ISM06

Wetting

Chapter 4 Hamley

Section 23.10 Atkins

Topics

- The pond and the sea
- Surface tension
- Surface pressure
- Gibbs adsorption equation
- Droplets on smooth surfaces
- The coffee experiment
- Droplets on heterogeneous surfaces
- Lotus leafs
- Droplets on liquid surfaces
- The surface of soup

The sea I

'Remember to throw into the sea the oil which I gave you, when straightway winds will abate, and a calm and smiling sea will accompany you throughout your voyage'
The Venerable Bede (born 672 or 673; died 735)
Ecclesiastical History of the English People, Book 3, Chapter 3.

Citation from Len Fisher, 'How to dunk a doughnut', Page 216

The sea II

Benjamin Franklin, on a sea voyage to England in 1757, noticed the wakes behind accompanying ships were smooth, while those behind his own were rough. He asked the captain for an explanation 'The Cooks, says he, have I suppose, been just emptying their greasy Water thro' the Scuppers, which has greased the Sides of those Ships a Little'

Len Fisher, pg 125

And the Pond

Arrived in England… and went to a pond in London's Clapham Common.

"the Oil tho'not more than a TeaSpoonful produced an instant calm, over a Space of several yards square, which spread, amazingly, and extended itself gradually, until it reached the Lee Side, making all of that Quarter of the Pond, perhaps, half an Acre, as Smooth as a Looking Glass."
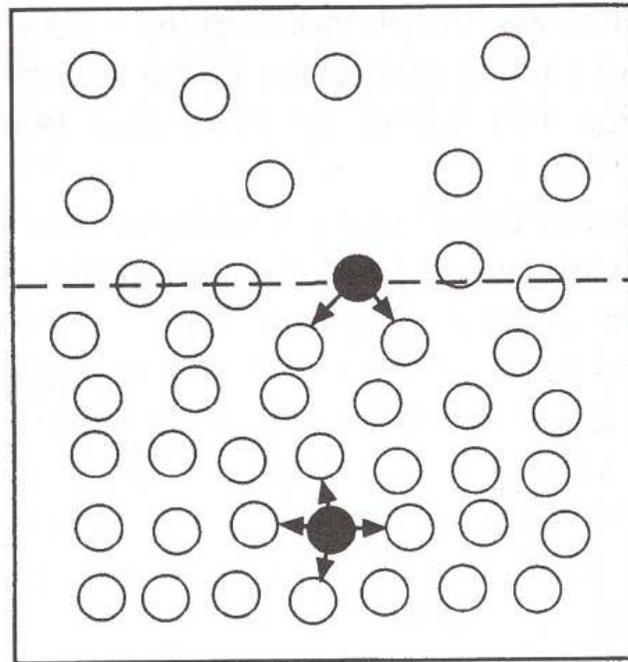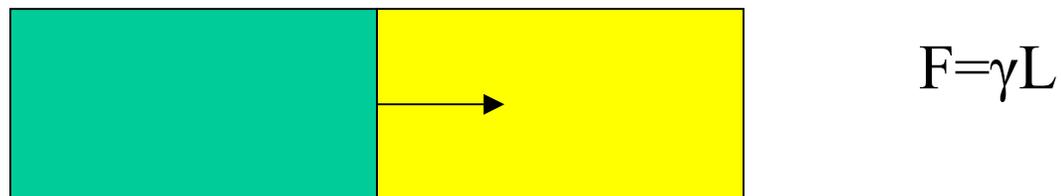
Len Fisher pg 126

Surface tension

Figure 4.5 Surface tension arises from the imbalance of forces on molecules at the liquid–gas interface

Operational definitions

From the work needed to increase the surface *area*

$$w=\gamma\Delta A$$

From the force perpendicular to the *contour* of the surface
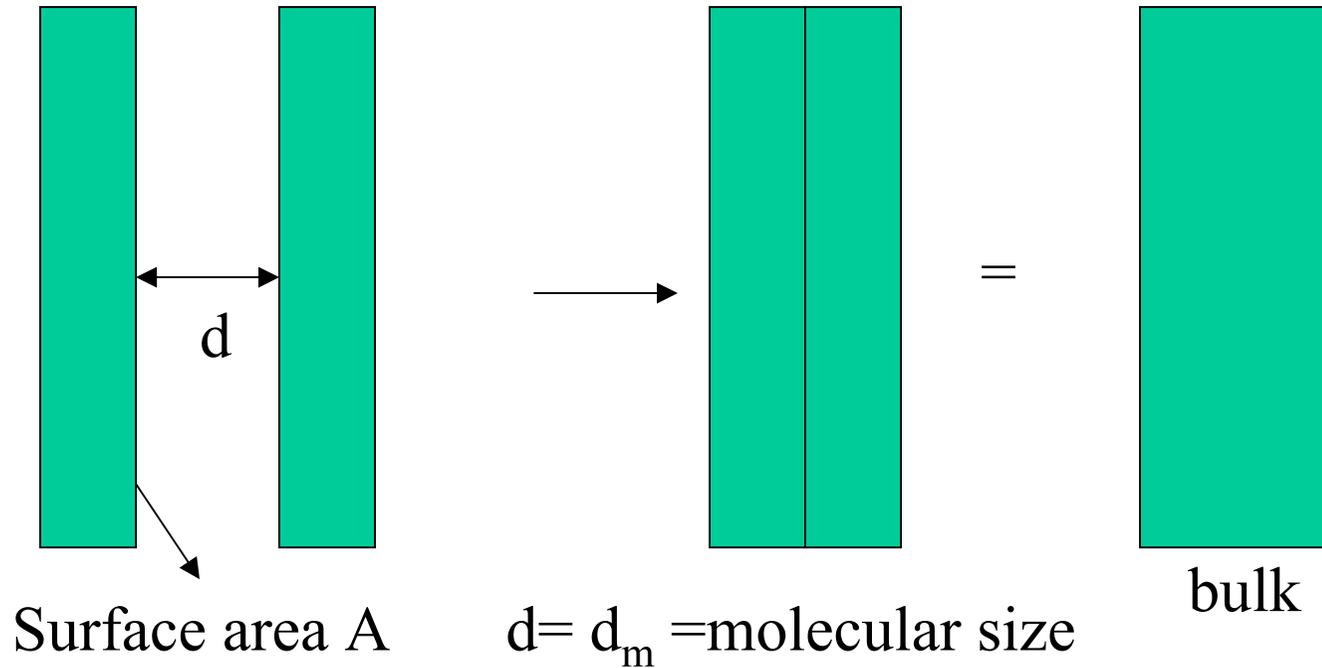
$$F=\gamma L$$

Value of surface tension

Determined by:

- Long range forces (e.g. dispersion)
- Short range specific forces (hydrogen bonding, complexation etc.)
- Entropical effects (in a liquid, the surface is usually slightly more disordered than the bulk)

Value of surface tension

Consider merging two half bodies of pure liquid

Exercise:
What is the relation between the Hamaker constant and the surface tension?
- for metals (e.g. Hg)
- for alkanes
- for water

d

bulk

Surface area A   d= d_m =molecular size

w=2γA =V(d=   )-V(d=d_m)

Surface pressure π

Two surfaces, separated by a barrier:

-'clean' water, surface tension γ_0

- water, covered with surfactants, surface tension γ

$$\pi = \gamma_0 - \gamma$$

to
force
transducer

film   Moveable
                    barrier

water

Requirement:
on the time scale of the experiment,
the surfactant does not dissolve in water
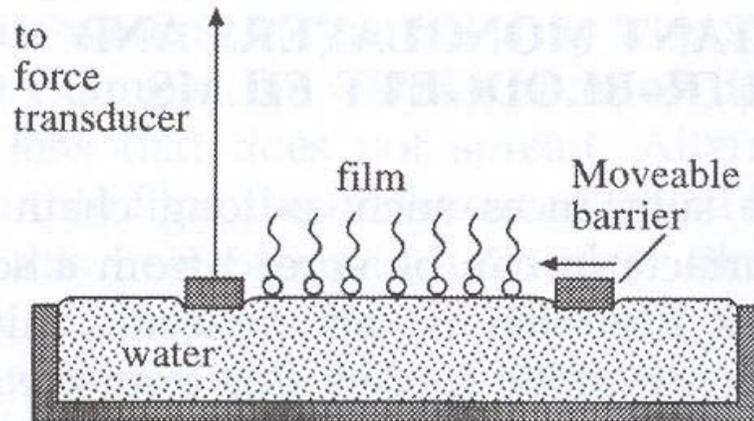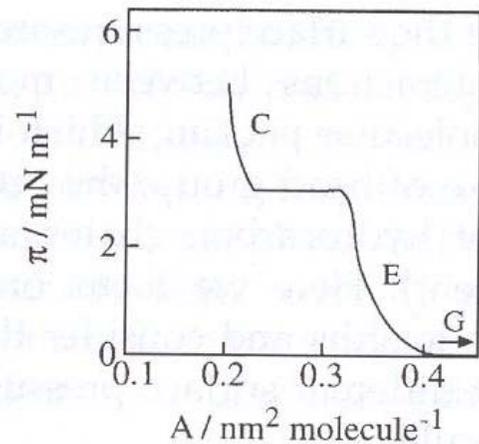
Figure 4.9   Schematic of a Langmuir trough
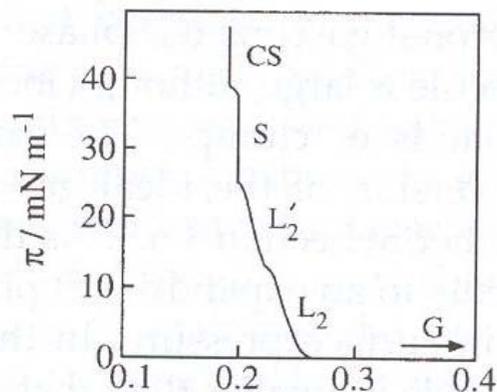
Surface pressure experimental results

n-hexadecanoic acid (short tail)
'G' gas phase
'E' expanded phase
'C' condensed phase

n-docosanoic acid (long tail)
Gas phase or
Condensed phases (L2-CS)
only

Figure 4.10 Surface pressure–area isotherms: (a) *n*-hexadecanoic acid on a subphase of 0.01 M HCl at 30 °C [data from N. R. Pallas and B. A. Pethica, *Langmuir*, **1**, 509 (1985)]; (b) *n*-docosanoic acid on a subphase of 0.01 M HCl [data from E. Stenhagen in *Determination of Organic Structures by Physical Methods*, E. A. Braunde and F. C. Nachod (Eds.), Academic Press, New York (1955)]

Surface pressure model
G-E-C phases

- G phase: the adsorbed molecules are very far apart, the surface layer behaves like a 2-dimensional ideal gas
- E phases: the adsorbed molecules are clustered, and on further compression form a 2-dimensional liquid
- C phases: the adsorbed molecules are closely packed, and form a 2-dimensional solid
- The behavior can be approximately described by 2-dimensional equation of state, according to van der Waals

for the gas phase:

$\pi = RT\Gamma$

Γ = adsorption in mol/m^2

Eq. 4.32

Gibbs adsorption equation

Experiment: we change the concentration of a surfactant *in solution*

$c/\text{mol dm}^{-3}$	0.0264	0.0536	0.1050	0.2110	0.4330
$\gamma/\text{mN m}^{-1}$	68.00	63.14	56.31	48.08	38.87

(question 4.2)

We notice that the surface tension drops.
The more surfactant we add, the easier it is
to create new surface, because the surfactant molecules are
happy on the surface…

Exercise: draw a cartoon of the solution in equilibrium
with the surface

Gibbs adsorption equation

$$\Gamma = -\frac{1}{RT}\left(\frac{\partial \gamma}{\partial \ln c}\right)_T$$ (ideal solution)

- When the adsorbed molecules are soluble,

  there will be an equilibrium between molecules in solution and molecules on the surface

- Since the surface tension depends on the amount of adsorbed molecules, there must be a *thermodynamic* relation between surface tension, adsorption and concentration in solution

- Thermodynamics means: it is always valid

Gibbs adsorption equation, justification I (adapted from Atkins)

p, T constant $\rightarrow$ Gibbs energy

$$dG = \gamma dA + \sum_I \mu_I dn_I \quad \text{change in total Gibbs energy}$$

$$dG^\alpha = \sum_I \mu_I dn_I^\alpha \quad \text{change in bulk Gibbs energy}$$

$$n^\sigma \equiv n_I - n_I^\alpha \quad \text{excess on surface}$$

$$G^\sigma \equiv G - G^\alpha \quad \text{surface Gibbs energy} = \text{excess Gibbs energy}$$

$$dG^\sigma = \gamma dA + \sum_I \mu_I dn_I^\sigma$$

Gibbs adsorption equation, justification II

$$dG^\sigma = \gamma dA + \sum_I \mu_I dn_I^\sigma$$

G^σ is extensive in A and n_I^σ (why?)

integrate over A and n_I^σ (how?)

$$G^\sigma = \gamma A + \sum_I \mu_I n_I^\sigma$$

$$dG^\sigma = \gamma dA + A d\gamma + \sum_I \mu_I dn_I^\sigma + \sum_I n_I^\sigma d\mu_I$$

$$A d\gamma = -\sum_I n_I^\sigma d\mu_I \qquad \text{Pure magic!}$$

Gibbs adsorption equation, justification, III

$$Ad\gamma = -\sum_I n_I^\sigma d\mu_I$$

$$\sum_I n_I^\alpha d\mu_I = 0 \quad \text{Gibbs-Duhem relation bulk}$$

$$d\gamma = -\sum_{I \neq w} \Gamma_I^{(w)} d\mu_I \quad \text{general Gibbs adsorption isotherm}$$

$$\Gamma_I^{(w)} \equiv \frac{1}{A}\left(n_I^\sigma - \frac{n_I^\alpha}{n_w^\alpha}n_w^\sigma\right)$$

when $c_I^\alpha << c_w^\alpha$ solute is dilute

$$\Gamma_I^{(w)} = \Gamma_I = \frac{n_I^\sigma}{A}$$

$$\Gamma_I^{(w)} \equiv -\left(\frac{\partial\gamma}{\partial\mu_I}\right)_{J \neq I, p, T} \quad \text{from general Gibbs isotherm}$$

Gibbs adsorption equation, justification, IV

$$\Gamma_I^{(w)} \equiv \frac{1}{A}\left(n_I^\sigma - \frac{n_I^\alpha}{n_w^\alpha}n_w^\sigma\right)$$

when $c_I^\alpha << c_w^\alpha$ solute is dilute

$$\Gamma_I^{(w)} = \Gamma_I = \frac{n_I^\sigma}{A}$$

$$\Gamma_I^{(w)} \equiv -\left(\frac{\partial\gamma}{\partial\mu_I}\right)_{J\neq I,p,T}$$ from general Gibbs isotherm

$$\left[\begin{array}{c}(\partial\mu_I)_{J\neq I,P,T} = RT\partial\ln c_I\\ \Gamma_I^{(w)} = \Gamma_I\end{array}\right]$$ when solution is ideal and dilute

$$\Gamma_I = -\frac{1}{RT}\left(\frac{\partial\gamma}{\partial\ln c_I}\right)$$

$$\Gamma = -\frac{1}{RT}\left(\frac{d\gamma}{d\ln c}\right)$$ when only one solute is present

Application of the Gibbs adsorption isotherm

The following specific adsorption model is given (more about this particular model in ISM07):

$$\Gamma = \Gamma_{\text{max}} \frac{Kc}{1 + Kc} \quad \text{Langmuir isotherm}$$

$$\Gamma_{\text{max}} = \text{maximal adsorption} = 3 \; \mu\text{mol}/\text{m}^2$$

$$K = \text{equilibrium constant} = 10^4 \; \text{M}^{-1}$$

Exercise:

Plot adsorption versus concentration

Plot surface pressure versus 1/adsorption (π-A isotherm)

Plot surface tension versus concentration

The answers...

$$\Gamma = -\frac{1}{RT}\frac{d\gamma}{d\ln c} \quad \text{Gibbs}$$

$$d\gamma = -RT\Gamma d\ln c = -RT\frac{\Gamma}{c}dc$$

$$\Gamma = \Gamma_{max}\frac{Kc}{1+Kc} \quad \text{Langmuir}$$

$$d\gamma = -RT\Gamma_{max}\frac{dKc}{1+Kc} \quad \text{integrate}$$

$$\gamma(c) = \gamma_0 - RT\Gamma_{max}\ln(1+Kc)$$

$$Kc = \frac{\Gamma}{\Gamma_{max}-\Gamma} \quad \text{Langmuir again}$$

$$\ln(1+Kc) = \ln(\frac{\Gamma_{max}}{\Gamma_{max}-\Gamma})$$

$$a \equiv 1/\Gamma \quad \text{area per mol}$$

$$\pi(a) = \gamma_0 - \gamma = \frac{RT}{a_{max}}\ln(\frac{a}{a-a_{max}})$$
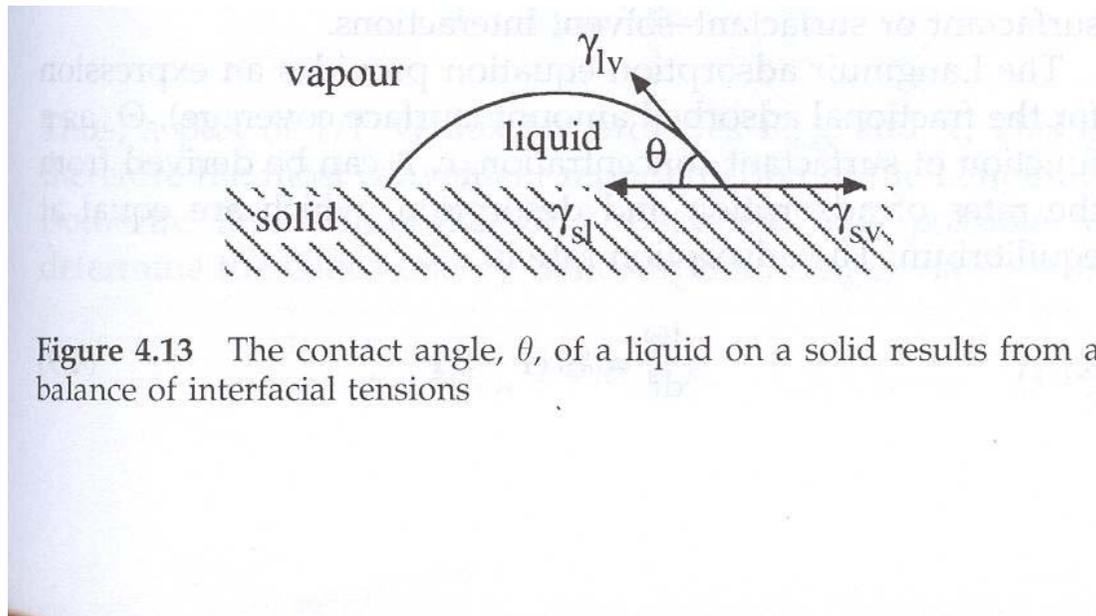
Droplets on smooth surfaces

Figure 4.13 The contact angle, θ, of a liquid on a solid results from a balance of interfacial tensions

Small droplets on a smooth surface have the shape of
a capped ideal sphere.
Large droplets feel gravity,
and have the shape of a flattened sphere.
In both cases the contact angle is the *same.*

Droplets on a smooth surface

Using the surface tensions of the separate two-phase interfaces, we can predict what happens

when $-1 \leq \dfrac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \leq 1$ finite contact angle **Incomplete wetting**

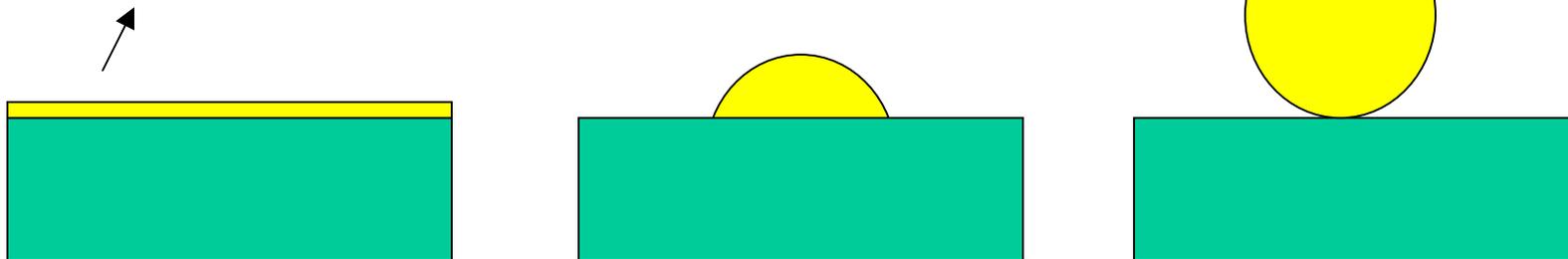$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta$$

$$\cos \theta = \dfrac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad \text{In equilibrium}$$

when $\dfrac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} > 1$ complete wetting (the drop spreads evenly over the surface)

when $\dfrac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} < -1$ no wetting at all (the drop is a perfect sphere, like a marble)

(complete wetting *in equilibrium*:
     Antonows rule, S=0)

contact angle

- The surface tension of metals is $O(1000)$ mJ/m^2
- The surface tension of apolar organic liquids is $O(20\text{-}40)$ mJ/m^2
- The surface tension of polar liquids is $O(50\text{-}80)$ mJ/m^2
- The surface tension of solid oxides is $O(100)$ mJ/m^2
- Water completely wets metals and oxides
- Water on an apolar substrate gives incomplete wetting
- No wetting (marble effect) is very difficult to achieve

contact angle

- The surface tension of the solid-liquid interface is difficult to measure independently, we use the contact angle value to do so

- In case of wetting of an apolar substrate by and apolar liquid (oil on plastic), a simple relation holds $$\gamma_{SL} \approx \sqrt{\gamma_{SL}\gamma_{LV}}$$
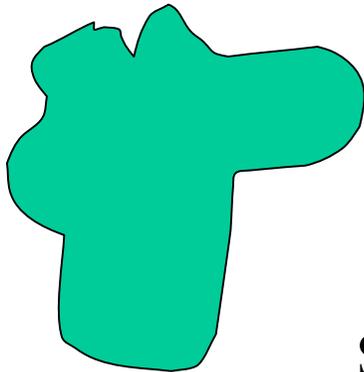
Exercise: derive this relation

The coffee experiment

Put a drop of coffee on …what you think is a smooth surface
Is it spherical?
NO!
The contour of a sessile drop is *very* irregular

The reasons:
- the surface is not smooth
- the surface has adsorbed 'dirt; which alters the contact angle locally

Surfaces with high surface tension are very difficult to keep clean: why is that?

Droplets on smooth but chemically heterogeneous surfaces

Almost, if not *all* natural every-day solid surfaces are heterogeneous
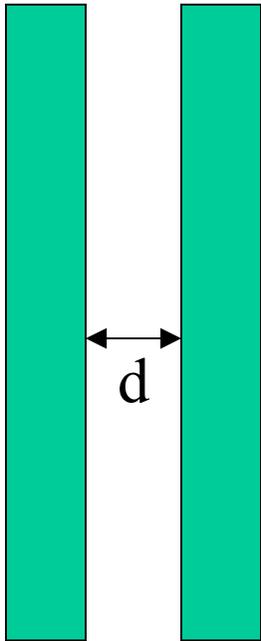
Exercise
A hydrophilic surface is covered with long stripes of hydrophobic 'dirt'.
We add a small drop with radius R.
draw cartoons explaining the shape of the sessile drop, in case R<<d, and R>>d

d

Droplets on rough but chemically homogeneous surfaces

On large scale, the drop looks symmetrical, and everything seems OK
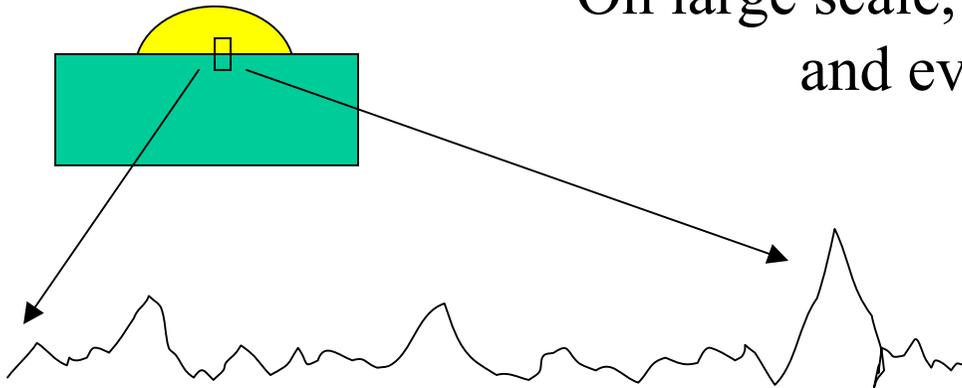
When the surface roughness has a very small length scale
(for water << 0.1 mm)
The drop looks spherical, but…
The effective contribution from the solid-interfacial energies
is higher than that for a smooth surface

Wenzel model for wetting rough surfaces

The surface roughness in effect
enlarges the surface area of contact between surface en liquid

$$\frac{A_r}{A}\gamma_{SV} = \frac{A_r}{A}\gamma_{SL} + \gamma_{LV}\cos\theta_{\text{rough}}$$

$$\frac{A_r}{A} = r = \text{ roughness factor}$$

$$\cos\theta_{\text{rough}} = r\frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} = r\cos\theta_{\text{smooth}}$$

Example:

$$\theta_{\text{smooth}} = 60^0 = \pi/3 \text{ radians}$$

$$r = 2$$

$$\cos\pi/3 = 0.5$$

$$\cos\theta_{\text{rough}} = 2 \times 0.5 = 1$$

$$\theta_{\text{rough}} = 0^0 \rightarrow \text{ complete wetting}$$

Exercise: repeat calculation for smooth contact angle 90^0 and 120^0

The Lotus effect

Lotus leafs have a mechanism for keeping the surface clean

The surface is covered with microscopic-size islands or patches of wax.

The heterogeneity enhances the hydrophobic effect enormously.
Small water droplets do not wet at all, remain spherical,
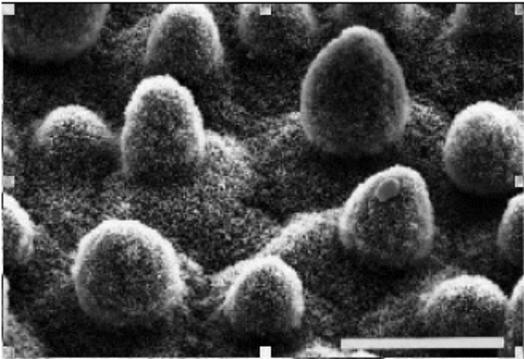and roll off the leaf upon minor disturbance.

Figure 6: SEM-image of lotus leaf. The micro
structural epidermal cells are covered with
nanoscopic wax crystals. Bar: 20 μm. (From
Barthlott et all.[1]).

(Stanley Lai's BSc ISM report 2003)

In several Asian religions the Lotus flower (*Nelumbo Nucifera*) is revered as the symbol of purity. The basis of this consideration is based on the self-cleansing property of the leaves of the Lotus flower: even when emerging from muddy waters the leaves unfold untouched by the pollution.

In order to describe the background of the Lotus-effect, an exact definition is in order: a surface which shows the Lotus-effect is superhydrophobic, expressed by a contact angle larger than 150º. Due to this superhydrophobicity, water tends to roll off the surface, even if the surface is tilted slightly, and cleans the surface of a contamination in its way (Figure 5).
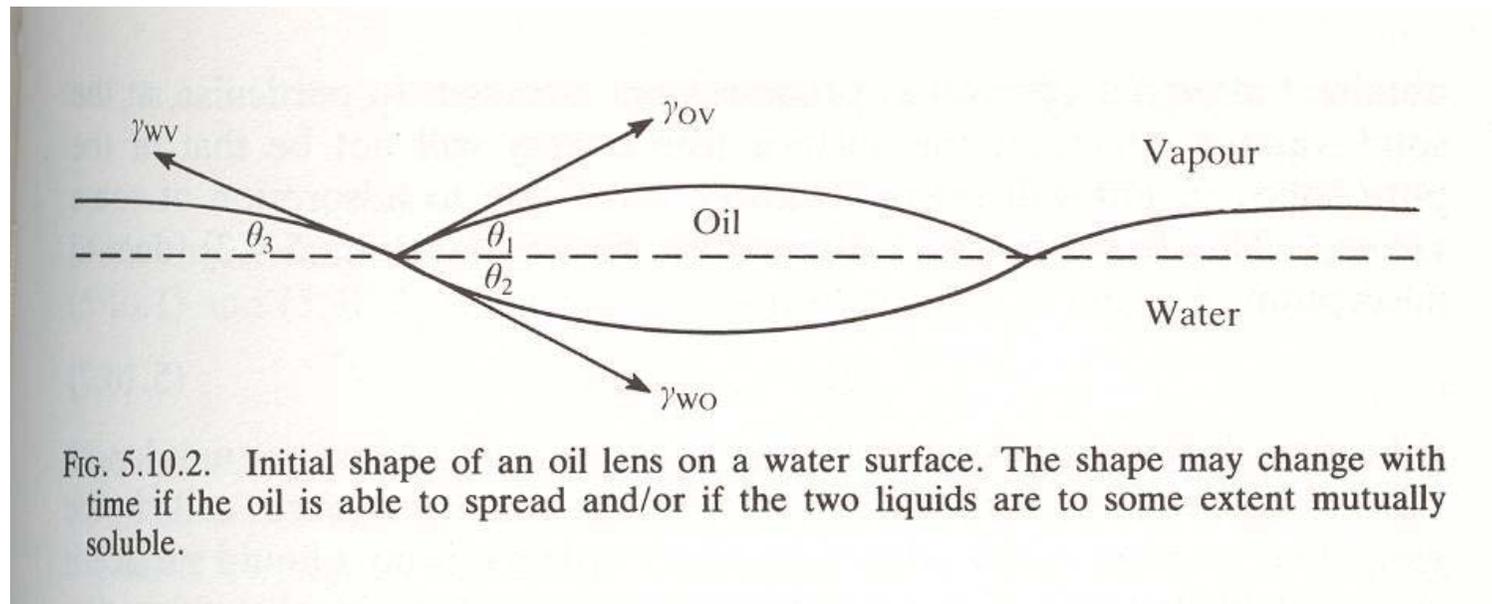

Figure 5: A droplet takes up the dust covering a lotus leaf.

(From http://www.botanik.uni-bonn.de/system/lotus/en/prinzip_html.html).

Text from Stanley Lai's BSc ISM report 2003

Wetting of liquid surfaces

When an oil does not wet water,
a tiny drop of oil has the shape of a lens

FIG. 5.10.2. Initial shape of an oil lens on a water surface. The shape may change with time if the oil is able to spread and/or if the two liquids are to some extent mutually soluble.

The angles are determined by force balance
in both horizontal and perpendicular direction

Spreading coefficient

air $\quad\quad\quad\quad\quad\quad\quad \gamma_{ow}$

oil

water $\quad\quad\quad\quad\quad \gamma_{oa} \quad \gamma_{wa}$
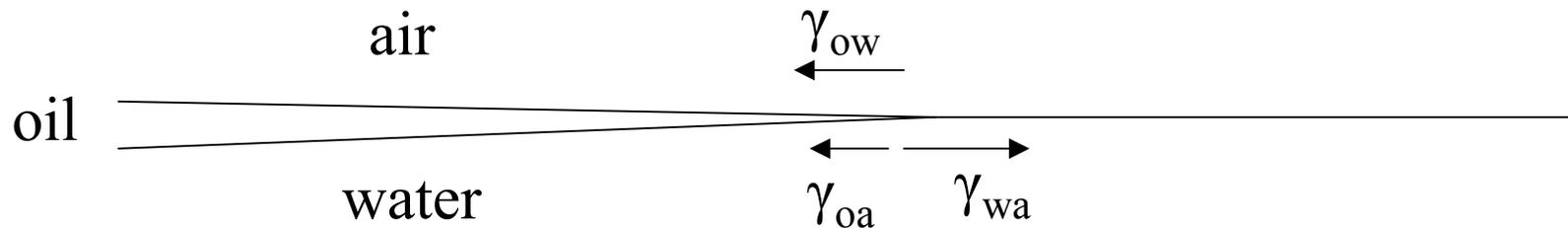
When the lense is very thin, all the contact angles
are very small, and we are left with forces in horizontal direction
only

The *spreading* coefficient S is defined as
$$S = \gamma_{wa} - (\gamma_{oa} + \gamma_{ow})$$
S > 0: the oil spreads into a thin film (complete wetting)
S < 0: the oil will spread into a lens of finite size
(incomplete wetting)

Wetting of liquids

Example: we add a drop benzene to the surface of water

Initially, benzene is not dissolved
Surface tensions:
water/air 72.8; benzene/air 28.9; benzene/water 35.0 mN/m
S > 0: spreading
After a short while, benzene leaks out of the spreading
drop onto the water/air
interface, the water/air surface tension drops to 62.4 mN/m
Now S<0, the spreading stops, and the oil retracts to a lens

The soup, sea and the pond

- explain the oil lenses on home-made 'bouillon' soup
- what happens if you add a bit of detergent?

- please explain the observations of Bede and Franklin

This ends file ISM06