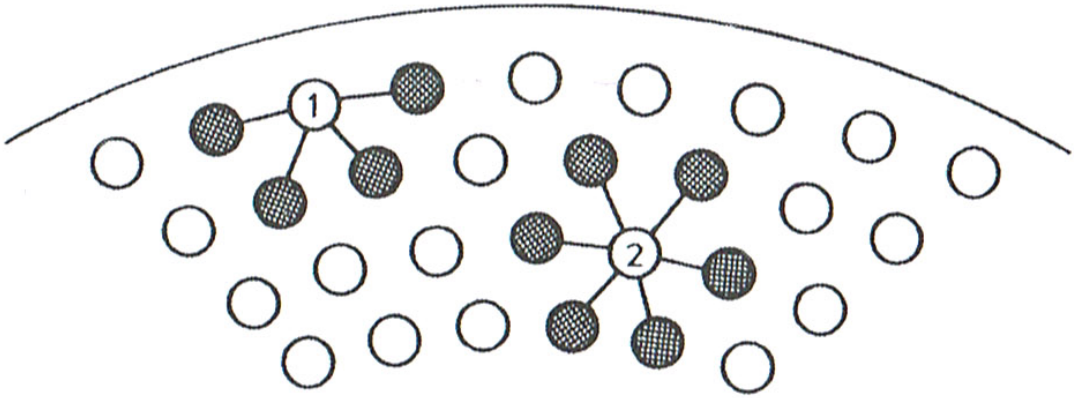
Physics of Life

PHYS-468

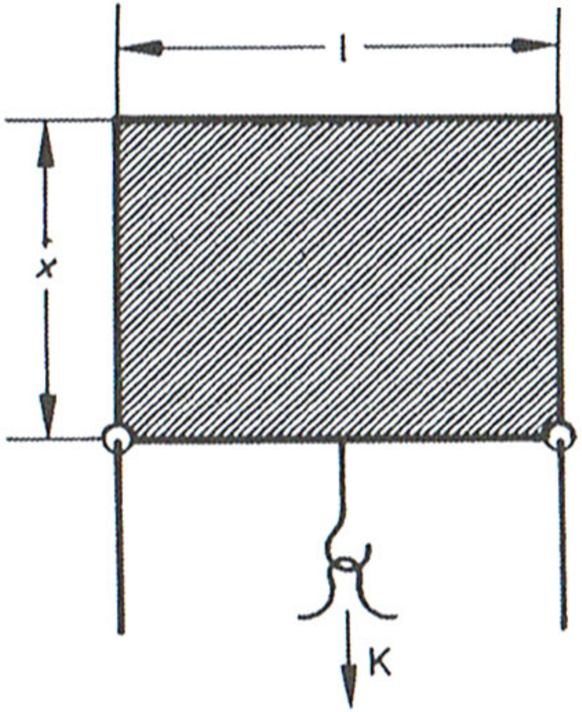
Surface Effects

Henning Stahlberg,
LBEM, IPHYS, SB, EPFL

Surface Tension



Surface tension will attempt to minimize the surface of the volume, to maximize the number of interactions between molecules.



A soap/water membrane in a wire construct will try to shrink its surface ***A=2*x*l*** (the factor "**2**" is because there is a front and a back surface), thereby exerting a **pulling force** ***K*** onto the lower wire. The length of the wire is "*l".*

The exerted *work* is:

$$dW = Kdx = \frac{K}{2l} 2l dx = \frac{K}{2l} dA = \gamma dA$$

Here, the **surface tension** γ is defined as:

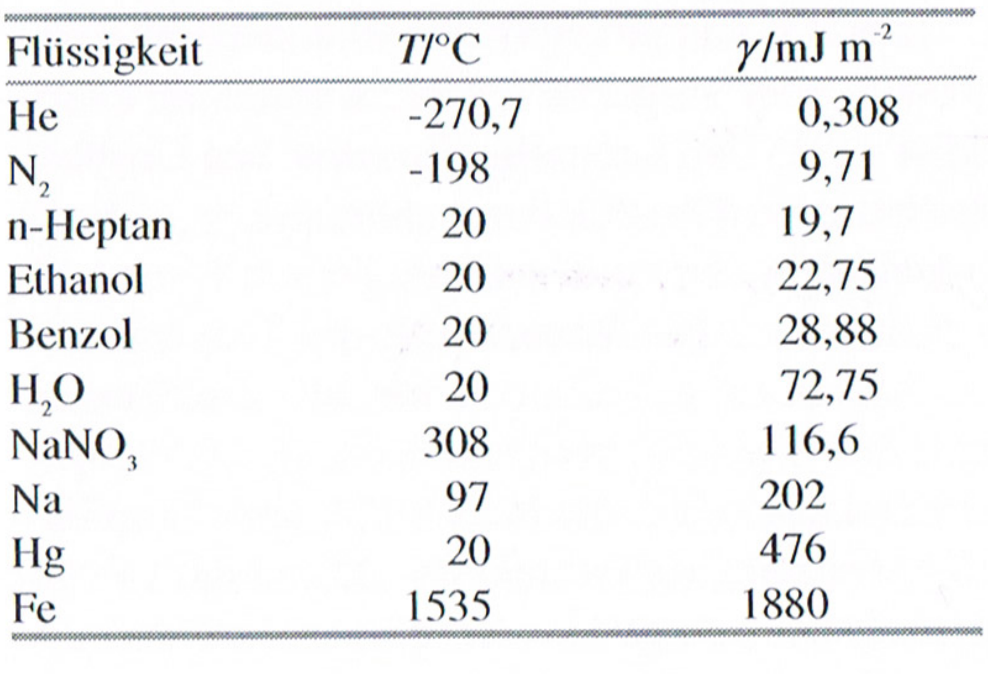
$$\gamma = \frac{K}{2l}$$

Or:

$$\gamma = \frac{dW}{dA}$$

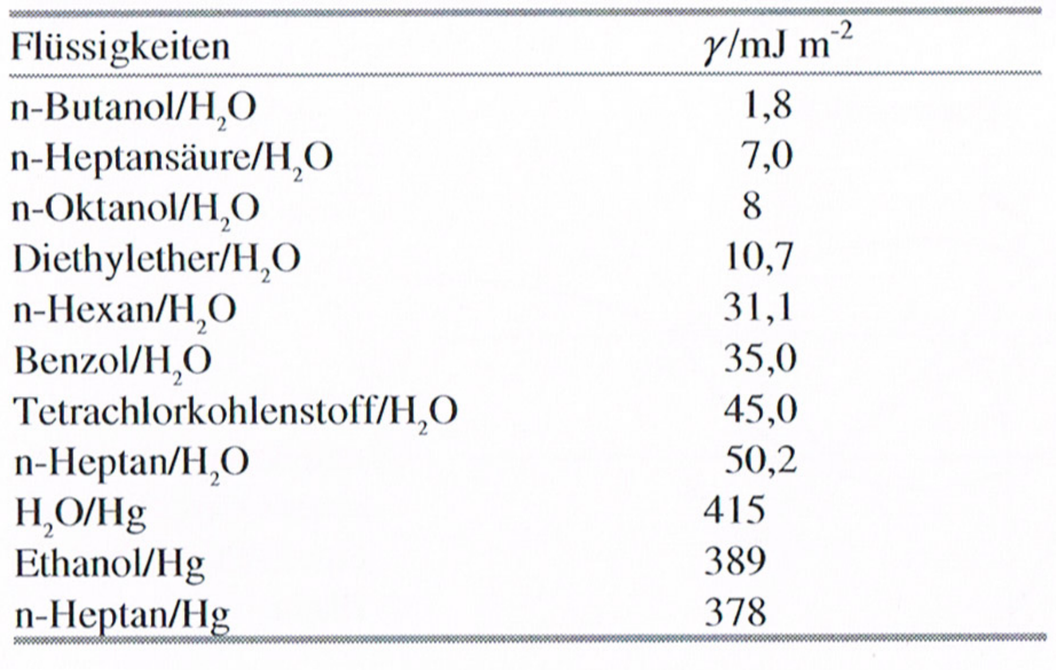
Surface Tension

Surface tension of liquids vs. air



Flüssigkeit	T/°C	γ/mJ m^{-2}
He	-270,7	0,308
N_2	-198	9,71
n-Heptan	20	19,7
Ethanol	20	22,75
Benzol	20	28,88
H_2O	20	72,75
$NaNO_3$	308	116,6
Na	97	202
Hg	20	476
Fe	1535	1880

Surface tension of liquids vs. liquids (at 20ºC)



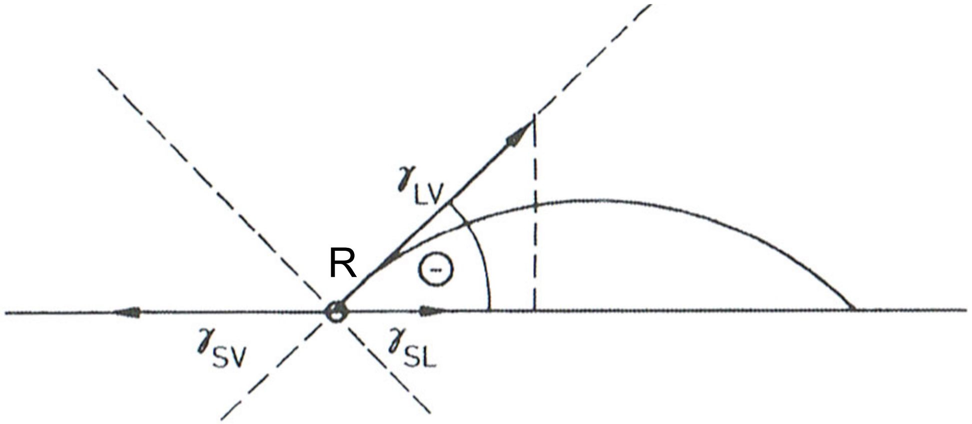
Flüssigkeiten	γ/mJ m^{-2}
n-Butanol/H_2O	1,8
n-Heptansäure/H_2O	7,0
n-Oktanol/H_2O	8
Diethylether/H_2O	10,7
n-Hexan/H_2O	31,1
Benzol/H_2O	35,0
Tetrachlorkohlenstoff/H_2O	45,0
n-Heptan/H_2O	50,2
H_2O/Hg	415
Ethanol/Hg	389
n-Heptan/Hg	378

The units of **surface tension** γ is Joule / m^2

Contact Angle of a Drop on a Surface

Surface tensions γ are vectors that pull on the contact edge R

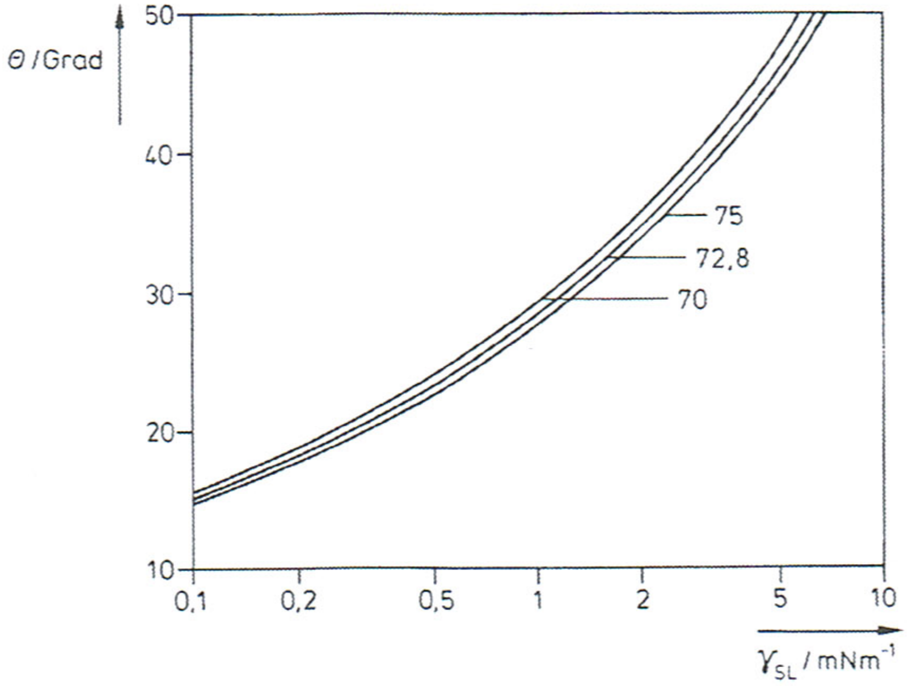
Shape and contact angle of a liquid drop on a solid surface.



$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cdot \cos\Theta$$

(Young-Gauss equation)

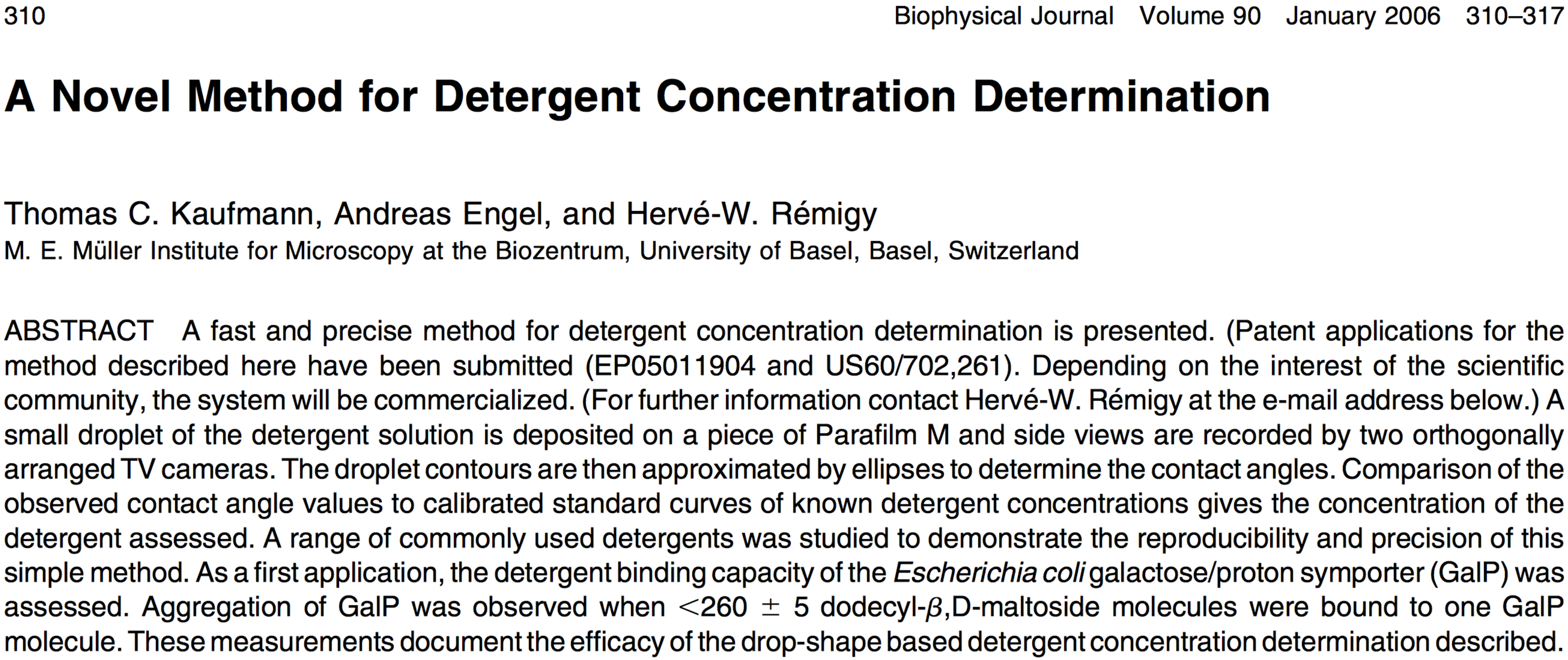
γ_{SV} = surface tension solid vs. volatile
γ_{SL} = surface tension solid vs. liquid
γ_{LV} = surface tension liquid vs. volatile



Graph to translate measured angle Theta into surface tension.
Curves are for water at
37ºC (γ_{SV} = 75.0 mJ/m2),
20ºC (γ_{SV} = 72.8 mJ/m2), and
4ºC (γ_{SV} = 70.0 mJ/m2).

Surface tensions are measured in N/m or in J/m2.

Contact Angle of a Drop on a Surface



310 Biophysical Journal Volume 90 January 2006 310–317

A Novel Method for Detergent Concentration Determination

Thomas C. Kaufmann, Andreas Engel, and Hervé-W. Rémigy
M. E. Müller Institute for Microscopy at the Biozentrum, University of Basel, Basel, Switzerland

ABSTRACT A fast and precise method for detergent concentration determination is presented. (Patent applications for the method described here have been submitted (EP05011904 and US60/702,261). Depending on the interest of the scientific community, the system will be commercialized. (For further information contact Hervé-W. Rémigy at the e-mail address below.) A small droplet of the detergent solution is deposited on a piece of Parafilm M and side views are recorded by two orthogonally arranged TV cameras. The droplet contours are then approximated by ellipses to determine the contact angles. Comparison of the observed contact angle values to calibrated standard curves of known detergent concentrations gives the concentration of the detergent assessed. A range of commonly used detergents was studied to demonstrate the reproducibility and precision of this simple method. As a first application, the detergent binding capacity of the *Escherichia coli* galactose/proton symporter (GalP) was assessed. Aggregation of GalP was observed when $<260 \pm 5$ dodecyl-β,D-maltoside molecules were bound to one GalP molecule. These measurements document the efficacy of the drop-shape based detergent concentration determination described.

Contact Angle of a Drop on a Surface

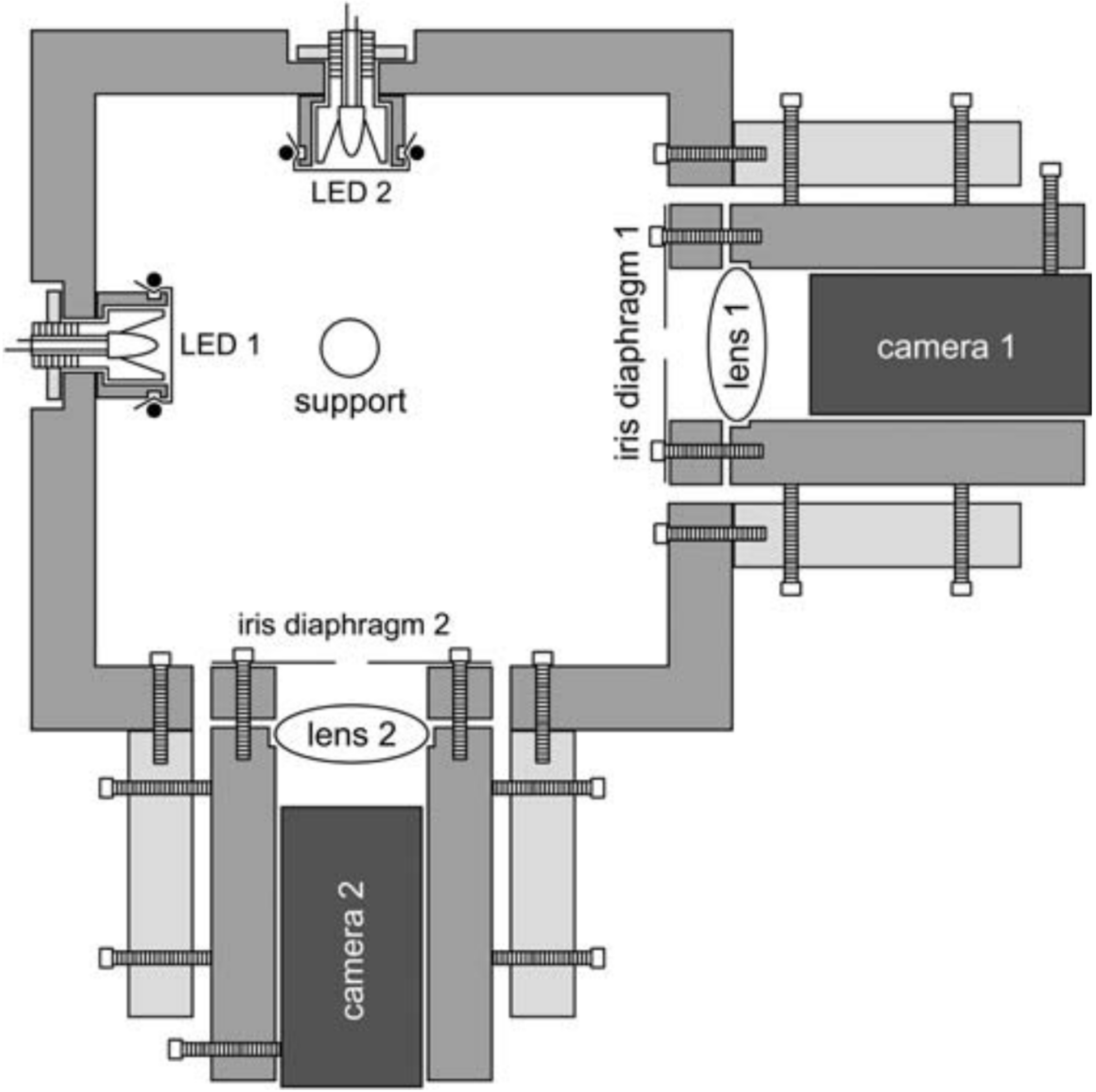
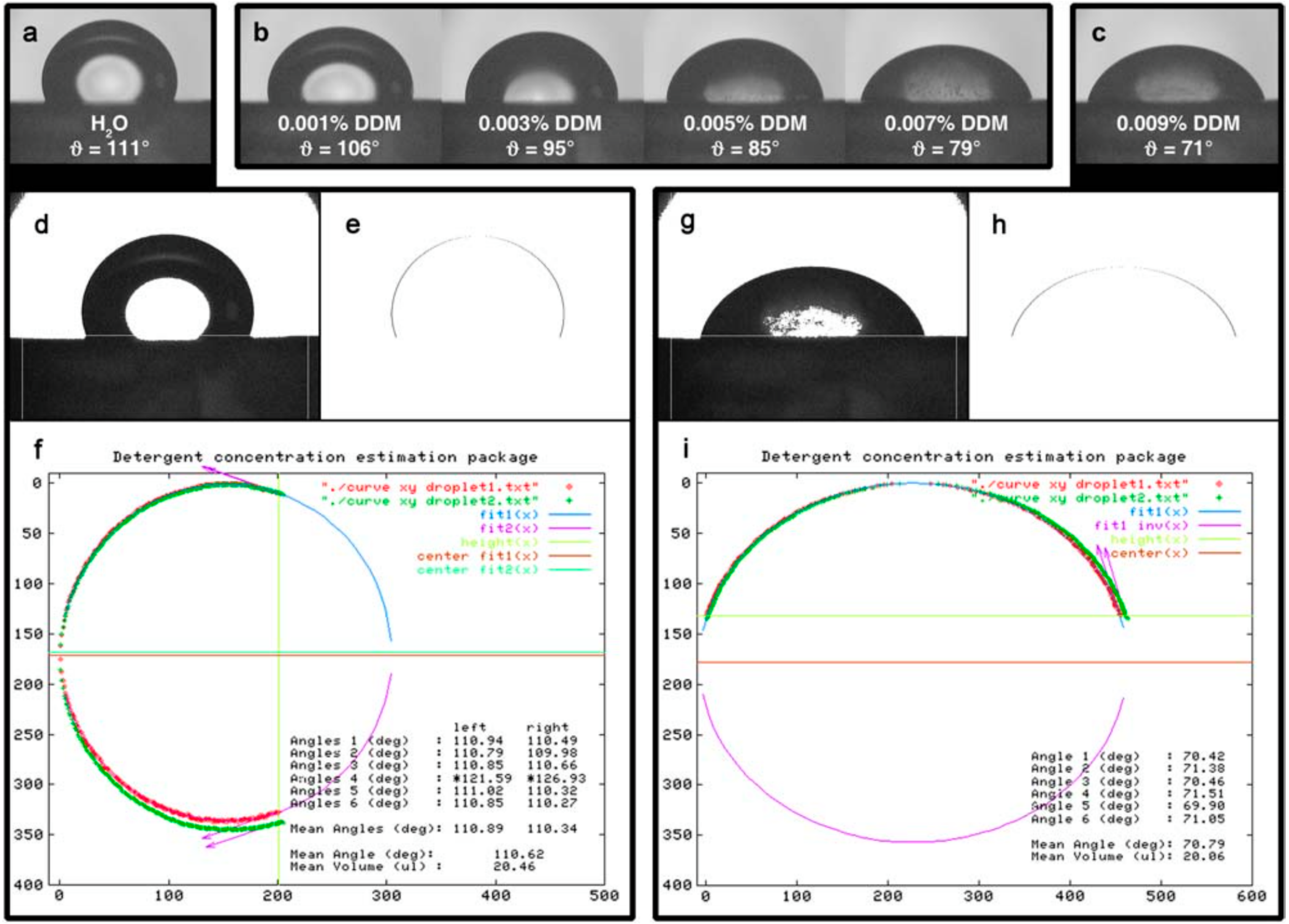


FIGURE 1 Schematic drawing showing the setup of the contact angle measuring device.

Contact Angle of a Drop on a Surface



```
                           left     right
Angles 1 (deg)      :  110.94   110.49
Angles 2 (deg)      :  110.79   109.98
Angles 3 (deg)      :  110.85   110.66
Angles 4 (deg)      : *121.59  *126.93
Angles 5 (deg)      :  111.02   110.32
Angles 6 (deg)      :  110.85   110.27

Mean Angles (deg):  110.89   110.34

Mean Angle (deg):         110.62
Mean Volume (ul) :        20.46
```

```
Angle 1 (deg)     : 70.42
Angle 2 (deg)     : 71.38
Angle 3 (deg)     : 70.46
Angle 4 (deg)     : 71.51
Angle 5 (deg)     : 69.90
Angle 6 (deg)     : 71.05

Mean Angle (deg): 70.79
Mean Volume (ul): 20.06
```

FIGURE 2 Image analysis procedure. (*a–c*) Raw images of the droplet series for DDM. (*d* and *g*) Pictures *a* and *c* respectively, with applied threshold. (*e* and *h*) Extracted droplet contours. (*f* and *i*) Output file from GNUPLOT displaying contact angles and mean volume. Note: In *f*, the contour has been rotated by 90° with respect to *e*.

Contact Angle of a Drop on a Surface

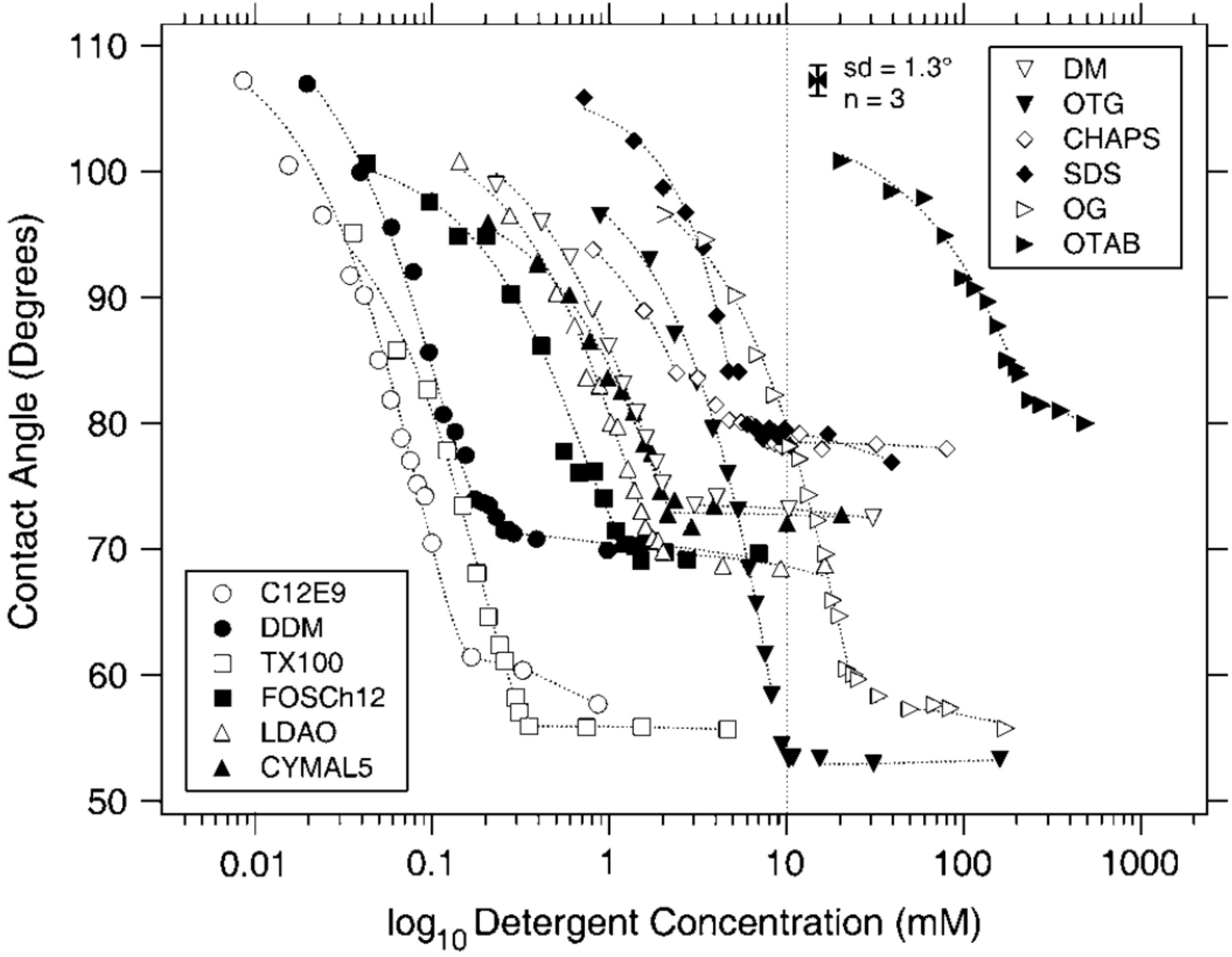


FIGURE 4 Semilogarithmic plot of the detergent concentration versus experimental contact angles for all calibrated detergents.

Contact Angle of a Drop on a Surface

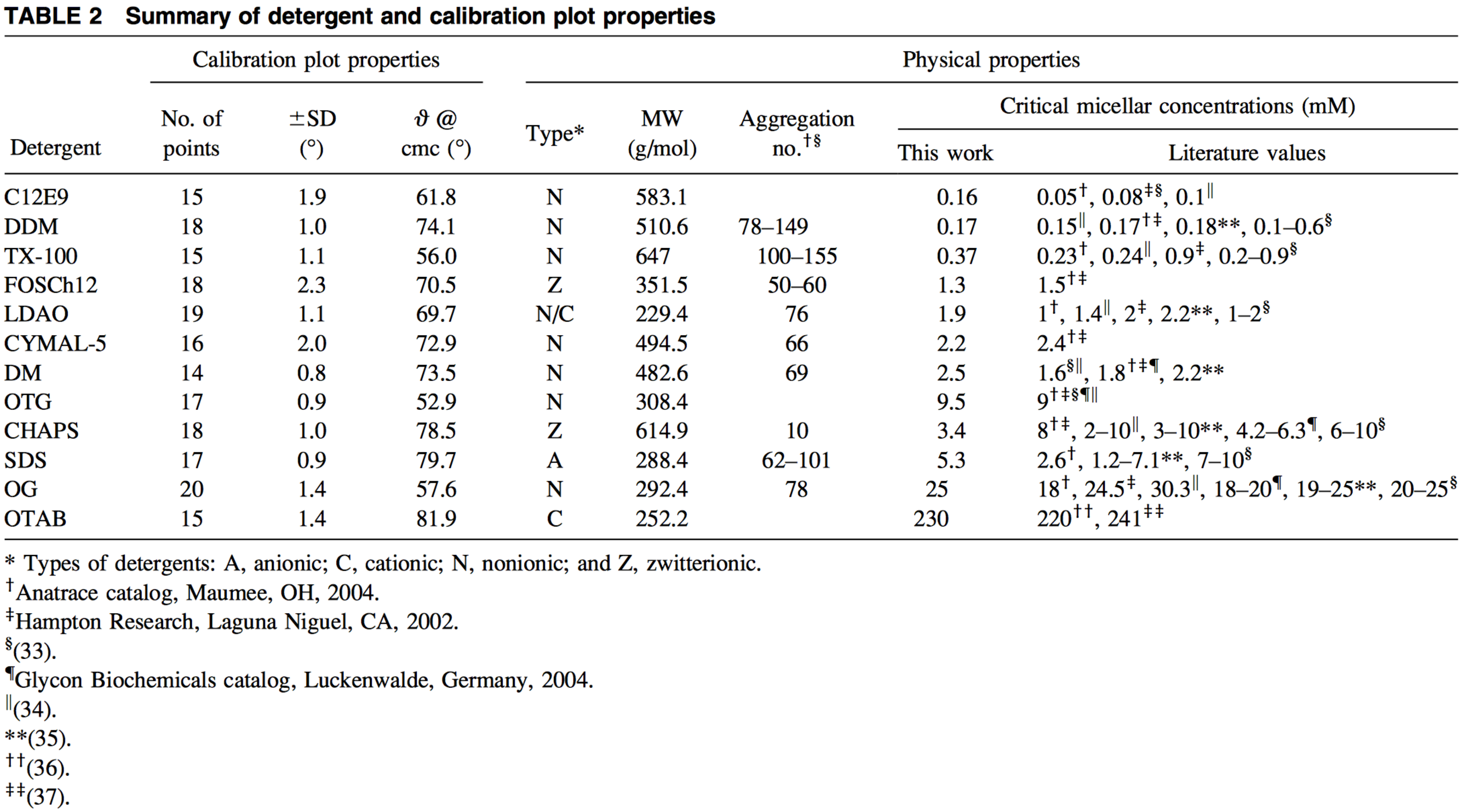


TABLE 2 Summary of detergent and calibration plot properties

	Calibration plot properties			Physical properties				
							Critical micellar concentrations (mM)	
Detergent	No. of points	±SD (°)	ϑ @ cmc (°)	Type*	MW (g/mol)	Aggregation no.[†§]	This work	Literature values
C12E9	15	1.9	61.8	N	583.1		0.16	0.05[†], 0.08[‡§], 0.1[‖]
DDM	18	1.0	74.1	N	510.6	78–149	0.17	0.15[‖], 0.17[††], 0.18[**], 0.1–0.6[§]
TX-100	15	1.1	56.0	N	647	100–155	0.37	0.23[†], 0.24[‖], 0.9[‡], 0.2–0.9[§]
FOSCh12	18	2.3	70.5	Z	351.5	50–60	1.3	1.5[††]
LDAO	19	1.1	69.7	N/C	229.4	76	1.9	1[†], 1.4[‖], 2[‡], 2.2[**], 1–2[§]
CYMAL-5	16	2.0	72.9	N	494.5	66	2.2	2.4[††]
DM	14	0.8	73.5	N	482.6	69	2.5	1.6[§‖], 1.8[†‡¶], 2.2[**]
OTG	17	0.9	52.9	N	308.4		9.5	9[†‡§¶‖]
CHAPS	18	1.0	78.5	Z	614.9	10	3.4	8[††], 2–10[‖], 3–10[**], 4.2–6.3[¶], 6–10[§]
SDS	17	0.9	79.7	A	288.4	62–101	5.3	2.6[†], 1.2–7.1[**], 7–10[§]
OG	20	1.4	57.6	N	292.4	78	25	18[†], 24.5[‡], 30.3[‖], 18–20[¶], 19–25[**], 20–25[§]
OTAB	15	1.4	81.9	C	252.2		230	220[††], 241[‡‡]

[*] Types of detergents: A, anionic; C, cationic; N, nonionic; and Z, zwitterionic.

[†] Anatrace catalog, Maumee, OH, 2004.

[‡] Hampton Research, Laguna Niguel, CA, 2002.

[§] (33).

[¶] Glycon Biochemicals catalog, Luckenwalde, Germany, 2004.

[‖] (34).

[**] (35).

[††] (36).

[‡‡] (37).

Surface Tension of a Soap Bubble

Surface of bubble (Factor 2 is for inside and outside):

$$A = 2 \cdot 4\pi R^2$$

If radius *R* changes by *dR*, then surface changes by:

$$dA = 16\pi R\, dR$$

$$\gamma = \frac{dW}{dA}$$

Surface work *dW*$_S$ is then:

$$dW_S = \gamma dA = \gamma 16\pi R\, dR$$

Volume work of the Gas *dW*$_G$ is:

$$dW_G = \Delta P\ dV = \Delta P\ d\left(\frac{4}{3}\pi R^3\right)$$

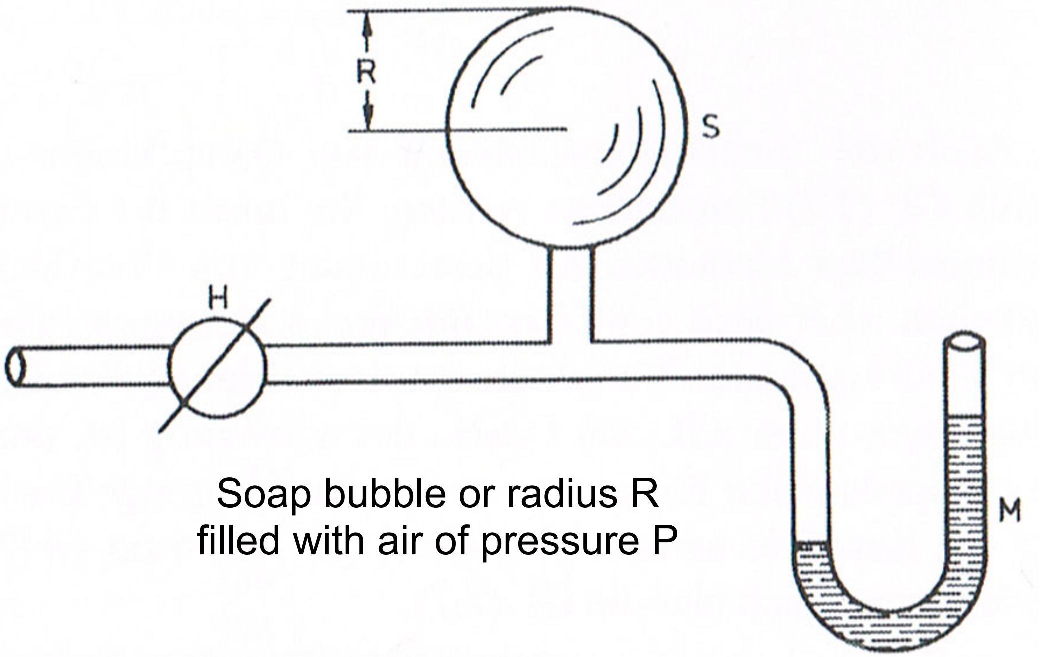
$$= \Delta P\ 4\pi R^2\ dR$$

Setting surface work and gas work equal:

$$dW_S = dW_G$$

Gives:

$$\Delta P = \frac{4\gamma}{R}$$



Soap bubble or radius R filled with air of pressure P

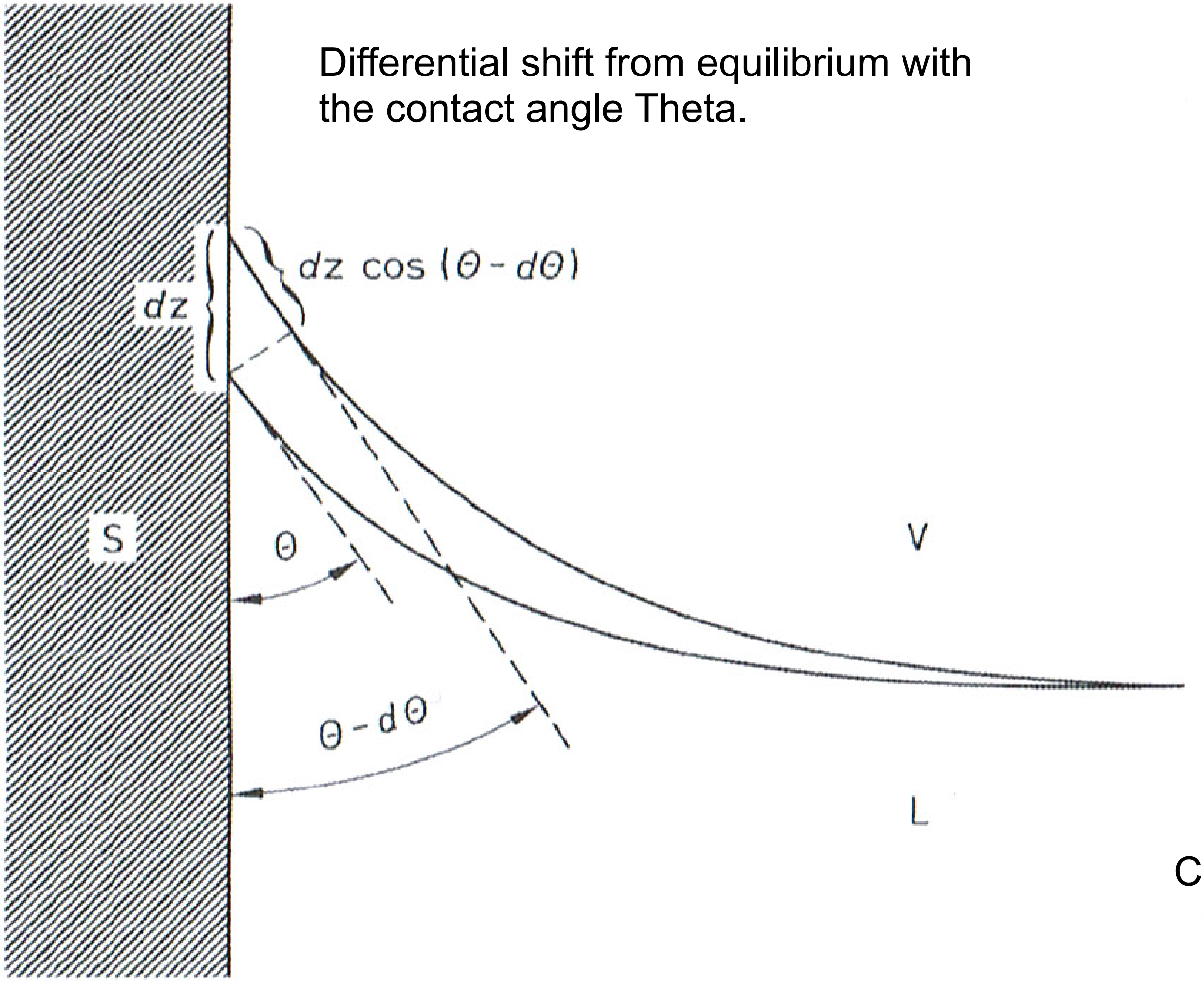
For a filled ball of liquid (only one surface):

$$\Delta P = \frac{2\gamma}{R}$$

(This is why inflating a balloon is most difficult at the beginning…)

Capillary Force

Differential shift from equilibrium with the contact angle Theta.



Three forces pull on liquid edge:

γ_{SV} = surface tension solid vs. volatile

γ_{SL} = surface tension solid vs. liquid

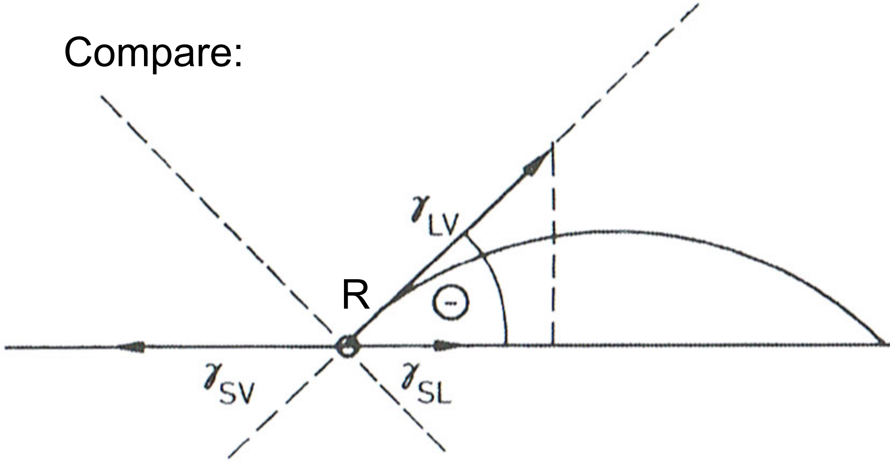
γ_{LV} = surface tension liquid vs. volatile

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cdot \cos\Theta$$

(Young-Gauss equation)

The capillary force results in a capillary rise at a vertical wall.

Compare:



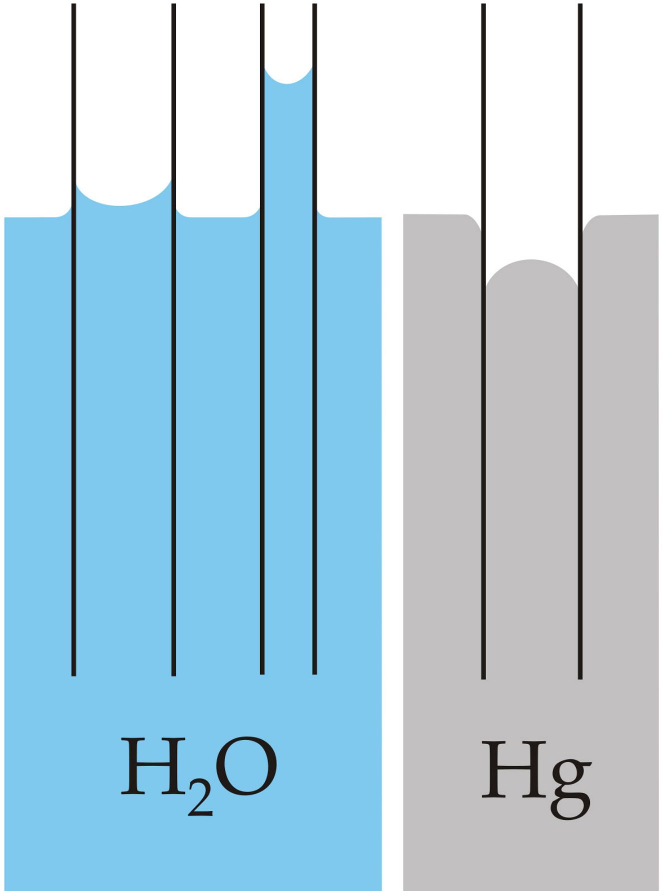
From before:

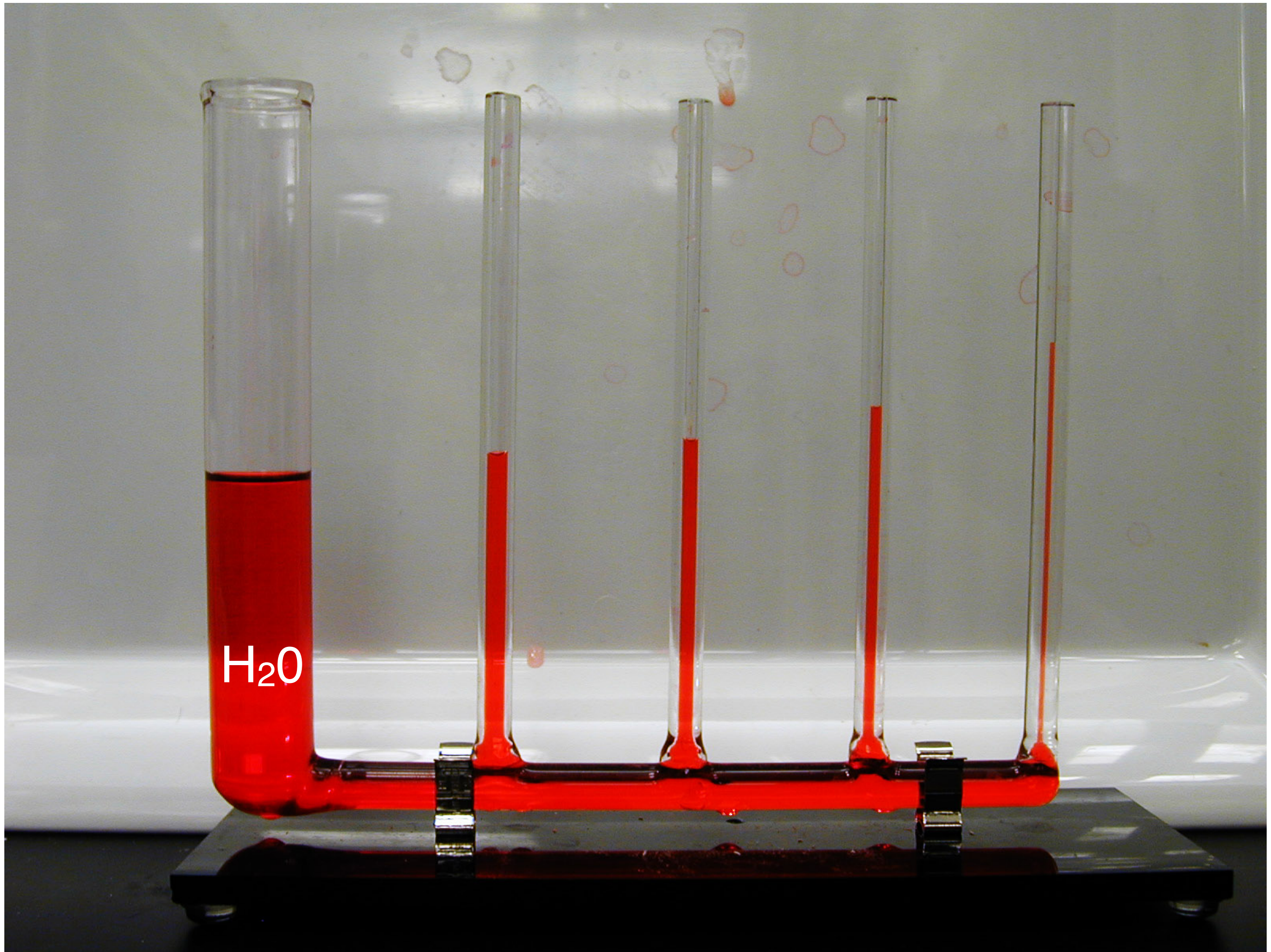
$$\gamma = \frac{dW}{dA}$$

Capillary Force

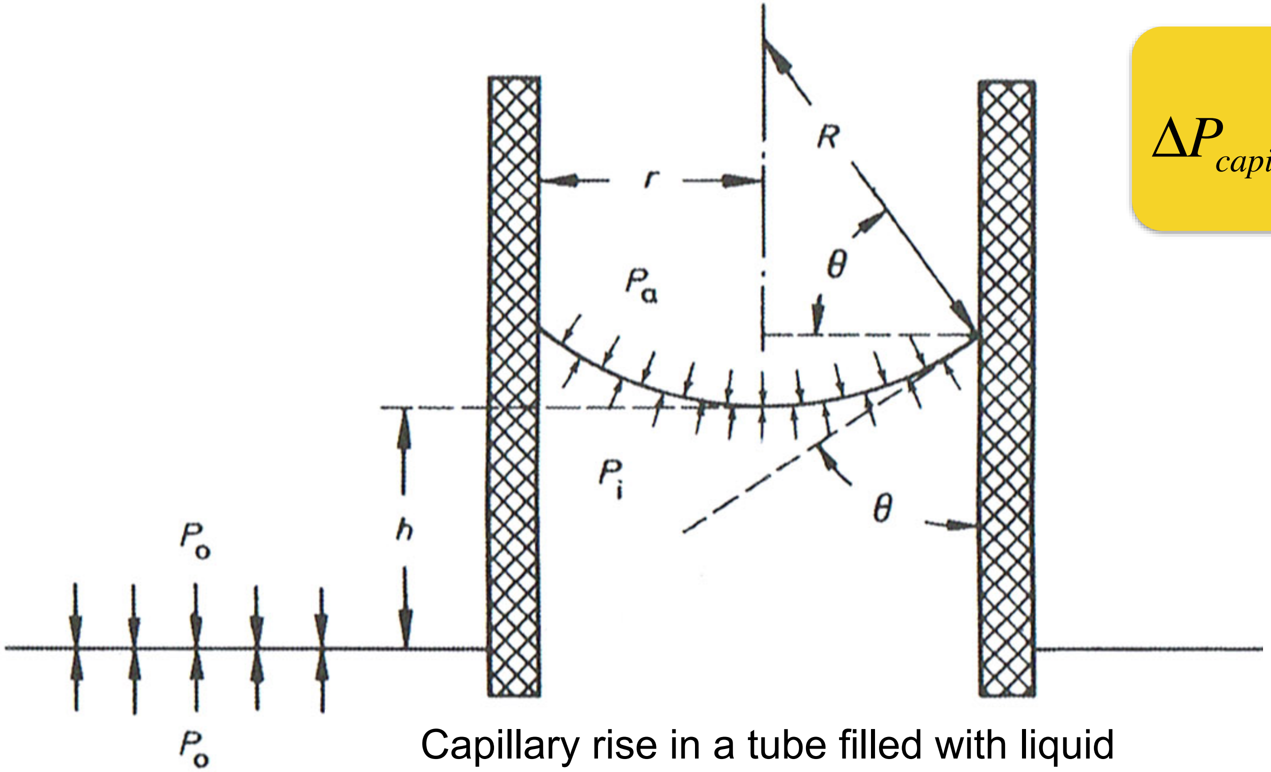
Water rises in a hydrophilic straw.
This effect is stronger, the thinner the straw is.
In a hydrophobic straw, water would be pushed down.

Mercury is a liquid metal. It is electrically conductive
and will be pushed down in a hydrophilic straw.





Capillary Force



Capillary rise in a tube filled with liquid

$$\Delta P_{capillary} = P_a - P_i = \frac{2\gamma}{R} = \frac{2\gamma \cdot \cos\Theta}{r}$$

P_a = pressure above liquid
P_i = pressure in liquid
P_o = pressure outside of capillary
γ = surface tension
R = radius of liquid
r = radius of tube
Θ = contact angle liquid vs. tube

$$\cos(\Theta) = \frac{r}{R}$$

Gravity pull on liquid column:

$$\Delta P_{gravity} = P_i - P_a = \rho g h$$

ρ = density of liquid [g/l]
g = gravity constant on earth (9.81 N/kg)
h = height of water column [m]

In equilibrium, forces are equal. Then: $\Delta P_{gravity} = \Delta P_{capillary}$

This gives:

$$\gamma = \frac{\rho g h \cdot r}{2 \cdot \cos\Theta}$$

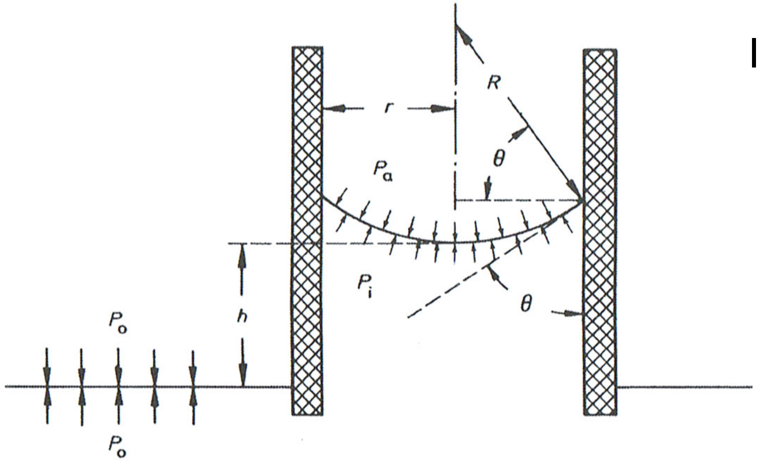
Or:

$$h = \frac{2\gamma \cdot \cos\Theta}{\rho g r}$$

If surface is fully hydrated:

$$h = \frac{2\gamma}{\rho g r}$$

Capillary Force



If surface is fully hydrated:

$$h = \frac{2\gamma}{\rho g r}$$

$\gamma = 72.5\ mN/m$ (water at 20ºC on solid)

$\rho = 1000\ kg/m^3$

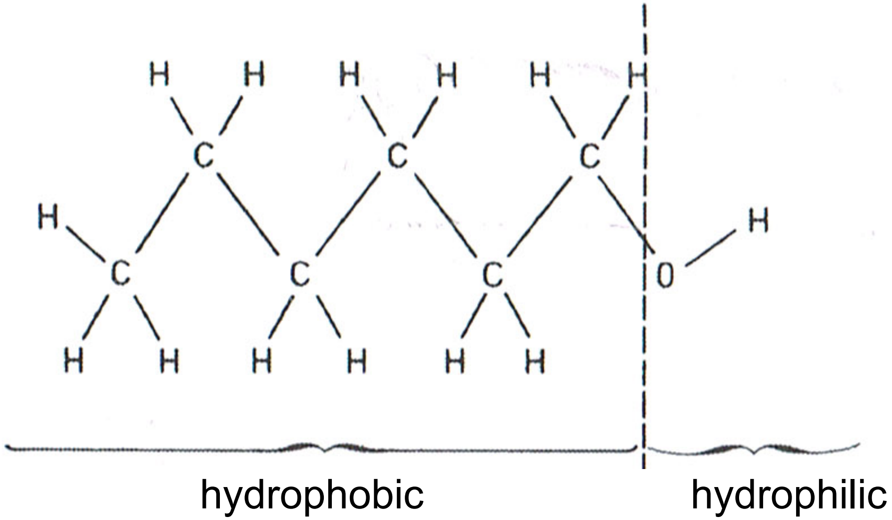
$g = 9.81\ N/kg$

For example:
In a capillary with 1 mm diameter (r = 0.0005 m), that is fully hydrated (Theta = 0), water can rise approximately 3 cm.

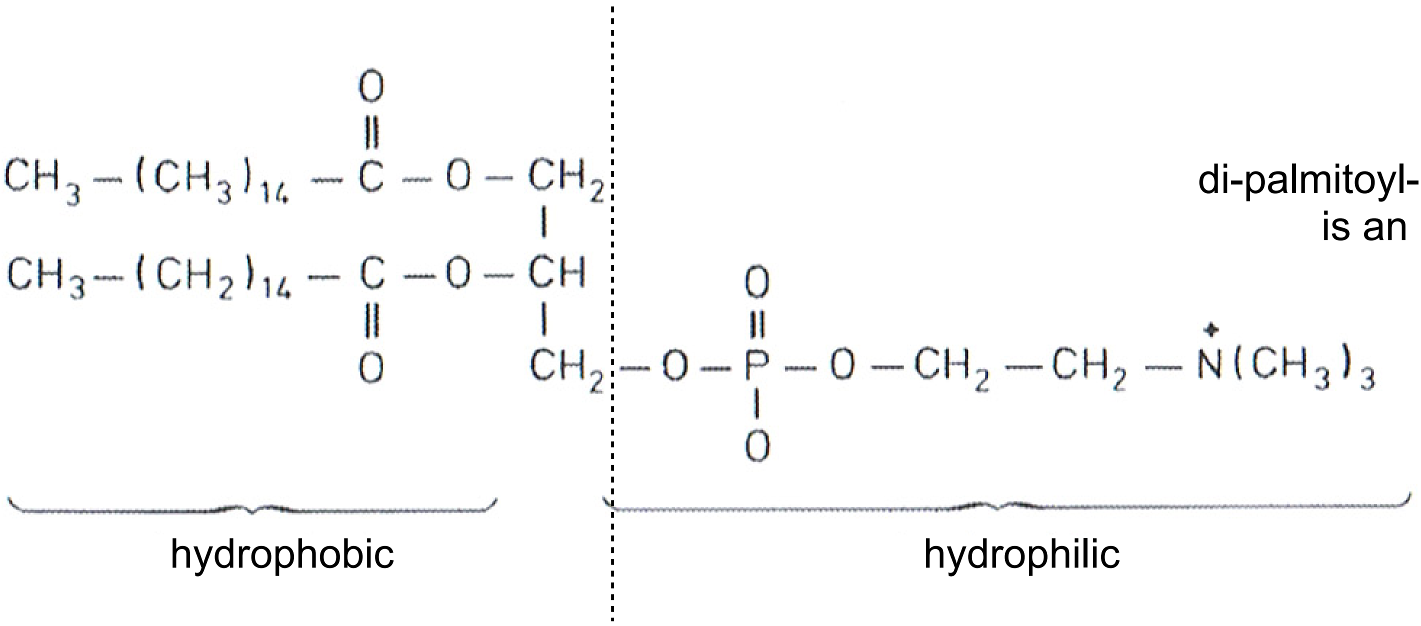
Or:
In a capillary with 10 µm diameter (r = 0.000005 m), that is fully hydrated (Theta = 0), water can rise approximately 3 meter.

A tree that is 30 meters high therefore must still have other means to get the water up.
This is the relative strength of the water "string" in a capillary, and the *transpiration suction*.

Surface Tension in the Presence of Surfactants



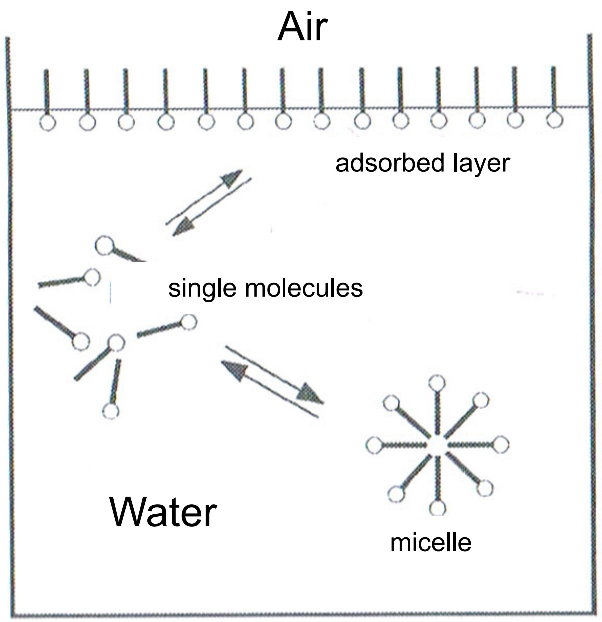
Hexanol is an
amphiphilic molecule



$$\begin{array}{l}
CH_3-(CH_3)_{14}-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2 \\
\qquad\qquad\qquad\qquad\qquad\quad\;\; | \\
CH_3-(CH_2)_{14}-\underset{\underset{\displaystyle O}{\|}}{C}-O-CH \\
\qquad\qquad\qquad\qquad\qquad\quad\;\; | \\
\qquad\qquad\qquad\qquad\qquad\quad CH_2-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{|}}{P}}-O-CH_2-CH_2-\overset{+}{N}(CH_3)_3
\end{array}$$

The lipid
di-palmitoyl-phosphatidyl-cholin (DPPC)
is an amphiphilic molecule

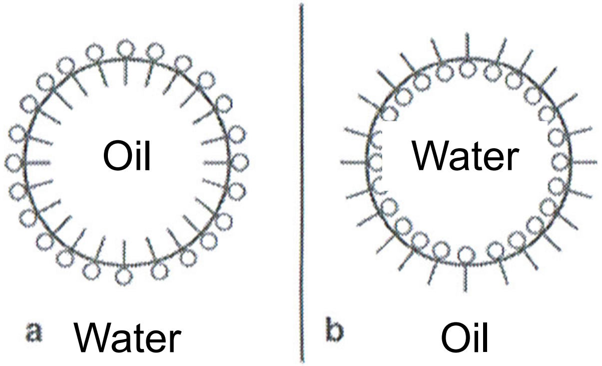
Surface Tension in the Presence of Surfactants



Surfactants are SURFace ACTive substances.
Other names are: Tensid or detergent.
These include soap or amphiphilic molecules.

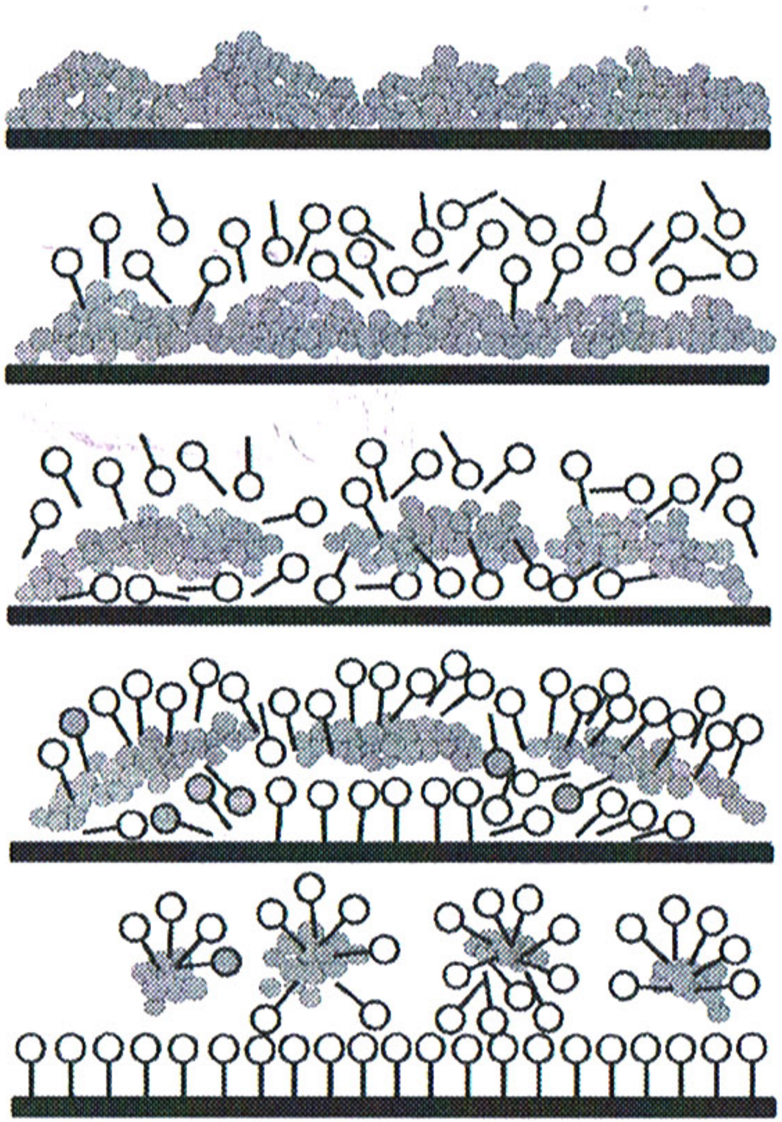
Molecules are at low concentration isolated in solution and tend to assemble at the surface.
At a concentration higher than the *critical micellar concentration* (cmc), they form micelles in the solution.

Surfactants can separate oil from water. They can solubilize oil in water via tiny droplets.



Surface Tension in the Presence of Surfactants

Surfactants can separate hydrophobic material from surfaces and clothing. This is how *soap* works.



Step 1

Step 2

Step 3

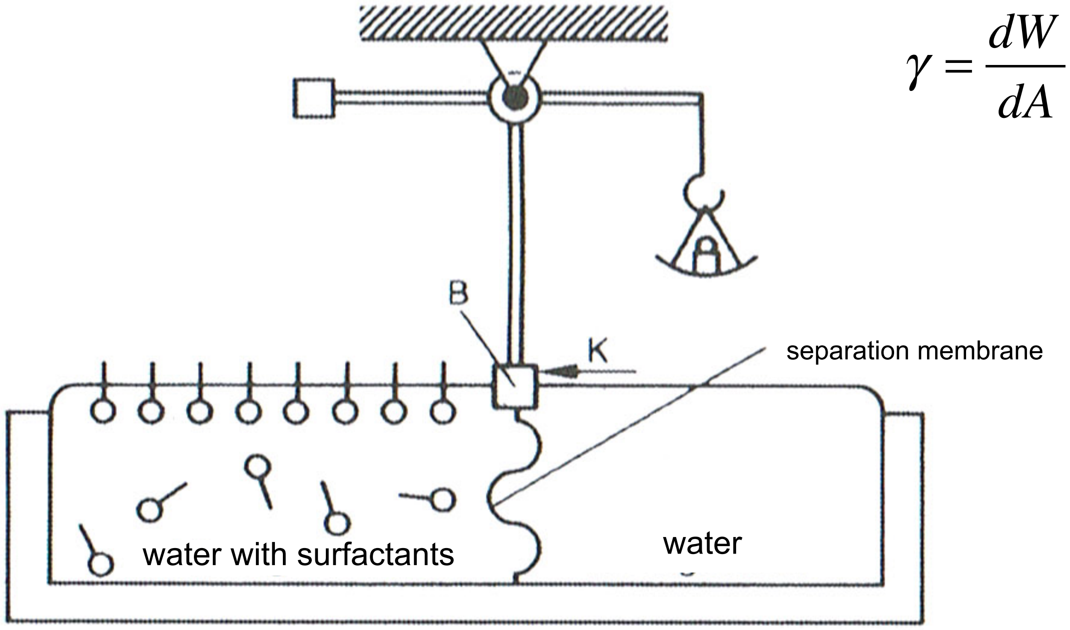
Step 4

Step 5

Surface Tension in the Presence of Surfactants

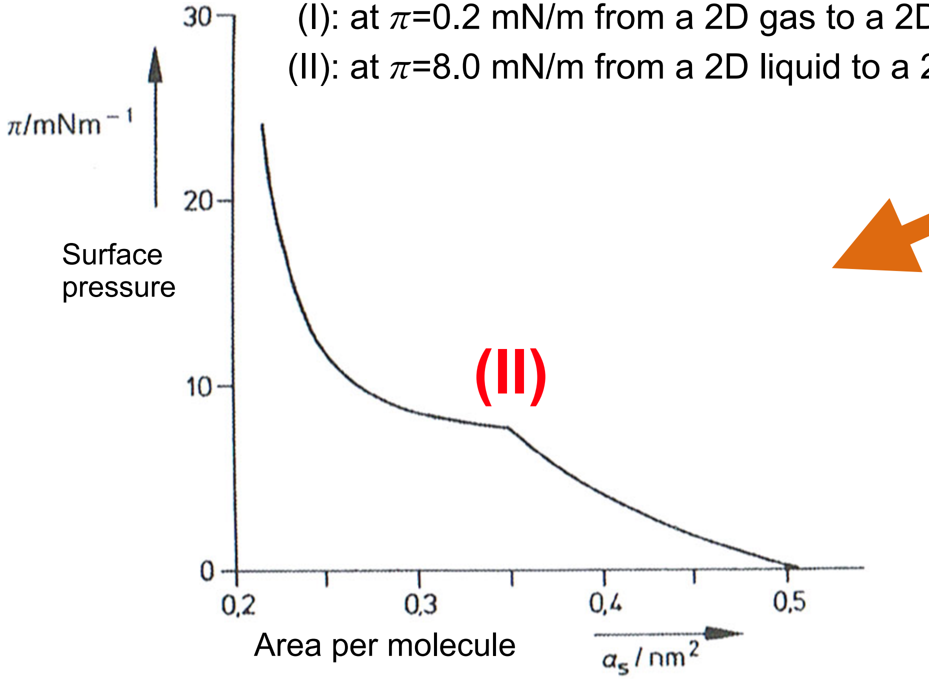
The **Langmuir-Blodgett trough** allows to measure the force K on the barrier B, therefore measuring the surface tension γ.

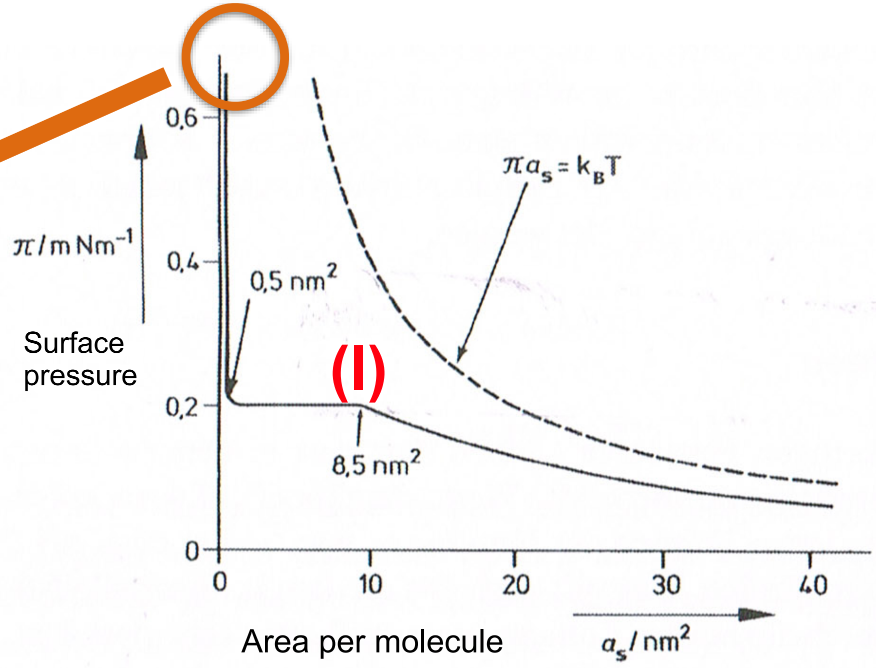
The barrier B is moved from right to left, while measuring the force K that is needed to compress the surface to the pressure π.



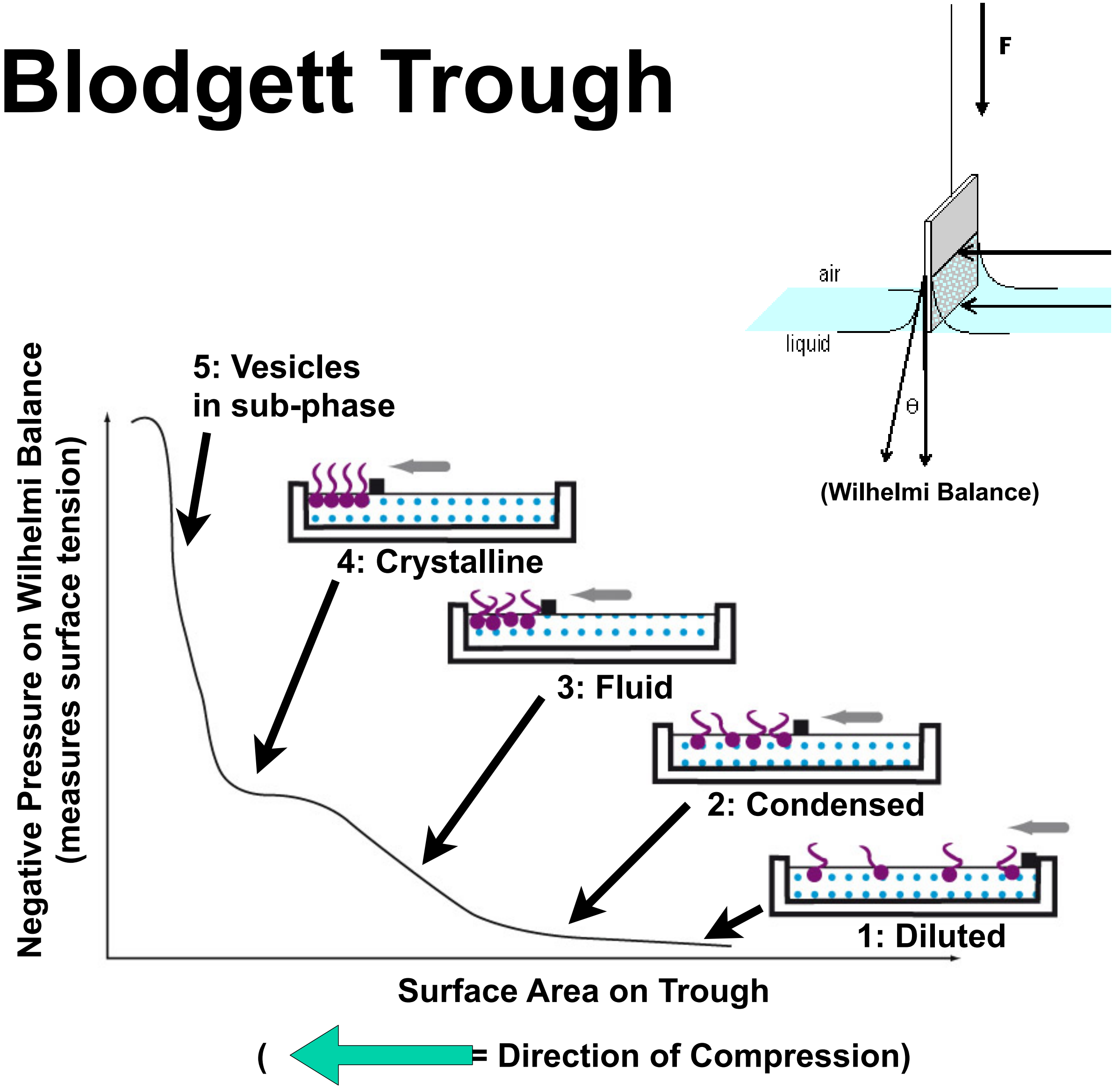
$$\gamma = \frac{dW}{dA}$$

Amphiphilic molecules on a water surface show two transitions:
(I): at π=0.2 mN/m from a 2D gas to a 2D liquid
(II): at π=8.0 mN/m from a 2D liquid to a 2D solid.



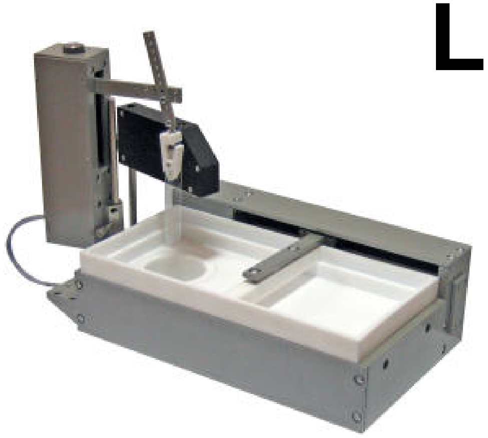


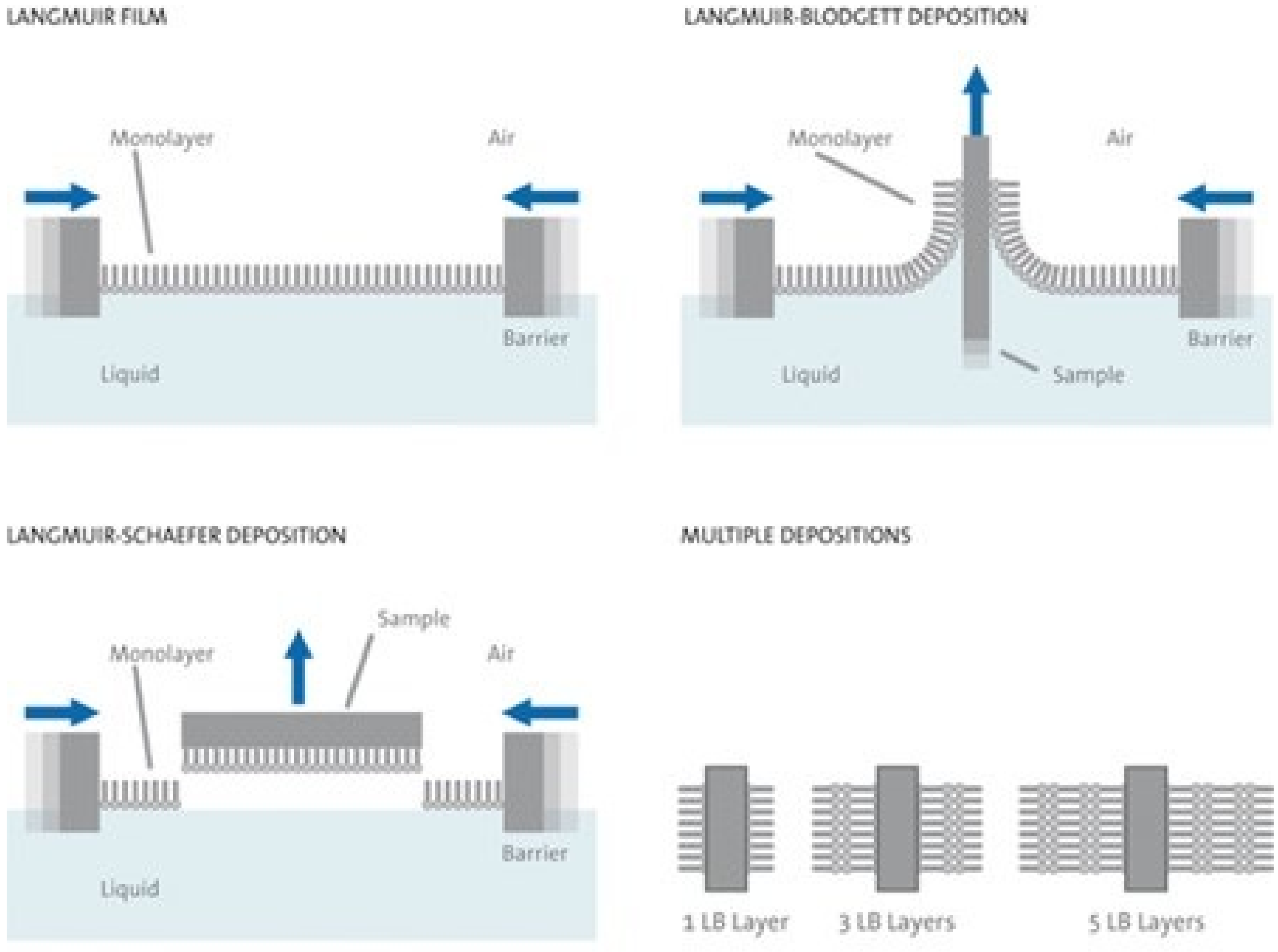
Langmuir Blodgett Trough



1,2) Without lateral pressure, lipids form a loose monolayer on the surface of a water bath.
3) Once the lateral pressure increases above a first critical value, lipids form a 2D fluid on the air-water interface.
4) With the lateral pressure above a second critical value, lipids form 2D crystals on the air-water interface.
5) Even higher pressure will drive the lipids into the sub-phase, where they form vesicles in the water.

Langmuir Blodgett Trough

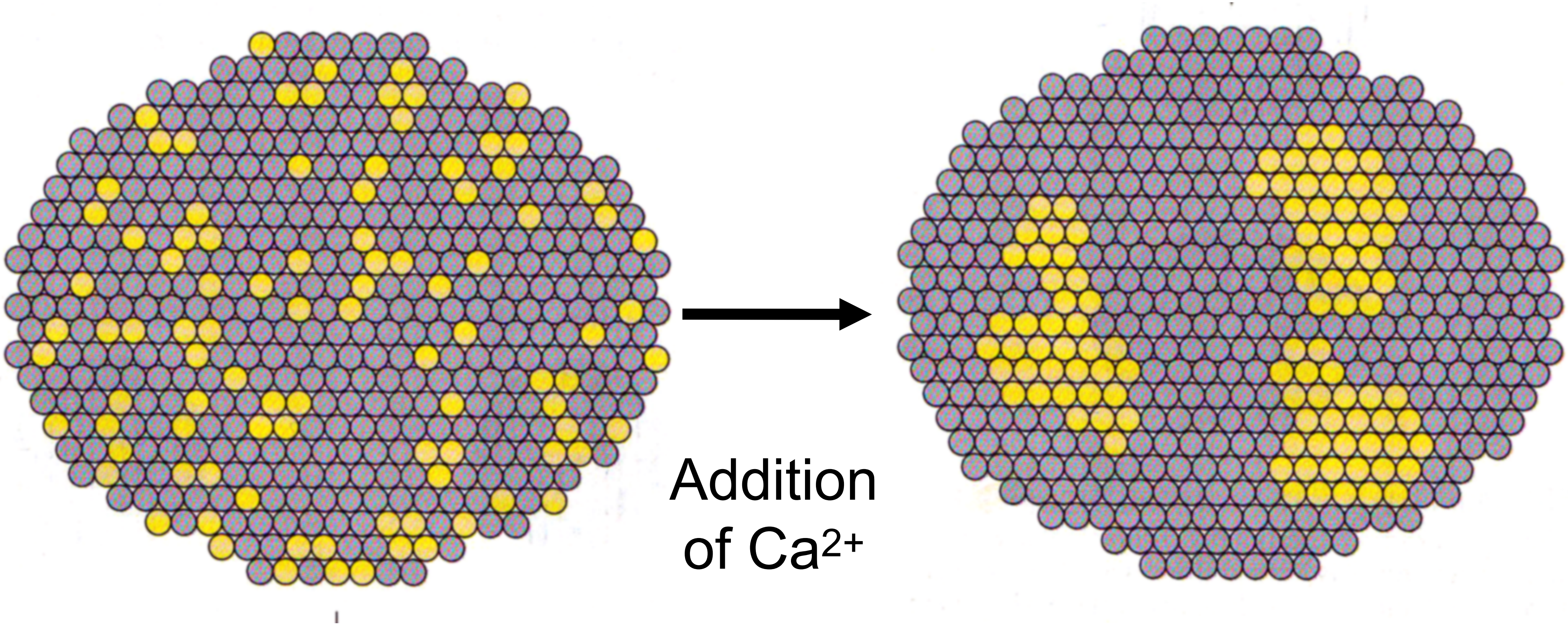




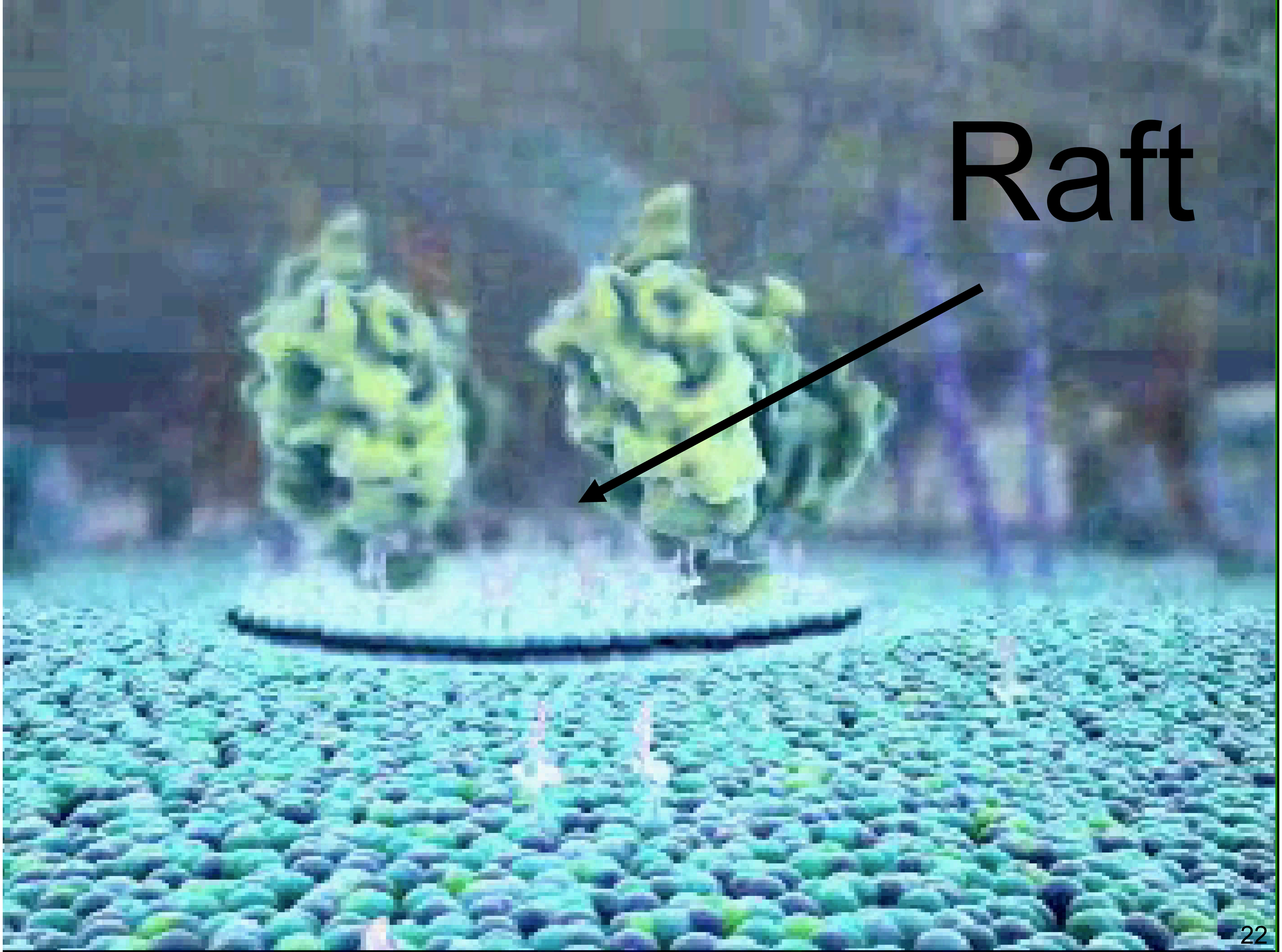
Transfer of the lipid monolayer film from the water surface onto a solid support (e.g., a microscopy slide or an electron microscopy grid):

- Top right: Rapidly inserting and then slowly vertically retracting a slide (Langmuir-Blodgett transfer). Slowly re-inserting and retracting will allow to buildup multiple layers of lipids (bottom right).
- Bottom left: Simple horizontal adsorption and pickup (Langmuire-Schaefer transfer).

Lipids can undergo phase separation

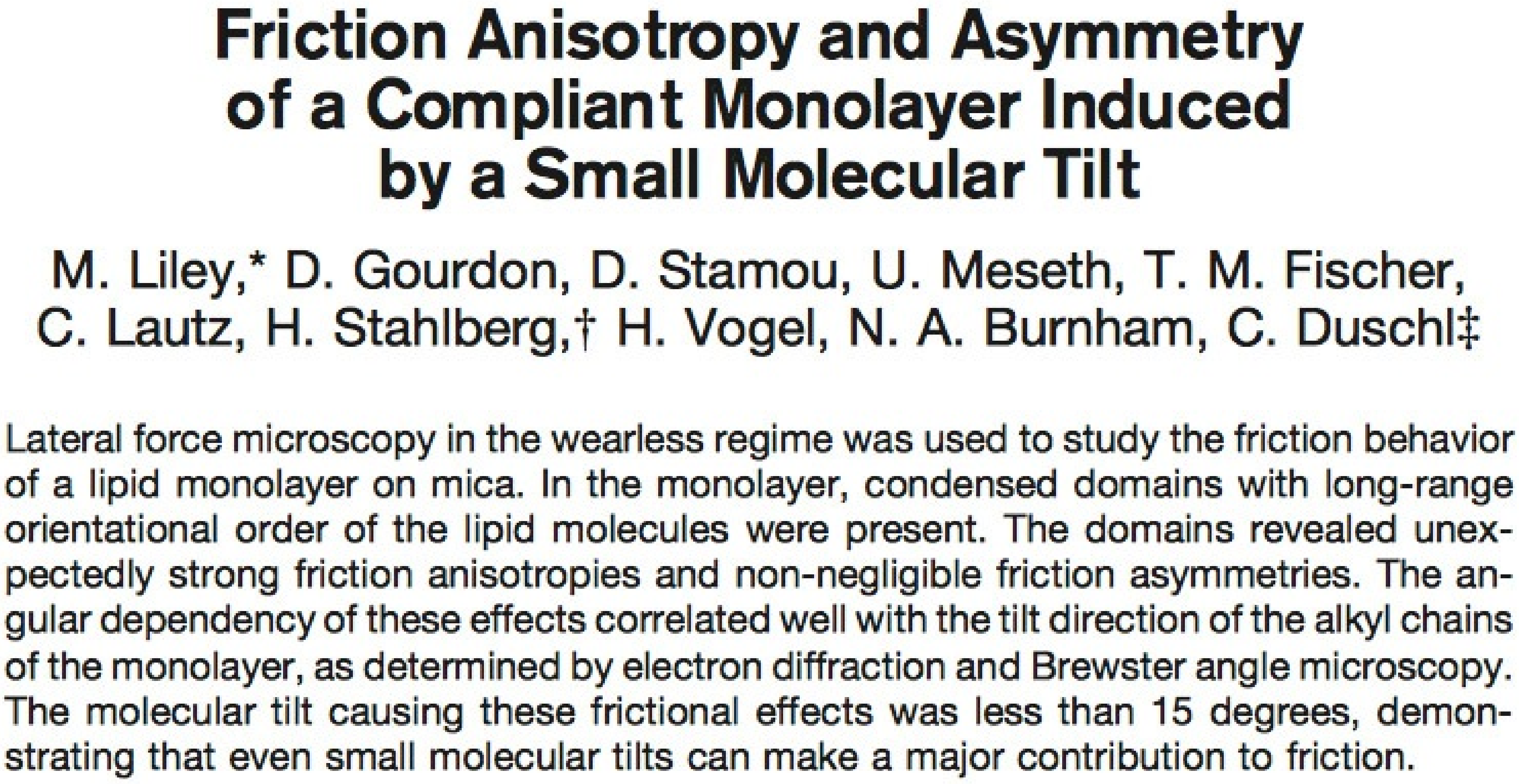


Addition of Ca^{2+}



Raft

Two different types of lipids on Langmuir-Blodgett Trough



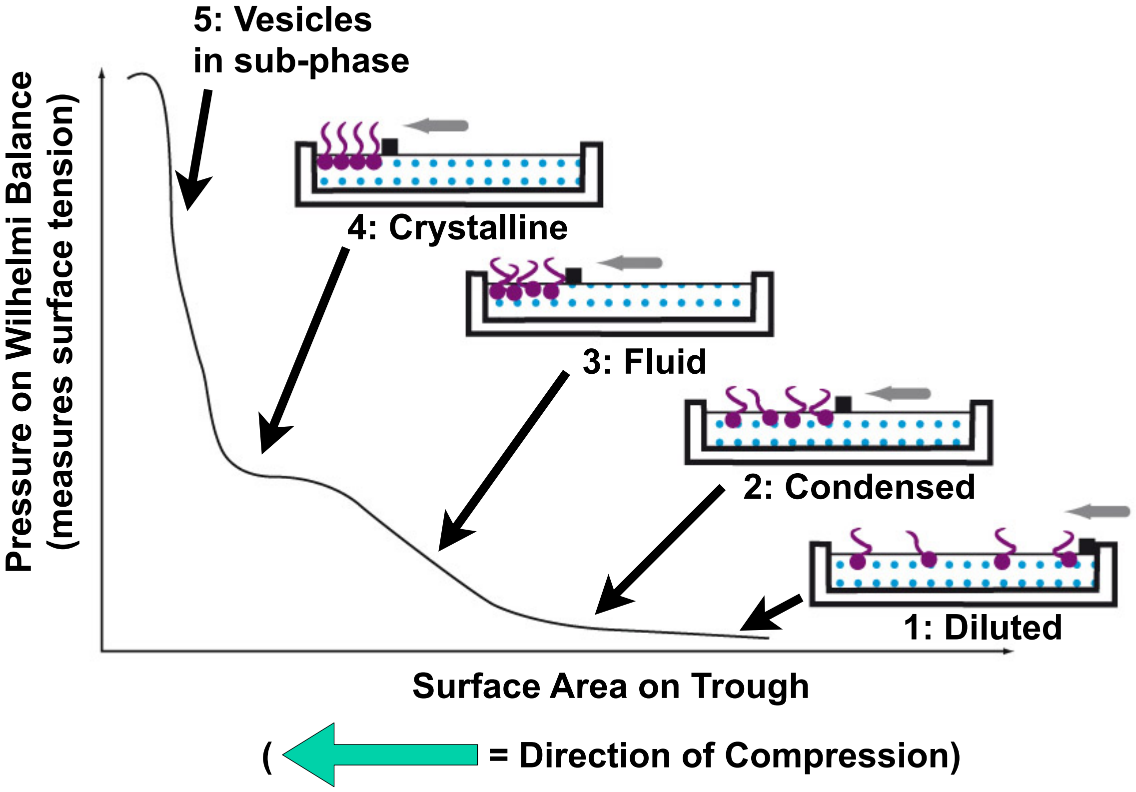
Friction Anisotropy and Asymmetry of a Compliant Monolayer Induced by a Small Molecular Tilt

M. Liley,* D. Gourdon, D. Stamou, U. Meseth, T. M. Fischer,
C. Lautz, H. Stahlberg,† H. Vogel, N. A. Burnham, C. Duschl‡

Lateral force microscopy in the wearless regime was used to study the friction behavior of a lipid monolayer on mica. In the monolayer, condensed domains with long-range orientational order of the lipid molecules were present. The domains revealed unexpectedly strong friction anisotropies and non-negligible friction asymmetries. The angular dependency of these effects correlated well with the tilt direction of the alkyl chains of the monolayer, as determined by electron diffraction and Brewster angle microscopy. The molecular tilt causing these frictional effects was less than 15 degrees, demonstrating that even small molecular tilts can make a major contribution to friction.

Liley et al., Science 280(5361), 273-275 (1998)
DOI: 10.1126/science.280.5361.273

Two different types of lipids on Langmuir-Blodgett Trough



5: Vesicles
in sub-phase

4: Crystalline

3: Fluid

2: Condensed

1: Diluted

Pressure on Wilhelmi Balance
(measures surface tension)

Surface Area on Trough

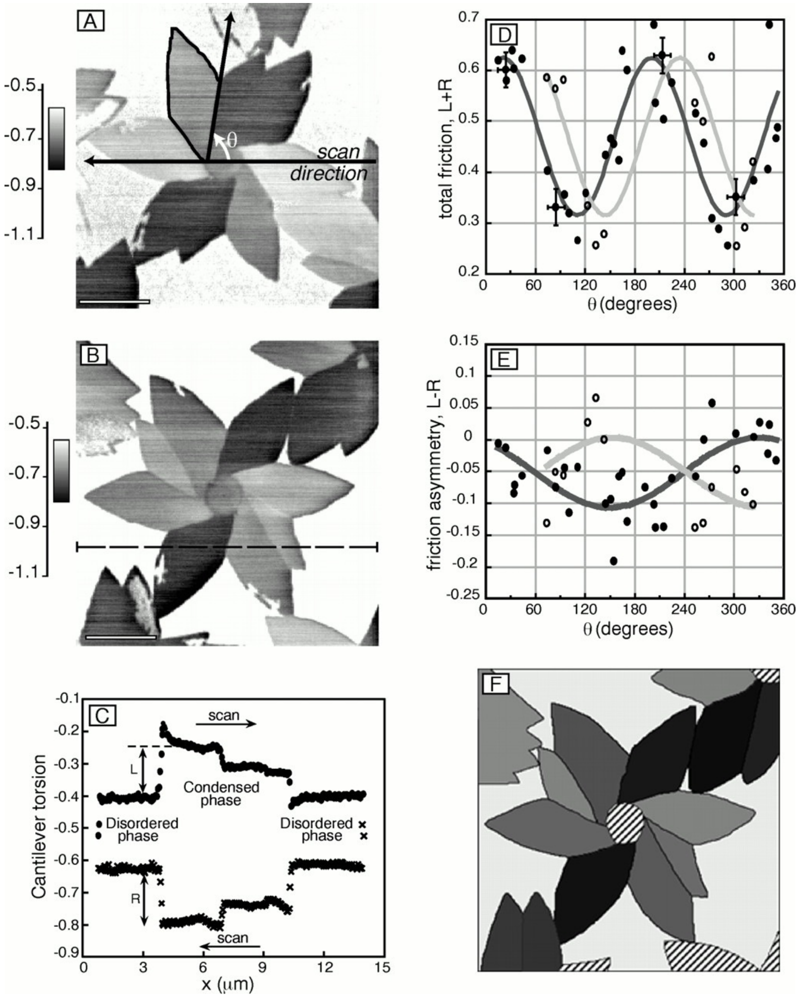
(← = Direction of Compression)

Setup: Two different lipids on air-water interface: Upon compression up to step 4 above (crystalline), the two lipid types demix, and one lipid starts to form 2D crystals first, in this case as a star-like shape, while the other lipid is still in the fluid phase. These phase-separated states were studied by various microscopy types, including fluorescence LM, AFM, TEM, and Brewster-angle LM.

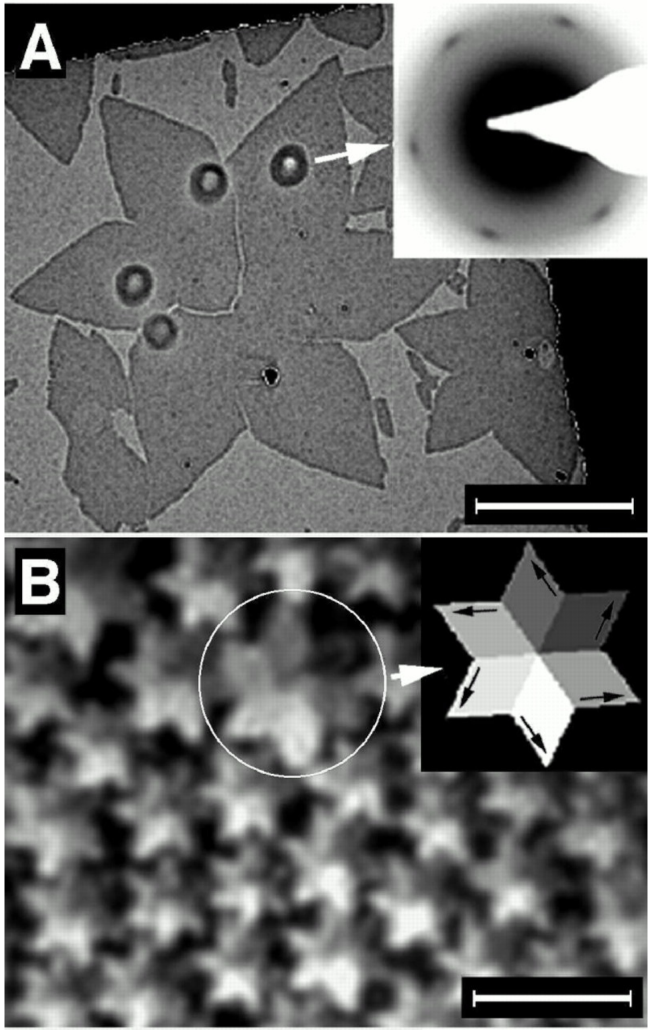
Liley et al., Science 280(5361), 273–275 (1998)
DOI: 10.1126/science.280.5361.273

Two different types of lipids on Langmuir-Blodgett Trough

Atomic Force Microscopy



(A) Transmission Electron Microscopy

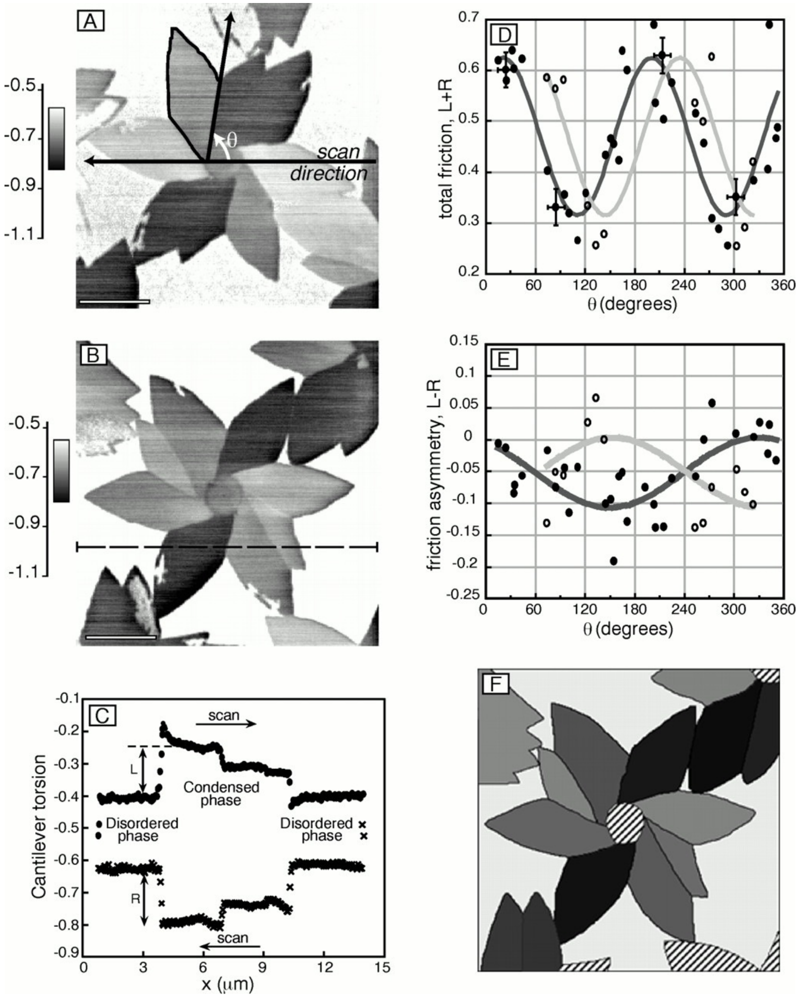


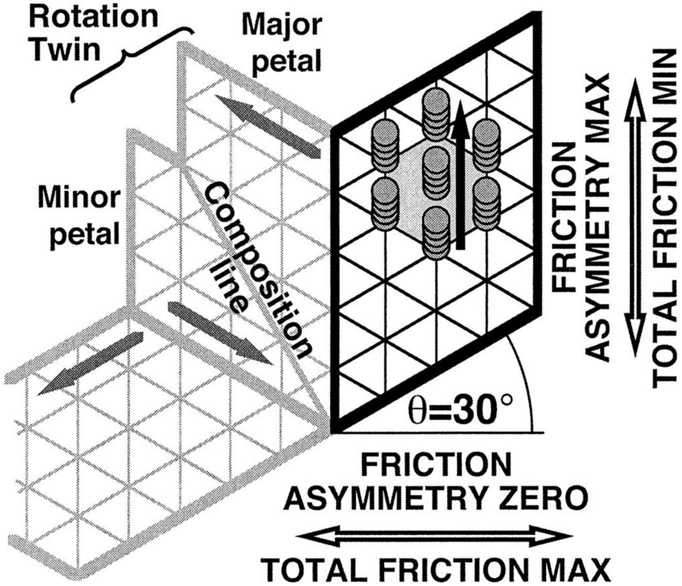
(B) Brewster Angle Light Microscopy

Liley et al., Science 280(5361), 273-275 (1998)
DOI: 10.1126/science.280.5361.273

Two different types of lipids on Langmuir-Blodgett Trough

Atomic Force Microscopy





Without lateral pressure, both lipids are fluid and mix with each other.
Under pressure, lipids undergo phase separation. One lipid 2D-crystallizes out, the other lipid stays fluid, surrounding the crystalline “star-shaped” crystals.

Liley et al., Science 280(5361), 273-275 (1998)
DOI: 10.1126/science.280.5361.273