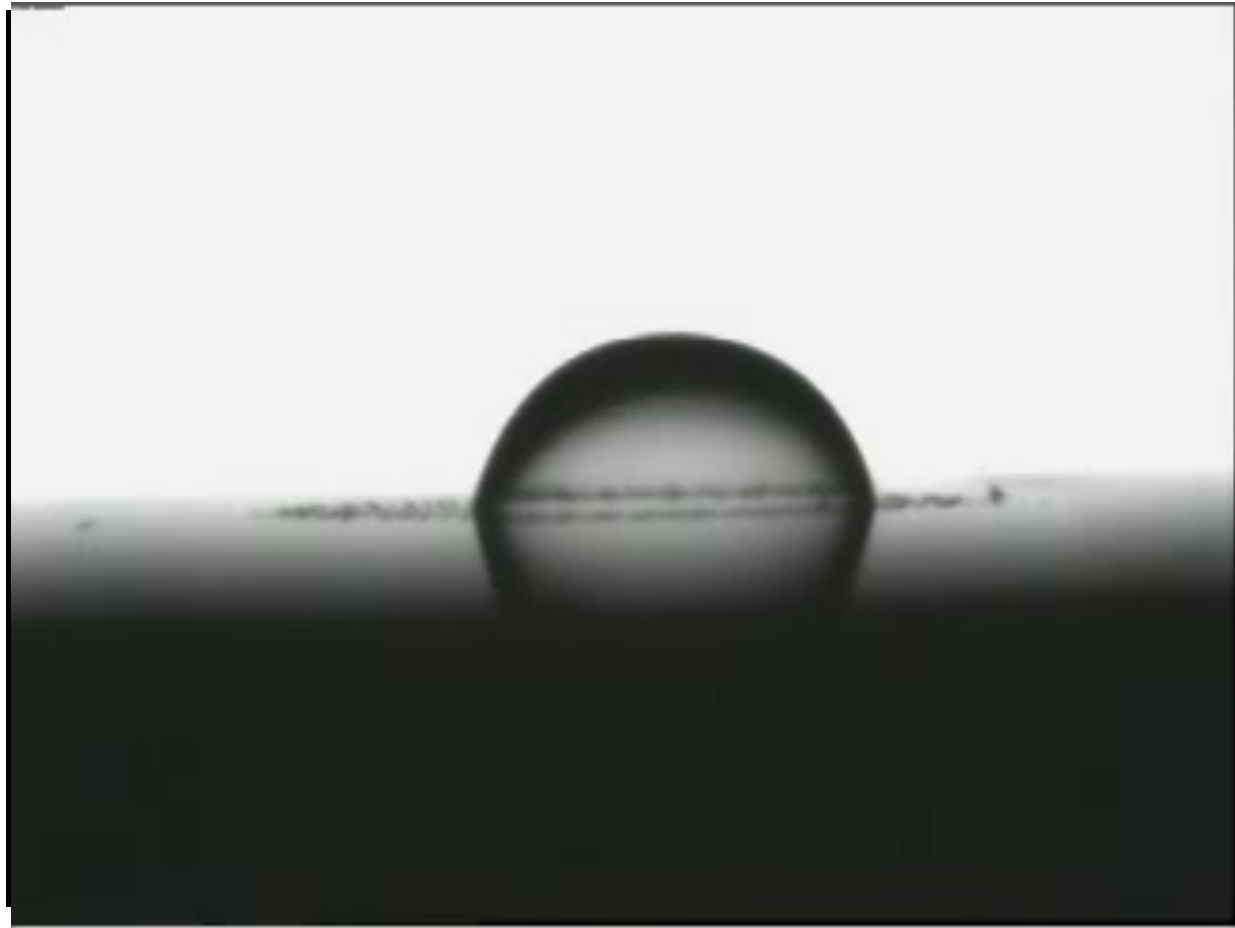


FIGURE 1.17. Controlling the wettability of a substrate through its roughness. Smooth surface (a); rough surface (b). Hydrophilic substrate becoming even more hydrophilic with a rough surface (top); hydrophobic substrate becoming “super-hydrophobic” (bottom).



# Electrowetting





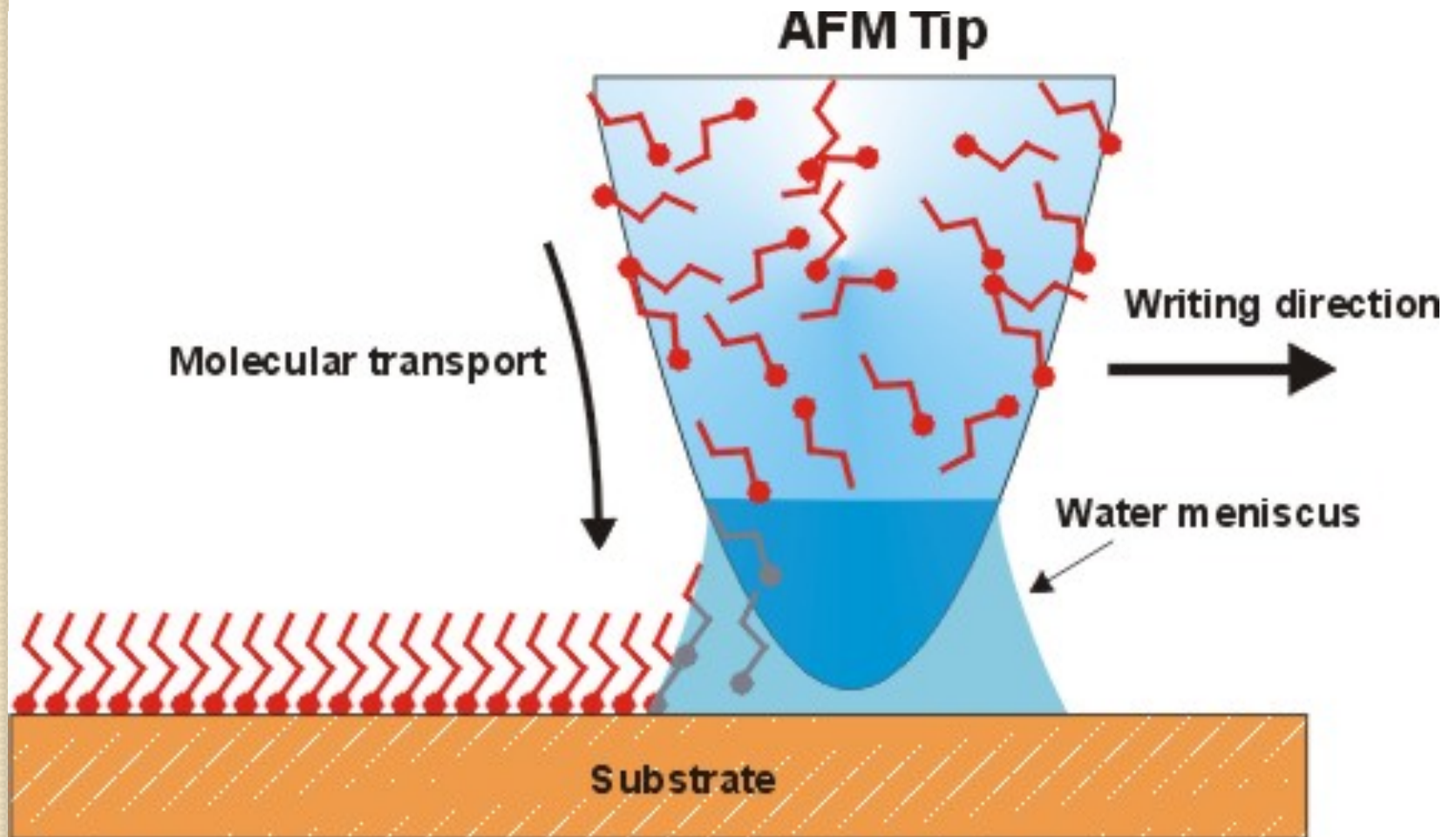
# Polymer Drop Breakup in Microfluidic Devices

## Filament Thinning & Breakup in Microchannels

P.E. Arratia, J.P. Gollub, & D.J. Durian

University of Pennsylvania  
Dept. Physics & Astronomy

# 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>

**C** **60 nm**

A diagram of a dip-pen nanolithography (DPN) tip, showing a central vertical line with two horizontal lines on either side, representing the tip's structure.

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.

A diagram of a conventional lithography tip, showing a central vertical line with two horizontal lines on either side, representing the tip's structure.

**400 nm** Richard P. Feynman, 1960

**Mirkin group at NWU**