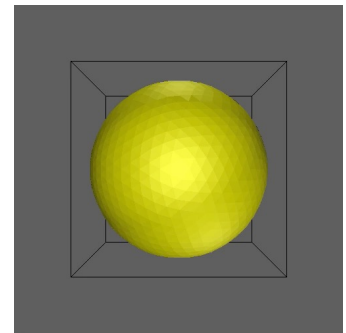
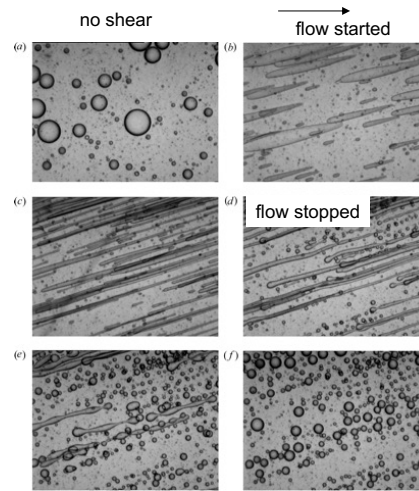


Complex fluids: Interfaces

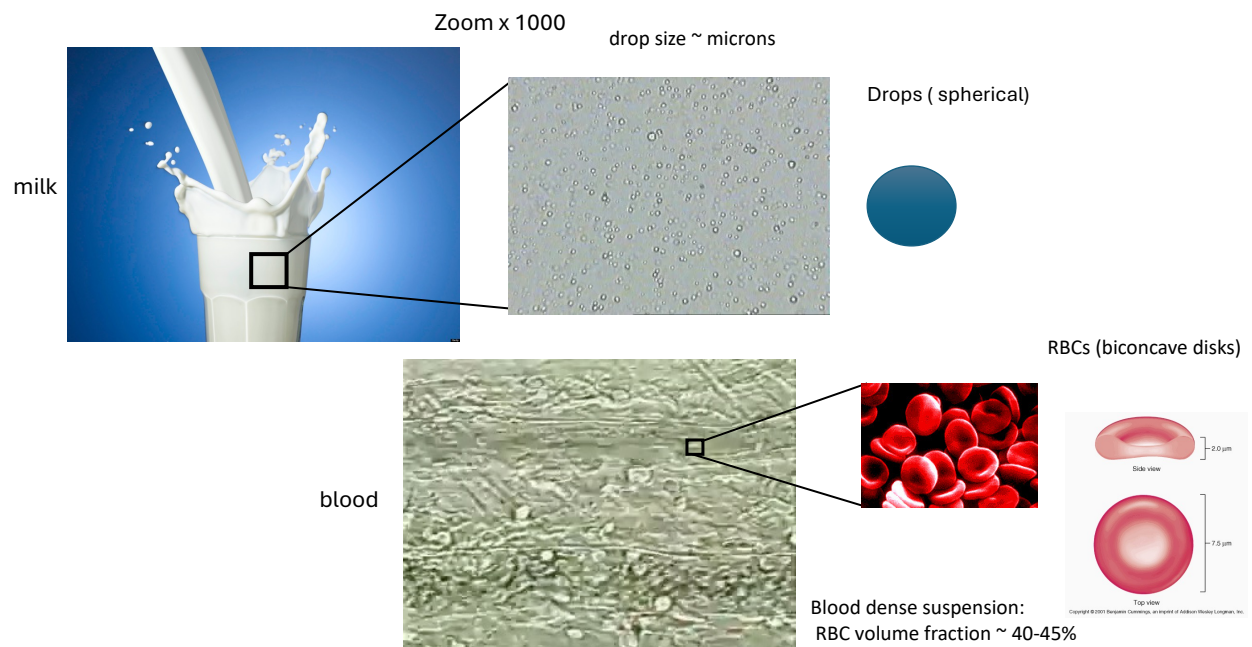
Petia M. Vlahovska
Northwestern University



Iza&Bousmina (2000)

1

Complex fluids/soft materials are structured



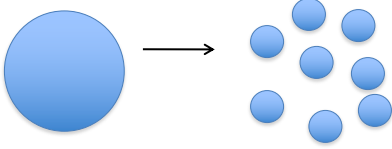
2

large surface to volume ratio

↕

unstable

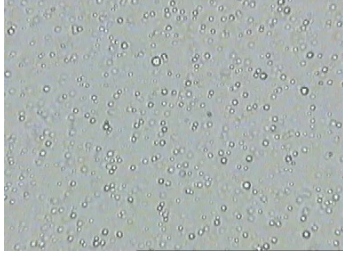
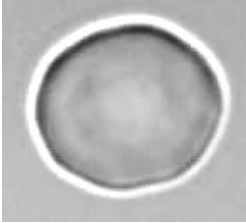
example: Take a sphere, chop it in N spheres,
same volume but area increases ?? fold



thermal noise is important

↕

Brownian motion, fluctuations

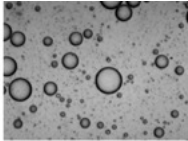
<https://www.youtube.com/watch?v=VwhNLaRCD-4>
 video Timo Betz
 Turtler et al. Nature Physics (2016)

deformable microstructure

↕

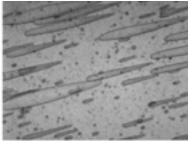
nonlinear response
(viscoelasticity,
non-Newtonian fluid mechanics,
nonlinear elasticity)

no shear



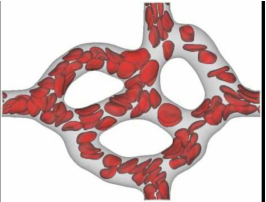
(mayonnaise spreading)

shear



Iza&Bousmina (2000)

blood flow in the microcirculation



3

Interfaces: simple and complex, statics and dynamics

- “simple” interfaces: surface tension, capillarity
- “complex interfaces”: surfactants, biological membranes, charged interfaces

4

Typical Length Scales, Energies, Forces:**Length:**

1 nm = 10^{-9} m, red blood cells $\sim 10 \mu\text{m} = 3\text{-}5 \times 10^{-6}$ m
 average cell in our body: approx. $50 \mu\text{m}$

Energy:

Thermal energy

$$1 k_B T = 4.16 \times 10^{-21} \text{ J}$$

$$\approx 0.6 \text{ kcal/mol} \approx 0.6 * 4.1868 \text{ kJ/mol}$$

$$= 2.5 \text{ kJ/mol (298K)}$$

$$= 4.1 \text{ pN nm}$$

$$\text{Boltzmann constant } k_B = 1.38 \times 10^{-23} \text{ JK}^{-1}$$

Force:

$$1 \text{ pN} = 10^{-12} \text{ N}$$

C-C bond: approx. $100 k_B T$ stable at room temperature

H-bond: approx. $10 k_B T$

Surface tension:

water/oil $10^{-3} \text{ N/m} \sim 25 k_B T/\text{nm}^2$

“SOFT”

5

What is the shape of a soap bubble?



surface tension keeps drops and bubbles spherical

What is surface tension?

How do describe and determine shapes?

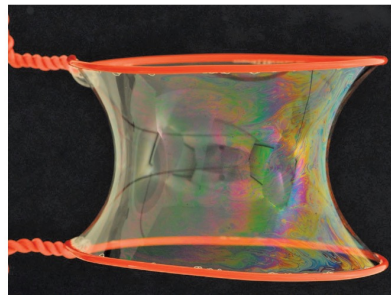


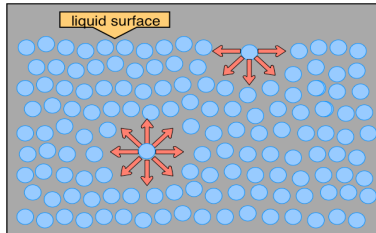
Figure 1. A minimal surface, like this soap film, is characterized by the property that small pieces minimize area for given boundary.

6

Surface tension

Surface tension can be interpreted both as surface energy per unit area (thermodynamic definition) and as a force per unit length (mechanical definition)

Surface tension as unbalanced intermolecular force



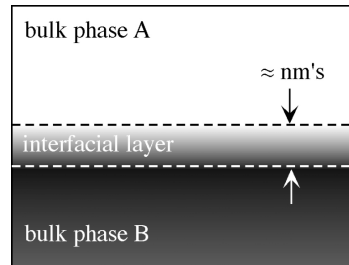
in the bulk: no net force on a molecule
at the surface: imbalance

=> stretched-membrane effect
water/air = 70 mN/m

$$\sigma \sim \frac{A}{b^2}$$

Hamaker constant
molecule size

Surface tension as pressure deficit in the interfacial layer



Interfaces are not sharp

(discuss Gibbs dividing surface)

For a flat surface

$$\sigma = \int_{-\infty}^{\infty} (p_N - p_T) dz \quad (\text{Bakker equation})$$

7

① Gibbs dividing surface (GDS)

Definition:
location of the GDS
 $z=0$ such that
 $\int_{-\infty}^0 (p(z) - p_m) dz + \int_0^{\infty} (p(z) - p_m) dz = 0$

② Hydrostatic definition of surface tension

In the vicinity of the interface pressure is nonisotropic

$$\underline{P} = \begin{pmatrix} P_T(z) & 0 & 0 \\ 0 & P_N(z) & 0 \\ 0 & 0 & P_N(z) \end{pmatrix}$$

at equilibrium $\nabla \cdot \underline{P} = 0 \Leftrightarrow \frac{\partial P_i}{\partial x_i} = 0$

$$\Rightarrow \frac{\partial P_T(z)}{\partial x} = 0 \quad \frac{\partial P_N(z)}{\partial y} = 0 \quad (\text{trivial})$$

$$\frac{\partial P_N(z)}{\partial z} = 0 \Rightarrow P_N = \text{const} = P_m$$

Fig. 2. A schematic of the pressure tensor distribution $\underline{P}$ as a function of the distance to the equilibrium dividing surface for a flat surface (see text at 6.3.3). (note: according to Eqs (3.15), (3.16), results of Cussler and Fortner (13))

define $\Delta p = P_N - P_T(z)$ characterizes the anisotropy of the pressure tensor

real force $\int_{-a}^a P_T(z) dz = \int_{-a}^a P_N dz - b \sigma$

force in the idealized system $\Rightarrow \sigma = \int_{-a}^a (P_N - P_T(z)) dz$

③ Laplace law

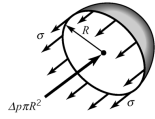
④ Mechanical equilibrium for general surface

assume that the patch is so small that $\hat{n}$ is the same everywhere. The calculation is in the lecture notes.

8

curved interface:

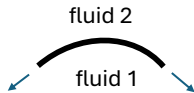
$$2\pi R\sigma = \pi R^2 (p_{in} - p_{out})$$



Laplace's law

$$\Delta p = \frac{2\sigma}{R}$$

What if the interface is not a sphere????



$$\frac{dt}{ds} = -H\mathbf{n}$$

$$\frac{dn}{ds} = H\mathbf{t} \leftrightarrow H = \nabla_s \cdot \mathbf{n}$$

$$f ds = \sigma(s+ds)\mathbf{t}(s+ds) - \sigma(s)\mathbf{t}(s)$$

$$\mathbf{f} = \frac{d}{ds}(\sigma\mathbf{t})$$

This local force is balanced by the jump in hydrodynamic traction,

$$\mathbf{f} + (\mathbf{T}_2 - \mathbf{T}_1) \cdot \mathbf{n} = 0$$

note: normal points into 2

Mechanics of interfaces: surface tension

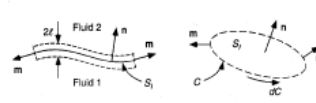


Figure 1: Figure from Dean "Analysis of Transport Phenomena"

Consider a surface area with normal $\mathbf{n}$. Conservation of momentum at the interface shows that inertia is negligible (due to its thinness, the interface mass is negligible). The mechanical equilibrium at the interface then reads

$$\int_S (\mathbf{T}_2 - \mathbf{T}_1) \cdot \mathbf{n} dS = \int_C \mathbf{f}_s dC \quad (4)$$

$(\mathbf{T}_2 - \mathbf{T}_1) \cdot \mathbf{n}$ is the jump in the bulk hydrodynamic stress. $\mathbf{f}_s$ are interfacial forces (surface tension, viscoelastic stresses, bending, etc...)

For an interface with surface tension $\mathbf{f}_s = \sigma \mathbf{n}$, $\mathbf{n} = \mathbf{t} \times \mathbf{n}$

$$\int_C \mathbf{f}_s dC = \int_S [(\mathbf{n} \times \nabla) \times (\sigma \mathbf{n})] dS \quad (5)$$

$$(\mathbf{n} \times \nabla) \times (\sigma \mathbf{n}) = (\sigma \nabla \cdot \mathbf{n}) \mathbf{n} - \nabla_s \sigma, \quad \nabla_s = (\mathbf{I} - \mathbf{n} \mathbf{n}) \cdot \nabla$$

Proof:

$$[(\mathbf{n} \times \nabla) \times (\sigma \mathbf{n})]_i = \varepsilon_{ijk} (\mathbf{n} \times \nabla)_j (\sigma n_k) = \varepsilon_{ijk} \varepsilon_{jpl} n_l \frac{\partial}{\partial x_q} (\sigma n_k) = \varepsilon_{ijk} \varepsilon_{jpl} n_l n_k \frac{\partial \sigma}{\partial x_q} + \varepsilon_{ijk} \varepsilon_{jpl} n_l \sigma \frac{\partial n_k}{\partial x_q} =$$

using that $\varepsilon_{ijk} = \varepsilon_{jki}$ and

$$\varepsilon_{jkl} \varepsilon_{jpq} = \delta_{kp} \delta_{lq} - \delta_{kq} \delta_{lp}$$

leads to

$$= n_k n_l \frac{\partial \sigma}{\partial x_l} + \sigma n_k \frac{\partial n_k}{\partial x_l} - n_l n_k \frac{\partial \sigma}{\partial x_k} - \sigma n_l \frac{\partial n_k}{\partial x_k} = [(\mathbf{I} - \mathbf{n} \mathbf{n}) \cdot \nabla \sigma + \sigma \mathbf{n} \cdot \nabla \mathbf{n} - \sigma \mathbf{n} \nabla \cdot \mathbf{n}]_i$$

note that $\mathbf{n} \cdot \nabla \mathbf{n} = 0$ because $\nabla(\mathbf{n} \cdot \mathbf{n}) = 0$

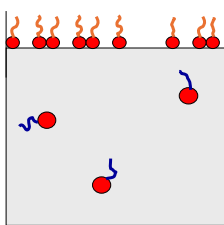
Thus

$$(\mathbf{T}_2 - \mathbf{T}_1) \cdot \mathbf{n} = (\sigma \nabla \cdot \mathbf{n}) \mathbf{n} - \nabla_s \sigma \quad (6)$$

9

Note: at equilibrium surface tension is uniform, and there are no gradients. If surface tension is nonuniform (e.g. due to temperature or surfactant nonuniformities) this drives flow

Surfactants: adsorb at interfaces and lower surface tension



a)

Amphiphilic molecules

Surfactant

● Polar head (likes water)

○ Oil-like tail (hates water)

Lipid

● Polar head

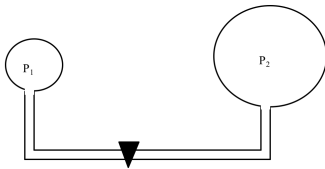
○ Fatty acid chains

Copolymer

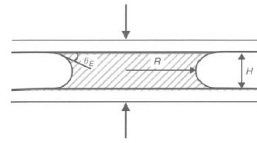


10

Questions:

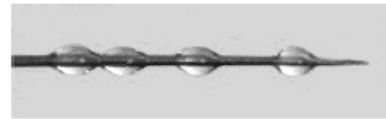


Two bubbles are connected by a tube.
What happens when you open the valve?



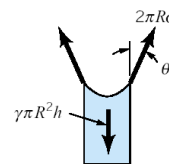
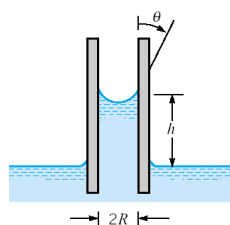
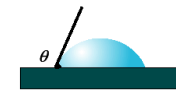
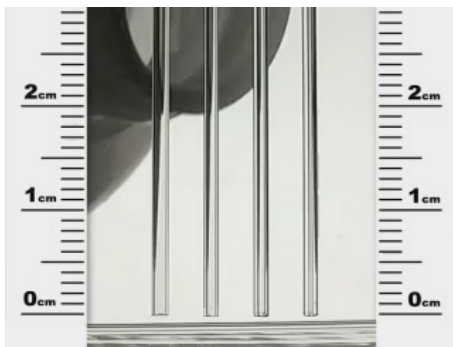
Capillary adhesion: Two wetted surfaces can
adhere strongly if the liquid wets both surfaces.
Estimate the force

Self-propelling drop. (see paper by Lorenceau and Quere "Drops on a
conical wire", J. Fluid Mech. 2003)
An asymmetric capillary device may prompt spontaneous drop
propulsion. An example of such
motion is illustrated in the Figure. A drop of silicone oil is deposited on a
conical copper wire (mean radius of 250 μm), whose radius increases
from the right to the left with a gradient dr/dz of the order of 1 %. Note
that silicone oil totally wets copper. Four successive photographs are
taken. The time interval between two snapshots is about 1 second.



In which direction does the drop move?

11



$$h = \frac{2\sigma \cos \theta}{\rho g R}$$

What if the liquid is nonwetting?



but why is the interface curved?

12

12

Wetting and contact angle

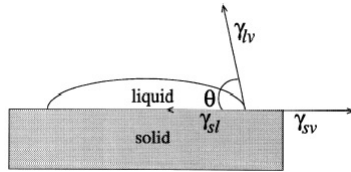
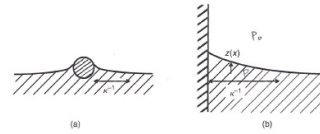
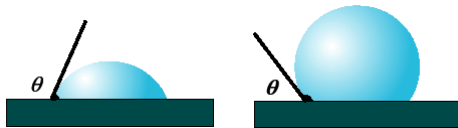


Fig. 1. Schematic of a sessile-drop contact angle system.

Kwok and Neumann, 1999

$$\gamma_{lv} \cos \theta_Y = \gamma_{sv} - \gamma_{sl}$$

Young's relation

FIGURE 2.2. A small floating object (a) or a wall (b) perturbs the surface of the liquid over a distance κ^{-1} called the "capillary length."

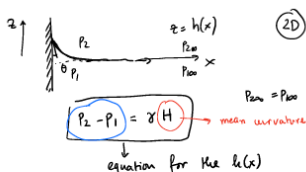
(de Gennes book)

Show that

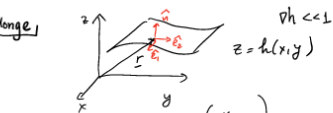
$$z(x) \sim \exp(-z\kappa)$$

(in axisym geometry – Bessel functions!)

13



Monge



$$\hat{e}_1 = \frac{\partial \mathbf{r}}{\partial x} = \begin{pmatrix} 1 \\ 0 \\ \frac{\partial h}{\partial x} \end{pmatrix}, \quad \hat{e}_2 = \frac{\partial \mathbf{r}}{\partial y} = \begin{pmatrix} 0 \\ 1 \\ \frac{\partial h}{\partial y} \end{pmatrix}$$

$$\hat{n} = \frac{\hat{e}_1 \times \hat{e}_2}{|\hat{e}_1 \times \hat{e}_2|} = \frac{\begin{pmatrix} \frac{\partial h}{\partial x} \\ \frac{\partial h}{\partial y} \\ 1 \end{pmatrix}}{\sqrt{1 + \left(\frac{\partial h}{\partial x}\right)^2 + \left(\frac{\partial h}{\partial y}\right)^2}}$$

$$\hat{n} = \begin{pmatrix} \frac{\partial h}{\partial x} \\ \frac{\partial h}{\partial y} \\ 1 \end{pmatrix} \frac{1}{\sqrt{1 + \left(\frac{\partial h}{\partial x}\right)^2 + \left(\frac{\partial h}{\partial y}\right)^2}}$$

<https://www.cmu.edu/biolphys/deserno/pdf/meniscus.pdf>

$$H = \nabla \cdot \hat{n} = \frac{\partial^2 h}{\partial x^2} + \frac{\partial^2 h}{\partial y^2} + \frac{\partial^2 h}{\partial z^2}$$

$$H = -\frac{\partial^2 h}{\partial x^2} - \frac{\partial^2 h}{\partial y^2}$$

$$p_2 - p_1 = -\gamma \left(\frac{\partial^2 h}{\partial x^2} + \frac{\partial^2 h}{\partial y^2} \right)$$

$$\frac{\partial^2 h}{\partial x^2} - \frac{\partial^2 h}{\partial y^2} = 0$$

tension is denoted by γ

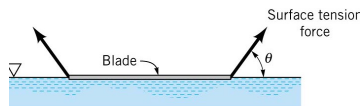
$$h(x) = A e^{-x/\ell_c} + B e^{x/\ell_c}$$

$$h(x) = A e^{-x/\ell_c} \quad \text{thw} \rightarrow \text{find } A$$

14



Q: The razor blade is heavier than the water. Why does it float?



15

The cheerios effect



16

The 'Cheerio Effect'

Dominic Vella and L. Mahadevana, Am. J. Phys. **73** 9, September 2005

FLOTATION FORCES
(effect driven by gravity)

(a) $\sin\psi_1\sin\psi_2 > 0$

IMMERSION FORCES
(effect driven by wetting)

(b) $\sin\psi_1\sin\psi_2 < 0$

(c) $\sin\psi_1\sin\psi_2 < 0$

(c) $\sin\psi_1\sin\psi_2 < 0$

(d) $\sin\psi_1\sin\psi_2 < 0$

(d) $\sin\psi_1\sin\psi_2 < 0$

(e) flotation forces disappear
for $R < 5 \mu\text{m}$

(e) flotation forces disappear
for $R < 5 \mu\text{m}$

(f) immersion forces exist
even for $R \approx 1 \text{ nm}$

(f) immersion forces exist
even for $R \approx 1 \text{ nm}$

P.A. Kralchevsky, K. Nagayama "Advances in Colloid and Interface Science" 85 (2000) 145-192

Figure 1. Photograph of the 2D array growth: the tracks of the particles rushing toward ordered phase are seen.

Denkov, N.; Velev, O.; Kralchevsky, P.; Ivanov, I.; Yoshimura, H.; Nagayama, K. (1992). "Mechanism of formation of two-dimensional crystals from latex particles on substrates". *Langmuir* 8: 3183

<https://www.youtube.com/watch?v=NlcNrsTlbVU>

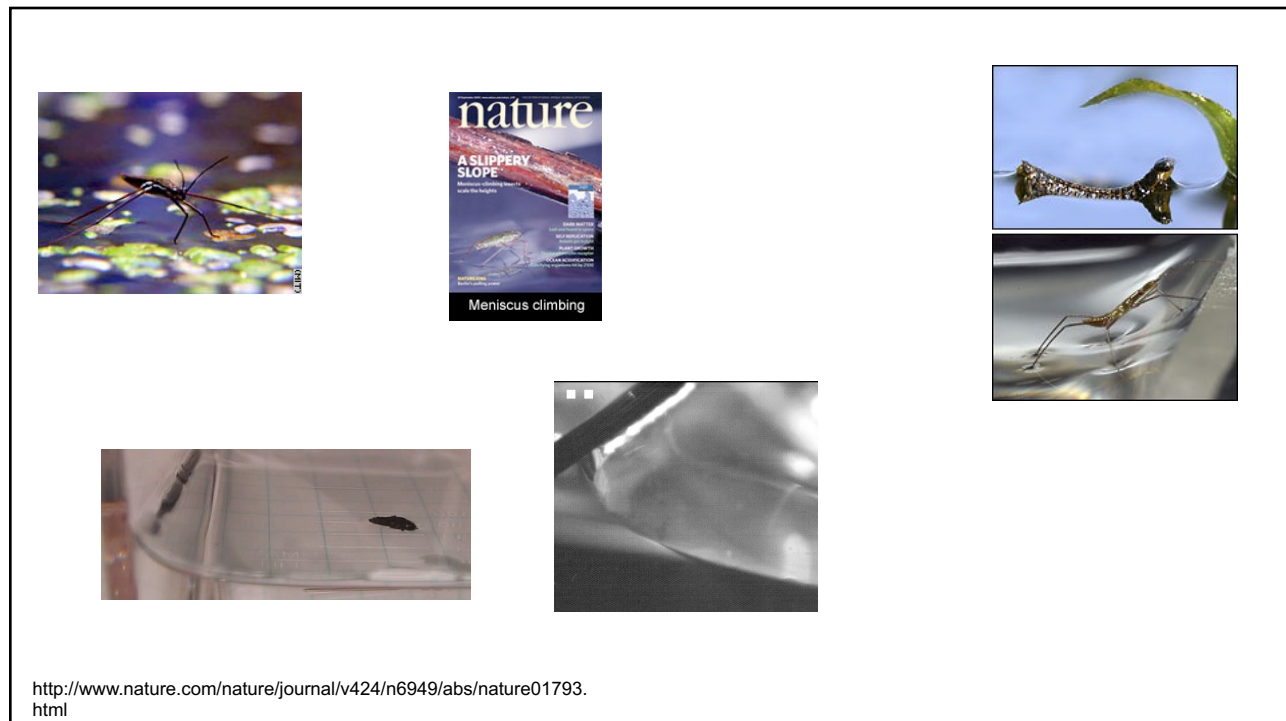
17

Fig. 1. Schematic of a curved oil–water interface with slope $-\tan \psi$ formed around a circular micropost. Cylindrical microparticles sediment through the oil phase, attach to the interface, and create deformations that interact with the interface curvature field. (Inset) Top view of the micropost with polar coordinates (r, θ) and of the particle-induced deformation, approximated as a quadrupole. The angle ϕ_p indicates the orientation of the quadrupolar rise axis, represented as a two-headed arrow. The angle ϕ indicates the orientation of the principal axis of curvature.

Cavallaro et al Curvature-driven capillary migration and assembly of rod-like particles PNAS 2011

18

9



19

Liquid interfaces are under tension → "Shape" of foam

For the intersection of soap film lamellae in a foam all tensions are the same, hence the angle is 120

Fruit fly eye

Physical modeling of cell geometric order in an epithelial tissue
Hilgenfeldt et al, PNAS 2008

Fig. 2. Nomenclature and geometry of the modeled ommatidium. Indicated are the C1 (anterior and posterior cone), C2 (equatorial and polar cone), and P (primary pigment) cells, and the angles α for the upper-right quadrant. The edge between the two C2 cells has length L_{C2} , and the widths of the secondary pigment cells attached to one (or two) C1 cells are shown. All edges carry E-cadherin, whereas the edges between C cells (blue) carry both E- and A-cadherin.

20

Note on geometry:

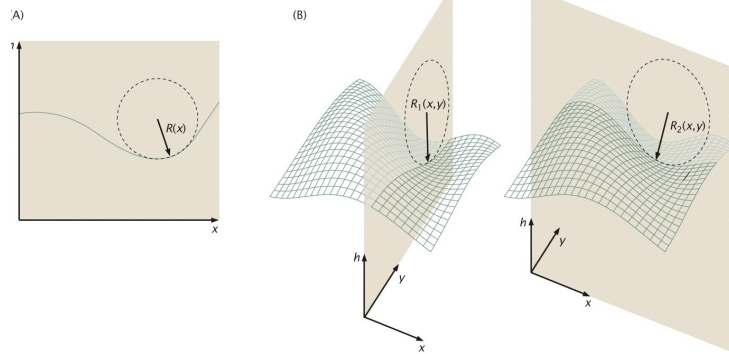


Figure 11.15 Physical Biology of the Cell, 2ed. (© Garland Science 2013)

Giomi, 2013 review

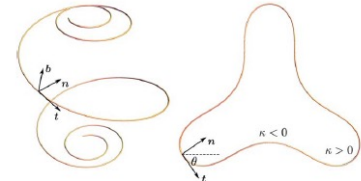


Fig. 1 Example of the Frenet frame in three (left) and two (right) dimensions. In three dimensions the curvature κ is conventionally taken with the positive sign and the normal vector n is directed toward the center of curvature. If a closed plane curve is oriented counterclockwise, on the other hand, n is directed toward the interior of the curve and $\kappa > 0$ ($\kappa < 0$) corresponds to points where the curve is convex (concave).

Frenet frame of the tangent $t = dr/ds$, normal n and binormal vector b is described by the Frenet-Serret formulae:

$$t' = \kappa n, \quad (1a)$$

$$n' = -\kappa t + \tau b, \quad (1b)$$

$$b' = -\tau n, \quad (1c)$$

as well as the following cross-product relationship:

$$t = n \times b, \quad n = b \times t, \quad b = t \times n. \quad (2)$$