Applications of Random Surfaces to Fluid Mixtures

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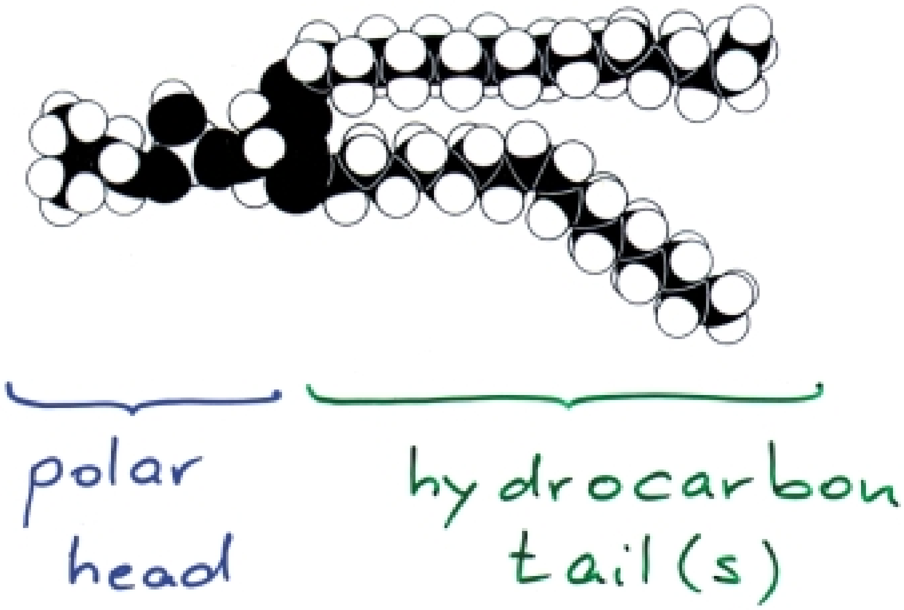
Supramolecular Aggregation

Amphiphiles and lipids

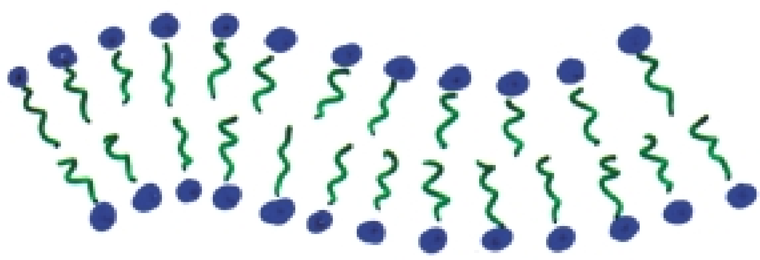


Hydrophobic effect:

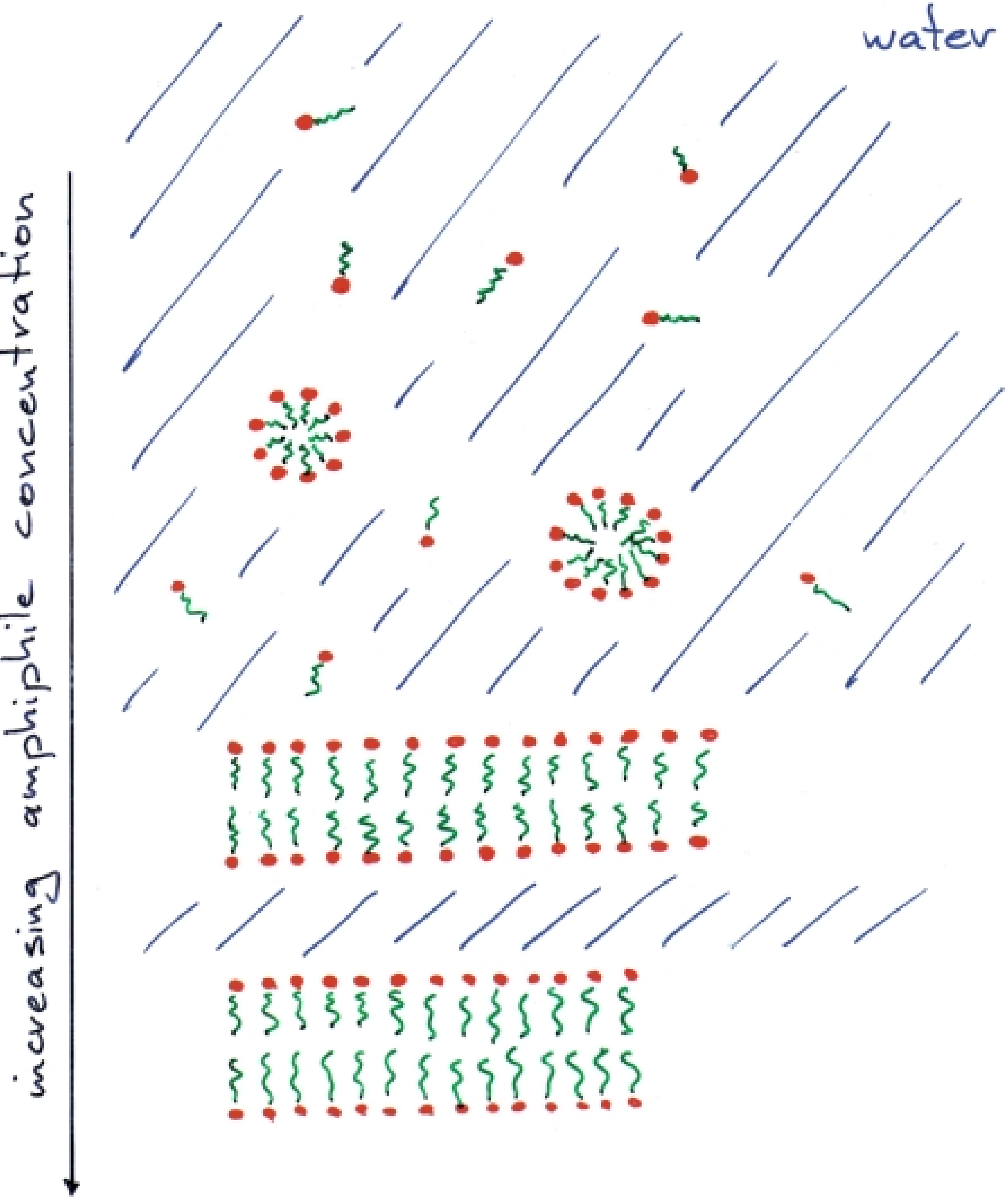
CH - tail wants to avoid contact with water

→ structure formation

membrane

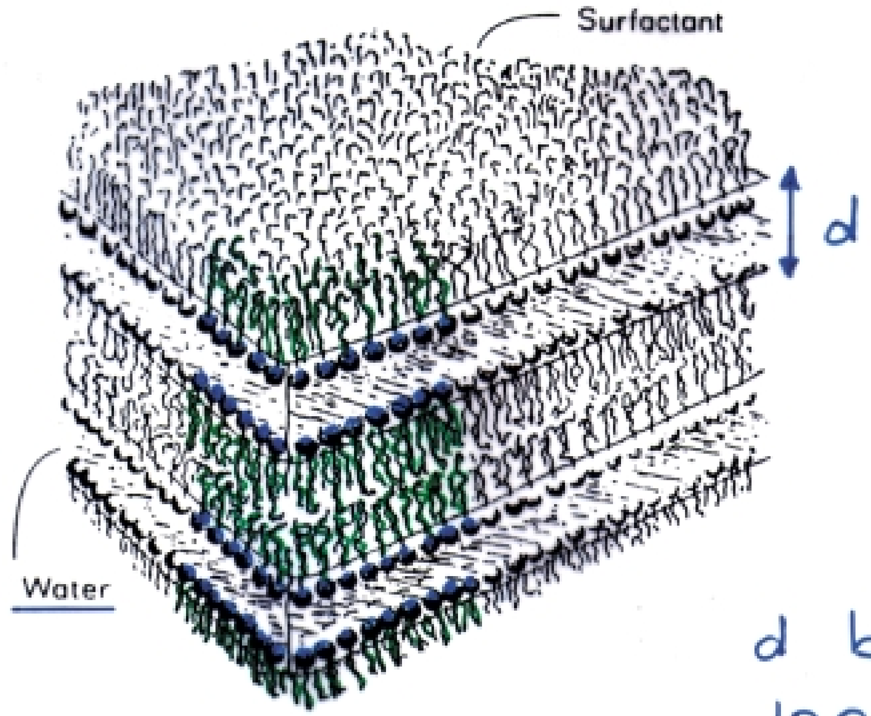


Self-Assembly of Amphiphiles



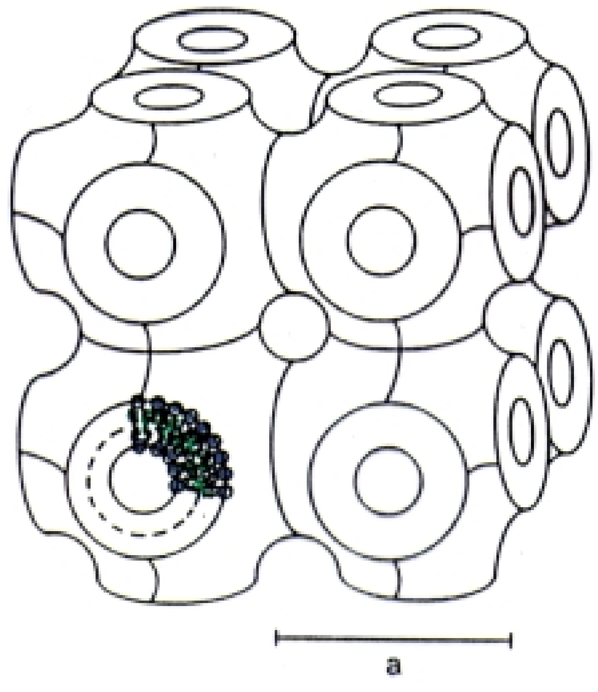
self-assembly into bilayers

Lamellare Phase:



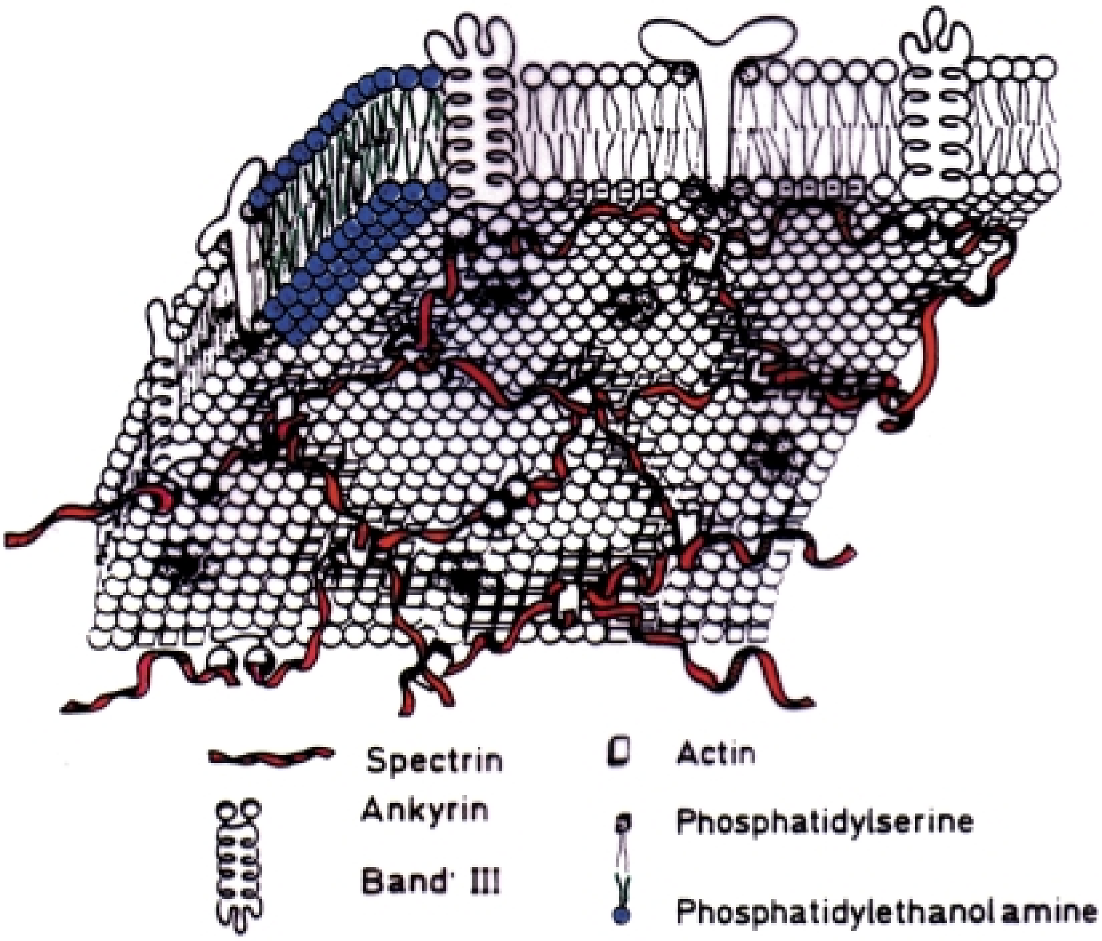
d bis zu 10 000 Å !

Kubisch (bikontinuierliche) Phase:



Biological Membranes

Sackmann et al.



Red Blood Cells
(Erythrocytes)

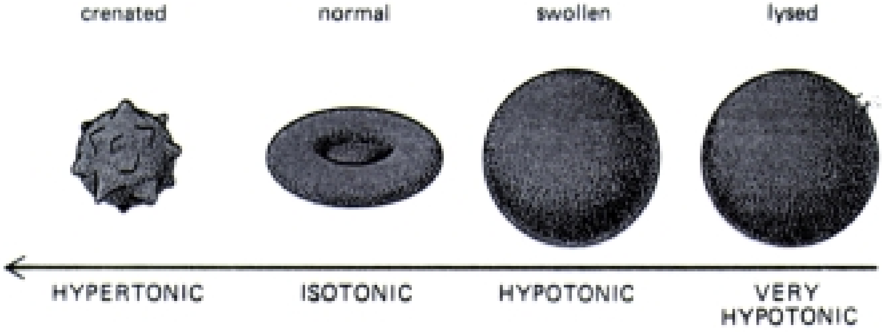


Figure 6–50 **Response of a human red blood cell to changes in osmolarity (also called *tonicity*) of the extracellular fluid.** Because the plasma membrane is freely permeable to water, water will move into or out of cells down its concentration gradient, a process called *osmosis*. If cells are placed in a *hypotonic solution* (i.e., a solution having a low solute concentration and therefore a high water concentration), there will be a net movement of water into the cells, causing them to swell and burst (lyse). Conversely, if cells are placed in a *hypertonic solution*, they will shrink (see also Panel 2–1, p. 47).

cubic
bicontinuous

hexagonal

Lamellar

microemulsion

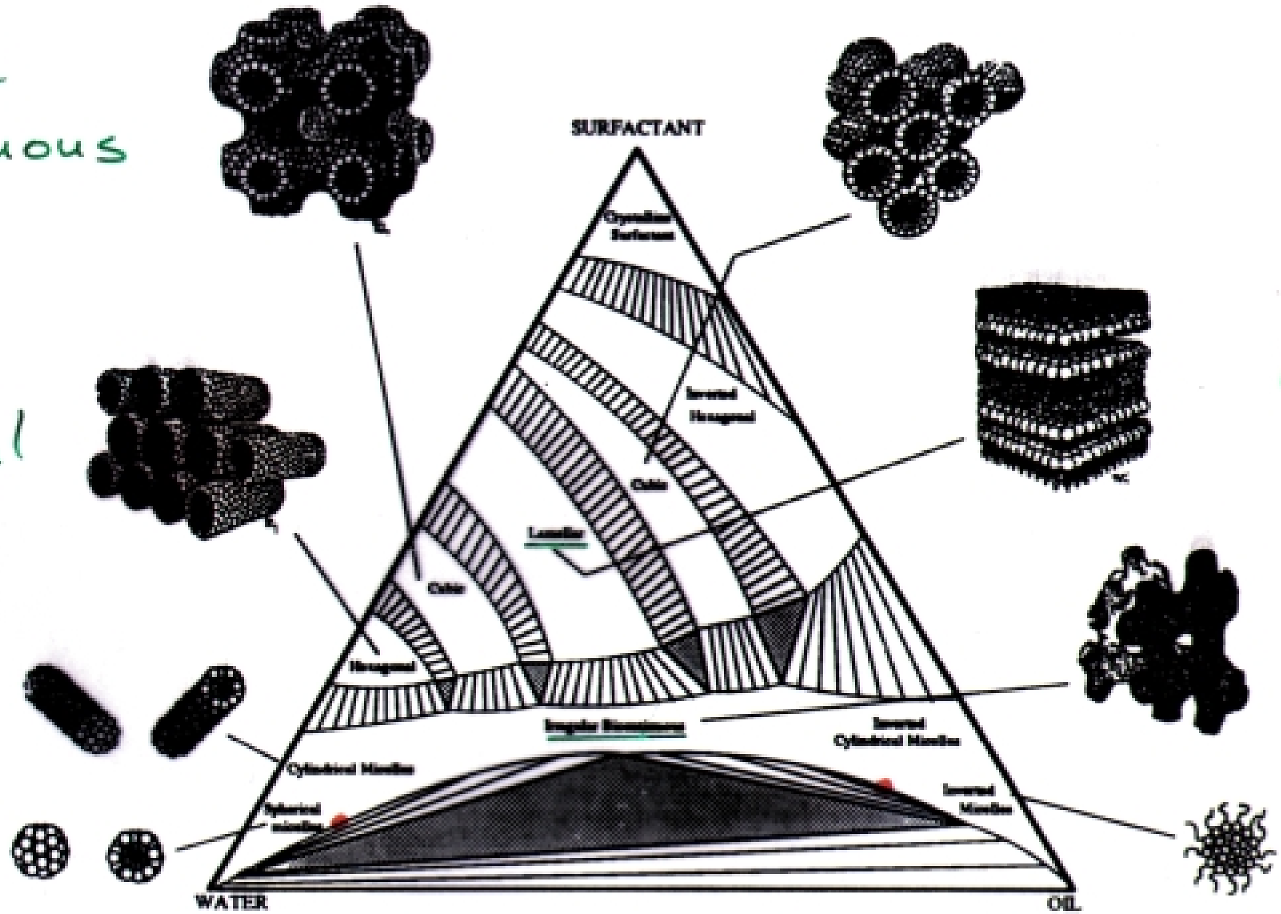
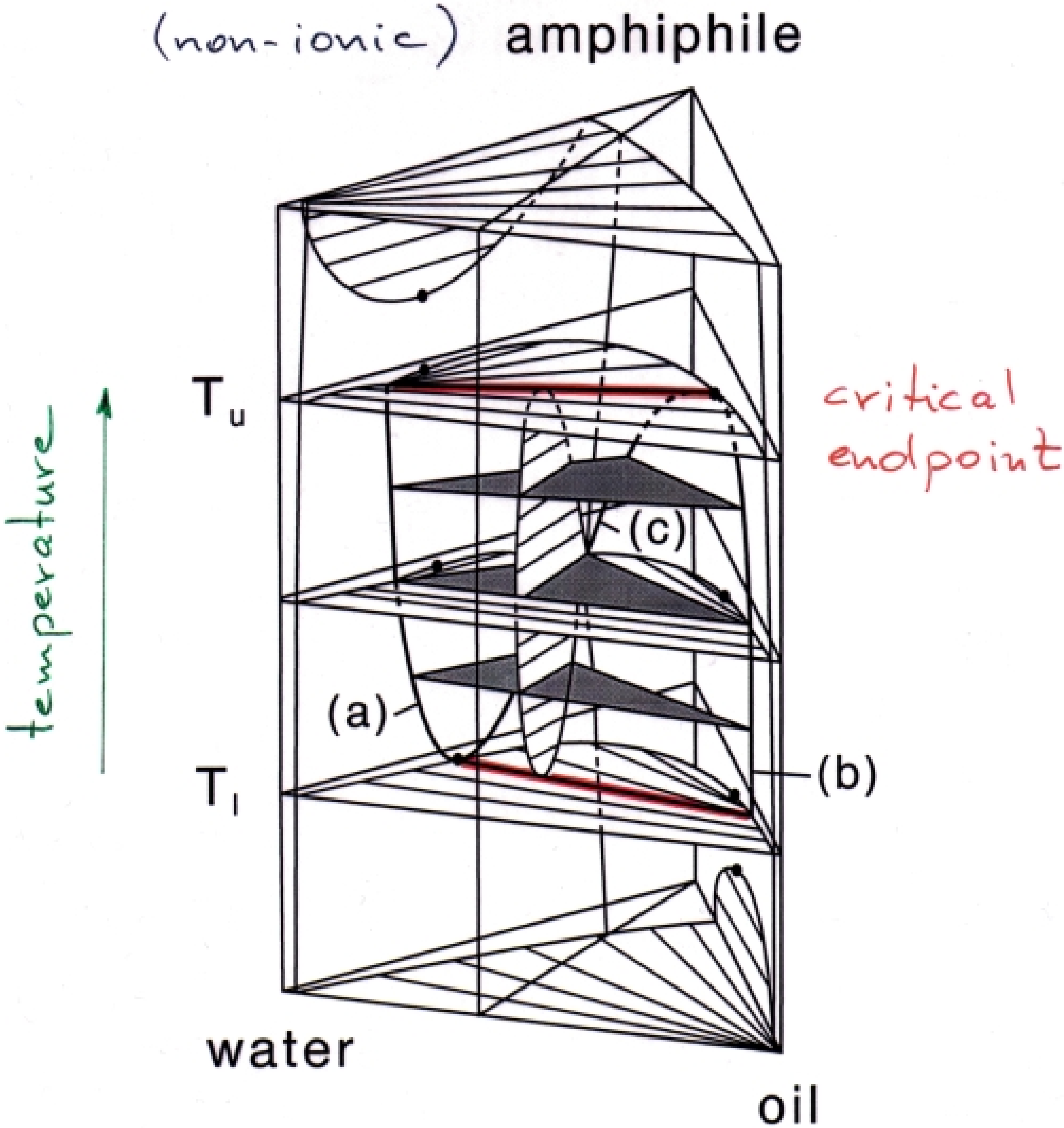


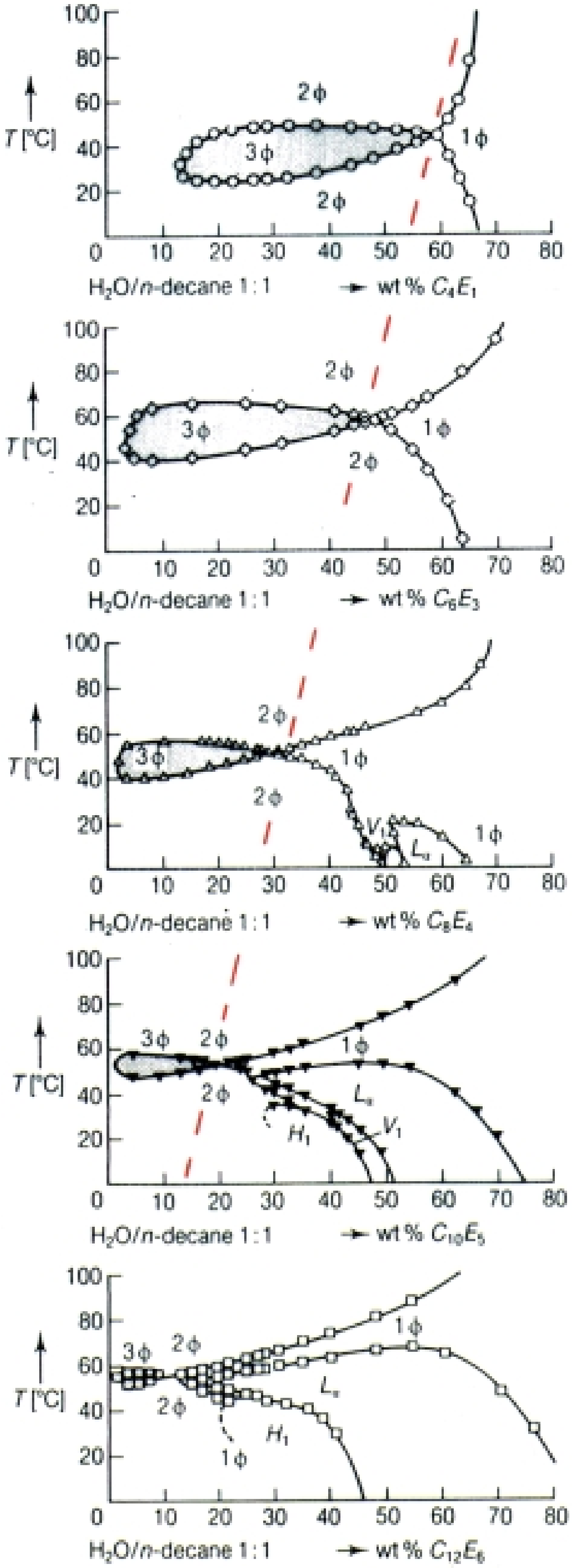
Figure 1. Schematic oil-water-surfactant phase diagram with microstructures depicted. Ref. 12.

(Davis et al. 1987)



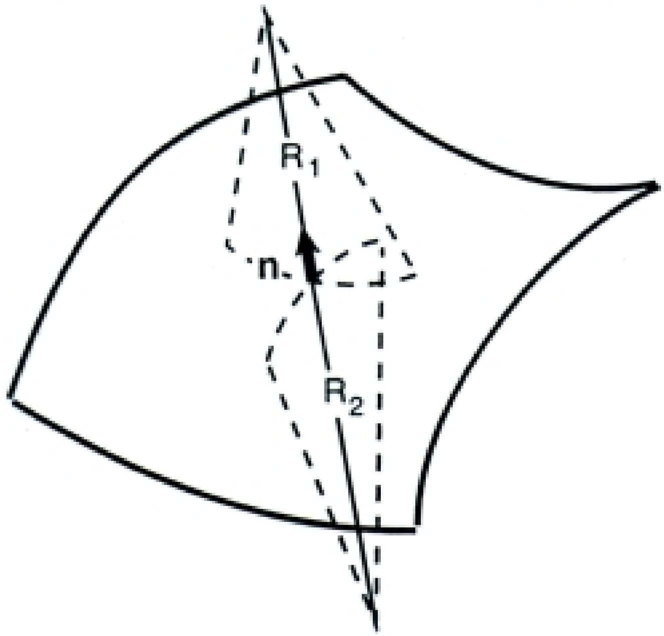
(Kahlweit et al. 1987)

Variation with Amphiphile Length



(Kahlweit et al. 1986)

Shape of membranes controlled by curvature elasticity



Energy:

$$\boxed{E = \int dS \left[\frac{\varkappa}{2} \left(\frac{1}{R_1} + \frac{1}{R_2} \right)^2 + \bar{\varkappa} \frac{1}{R_1 R_2} \right]}$$

$\varkappa$: bending rigidity

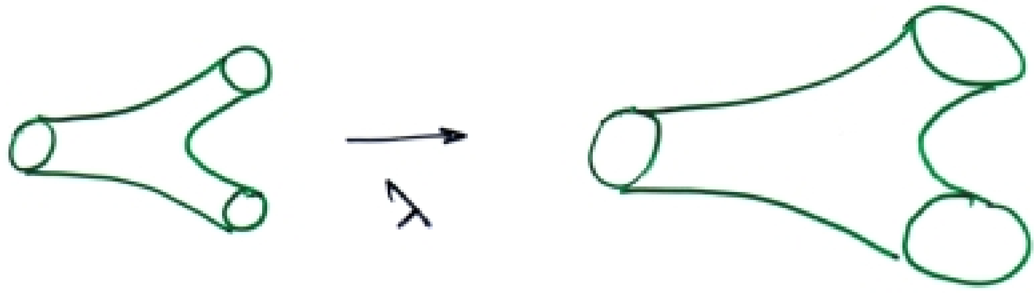
$\bar{\varkappa}$: saddle-splay modulus

(Canham 1970
Helfrich 1973)

Sponge Phases

A Scaling Argument

(Porte et al, 1989)



$$E = \varkappa \int dS\, H^2 \longrightarrow E' = \varkappa \int dS'\, H'^2$$

$$\left(\frac{1}{R_1} + \frac{1}{R_2}\right)^2$$

$$= \varkappa \int \lambda^2 dS\, \frac{1}{\lambda^2} H^2$$

$$\equiv E$$

(conformal invariance!)

Energy density:

$$\phi^{-3} \frac{E}{V} \longrightarrow \phi'^{-3} \frac{E'}{V'} = \phi^{-3} \frac{E}{V}$$

with amphiphile volume fraction

$$\phi = A/V$$

$$\rightsquigarrow \boxed{\frac{E}{V} \sim \phi^3}$$

Sponge Phases II:

The Role of Gaussian curvature

- Curvature energy:

$$\mathcal{H} = \int dS \left[\frac{1}{2} \kappa (c_1 + c_2)^2 + \bar{\kappa} c_1 c_2 \right]$$

Rewrite as

$$\mathcal{H} = \int dS \left[\frac{1}{2} \kappa_+ (c_1 + c_2)^2 + \frac{1}{2} \kappa_- (c_1 - c_2)^2 \right]$$

with: $\kappa_+ = \kappa + \frac{1}{2} \bar{\kappa}$

$\kappa_- = -\frac{1}{2} \bar{\kappa}$

- Stability of lamellar phase:

$$\kappa_+ , \kappa_- > 0$$

Instabilities:

$\kappa_+ = 0$ vesicles

$\kappa_- = 0$ plumber's nightmare

- Fluctuations on small scales

↷ renormalized, scale-dependent rigidities $\varkappa^R, \bar{\varkappa}^R$

$$\boxed{\varkappa^R_\pm(\xi) = \varkappa_\pm - \frac{\alpha_\pm T}{4\pi} \ln\frac{\xi}{a}}$$

with $\quad \alpha_+ = \alpha + \frac{1}{2}\bar{\alpha} = \frac{4}{3}$

$\qquad\quad \alpha_- = \quad -\frac{1}{2}\bar{\alpha} = \frac{5}{3}$

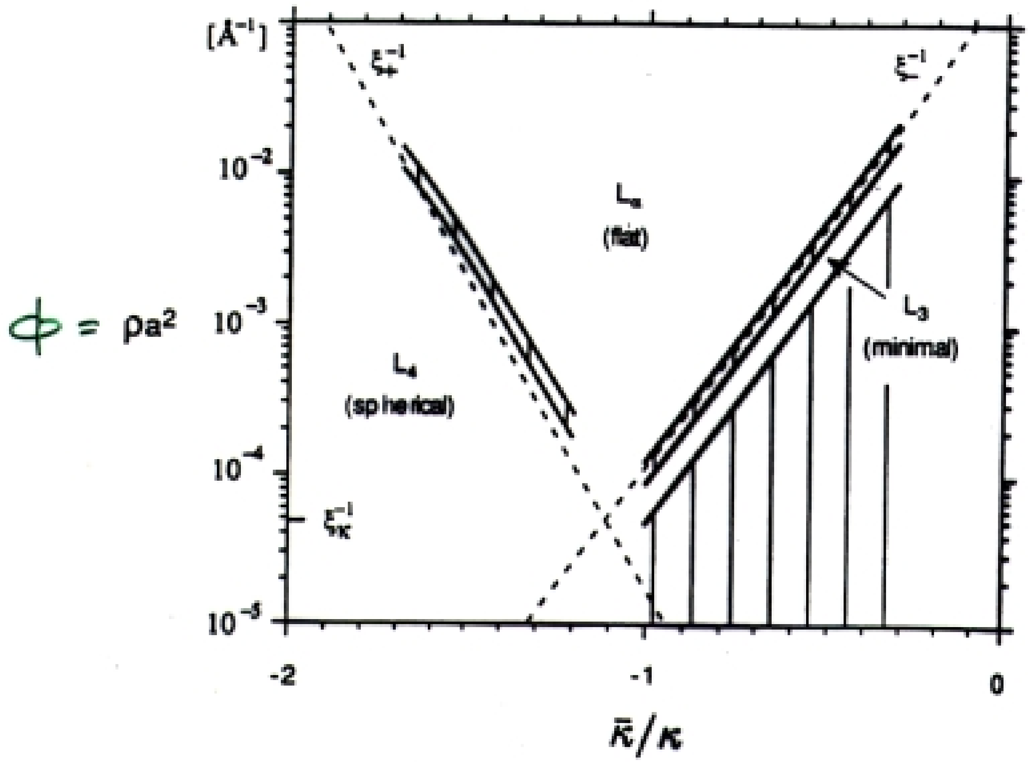
(Peliti & Leibler 1985, David 1989)

Instabilities: $\varkappa^R_\pm(\xi) = 0$

$\xi \sim \phi^{-1}$ ↷ $$\boxed{\ln\phi = -\frac{4\pi}{\alpha_\pm}\,\frac{\varkappa_\pm}{T}}$$

(Morse 1994)

Phase Diagram



(Morse, 1994)

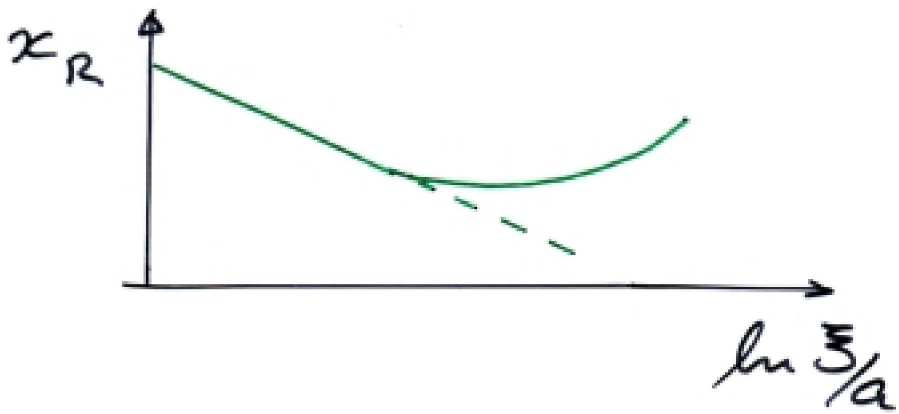
Sponge Phases III : Monte Carlo Simulations

of

Dynamically Triangulated Surfaces

Why simulations?

- Higher-order terms in $\frac{T}{\kappa}$ could stiffen membranes



- Universal value of $\alpha, \bar{\alpha}$

$\alpha = 3 \qquad \bar{\alpha} = \frac{10}{3}$ (Peliti & Leibler '85)

$\alpha = 1 \qquad \bar{\alpha} = 0$ (Helfrich '85)

$\alpha = -1 \qquad \bar{\alpha} = 0$ (Helfrich '98)

- Self-avoidance could stiffen fluid membranes

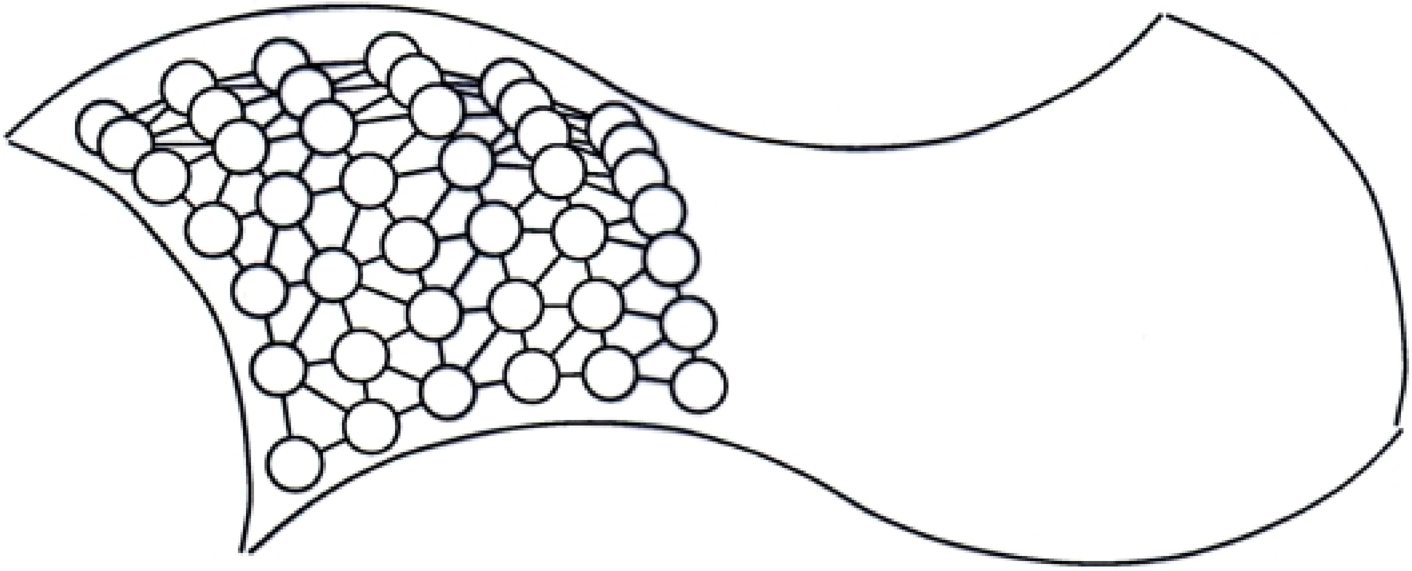
  Compare : crystalline membranes

  Crumpling transition suppressed by self-avoidance

- Test simple instability argument

- Structure and free energy of sponge phases

Dynamically triangulated surfaces

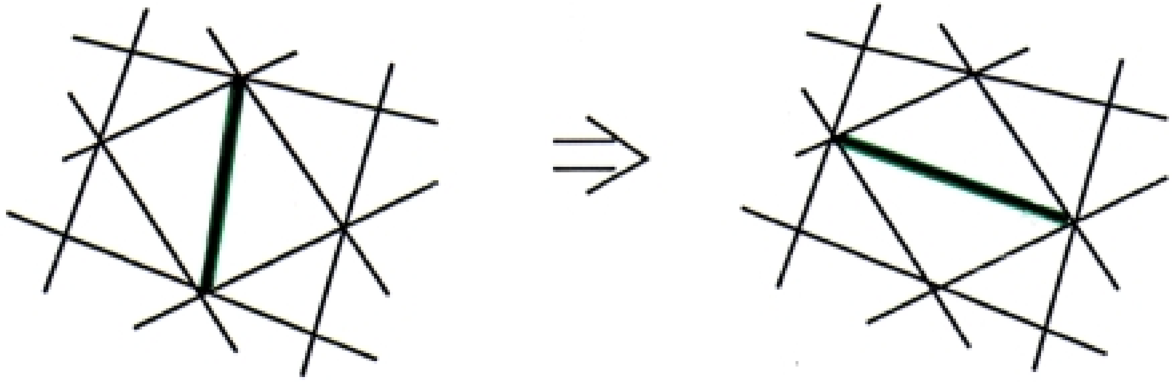


Hard-core radius σ_o

Tether length L: $\sigma_o < L < 1.7\,\sigma_o$

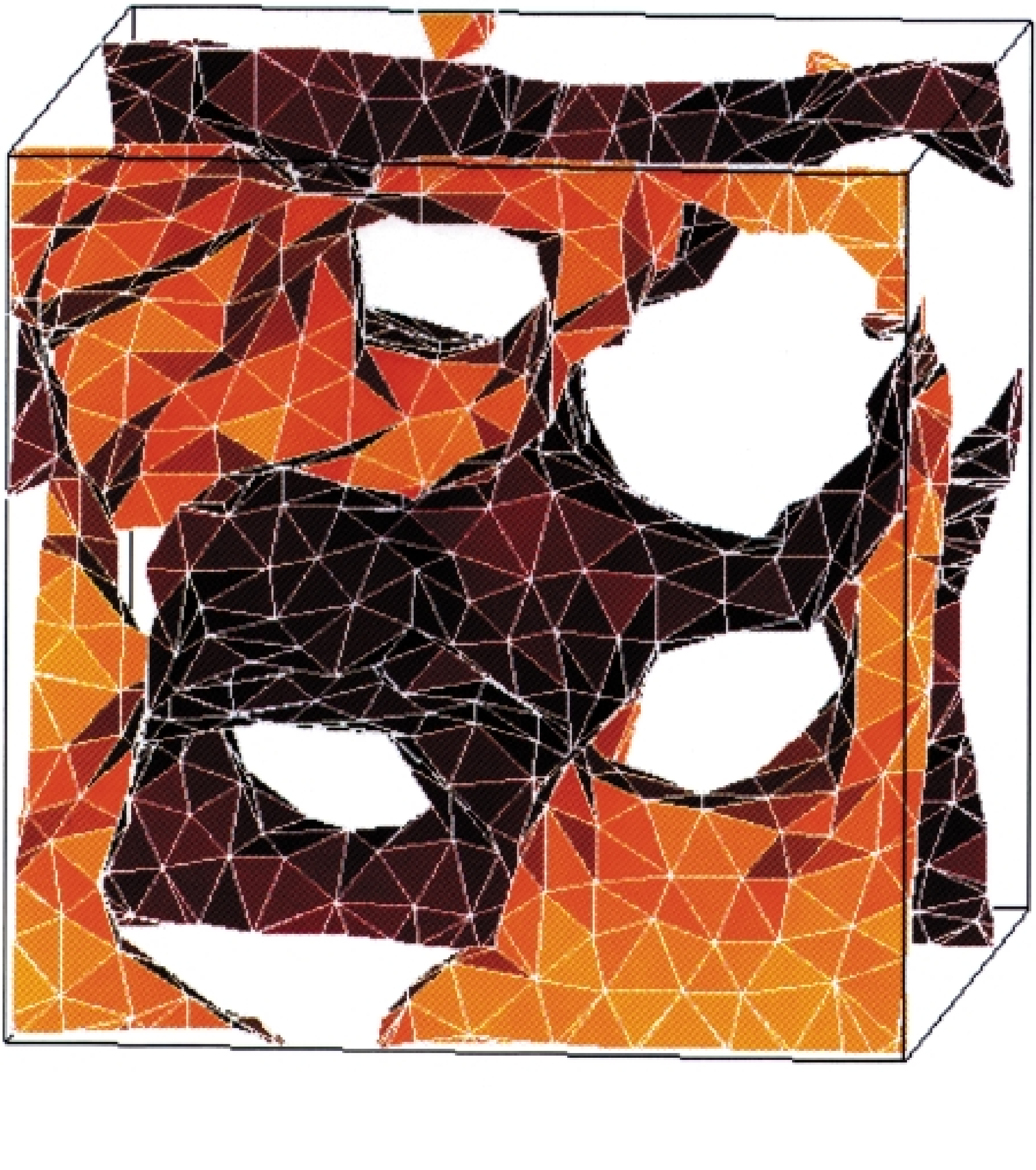
$\rightarrow$ self-avoidance

Dynamic triangulation:



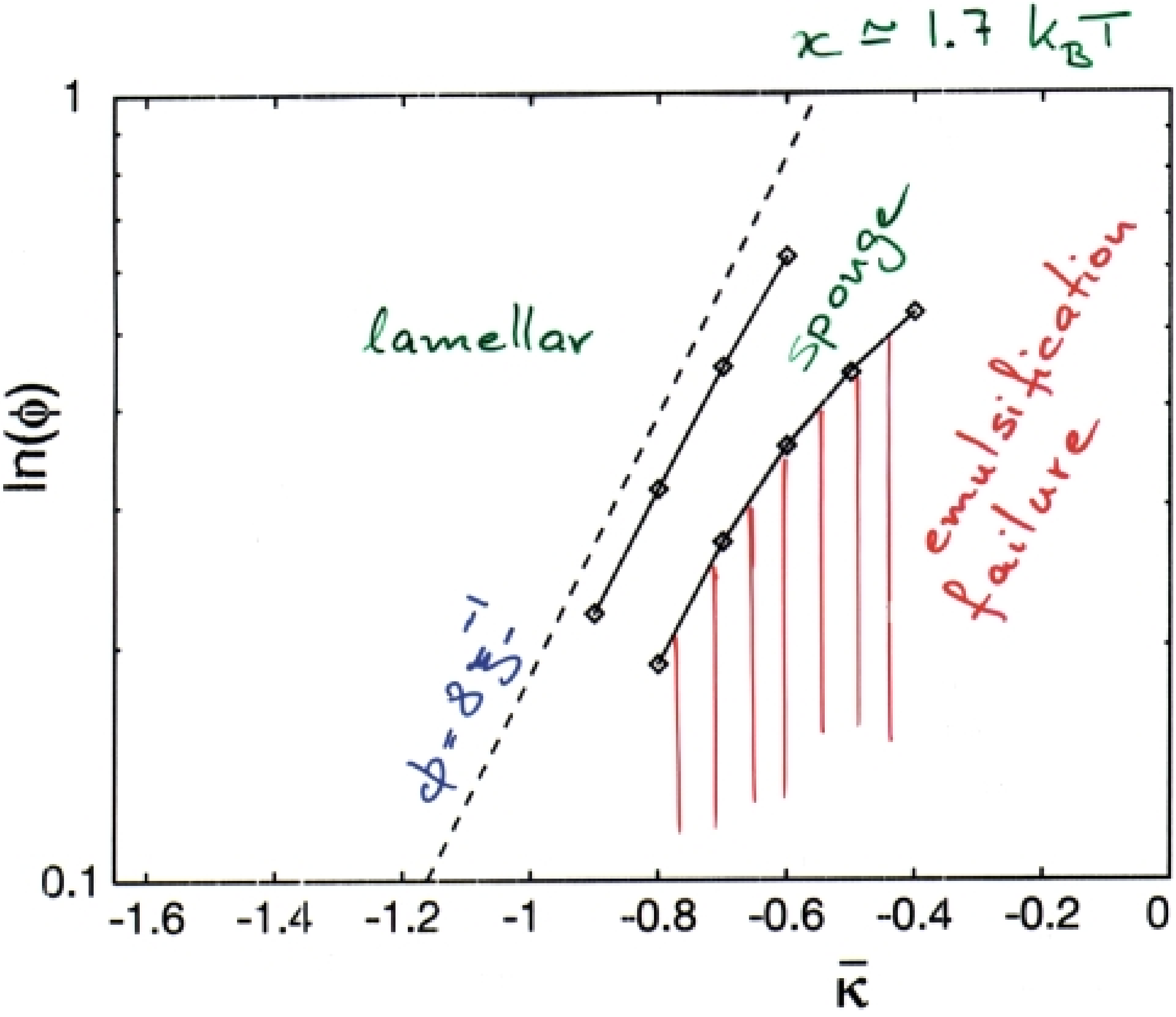
Monte-Carlo step to change topology of a triangulated surface

(a) (b)



Phase Diagram

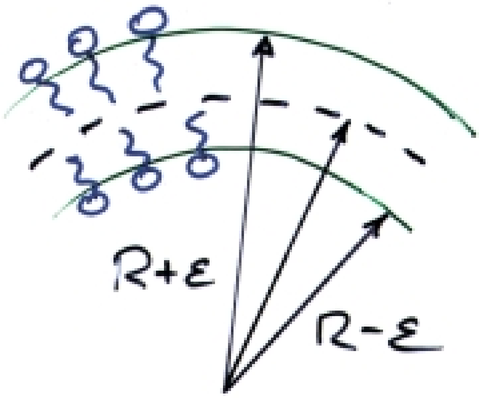
(G.G. & Kroll 1998)



Sponge Phases IV: Experimental Evidence

- Gaussian rigidity of bilayers:

  (Porte et al. 1989)



$$E_{mono} = \frac{1}{2} \kappa \int dS \, (c_1 + c_2 - 2c_0)^2$$

$$E_{tot} = E_{outer} + E_{inner}$$

$$\boxed{\bar{\kappa} = -4 c_0 \varepsilon \, \kappa}$$

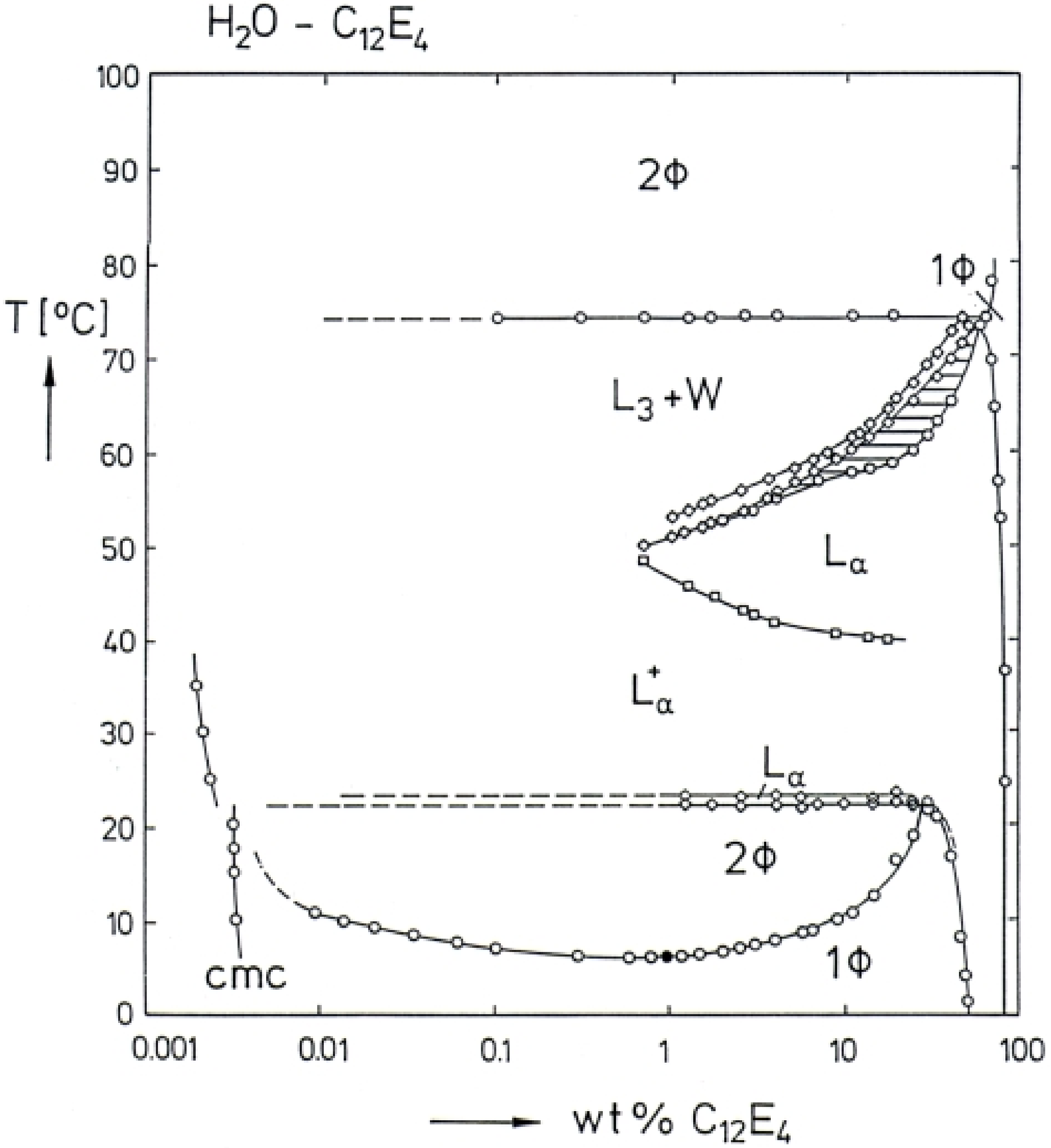
- Experiment for ternary mixtures

$$\boxed{c_0(T) \sim \bar{T} - T}$$

(Strey '94)

• Phase Diagram

(Strey 1996)



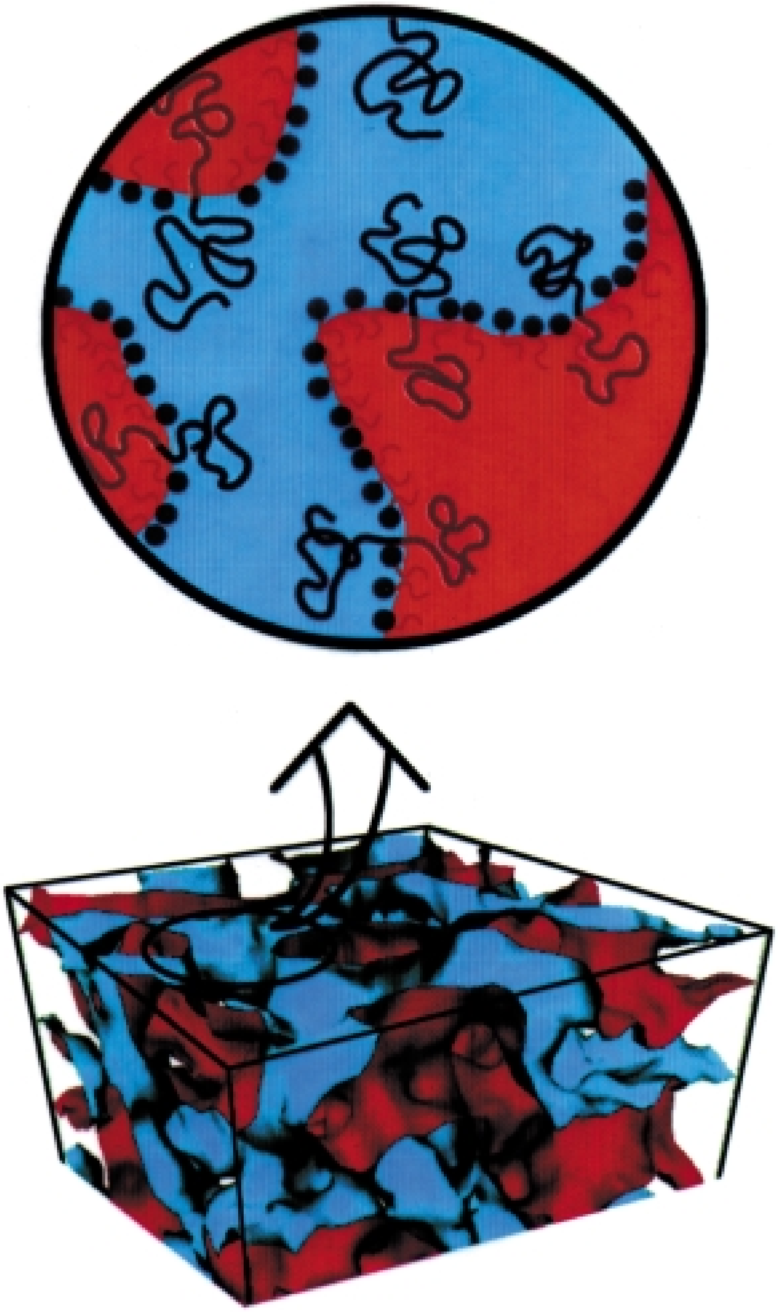
Membranes Decorated

by

Amphiphilic Block-Copolymers

(Endo, Allgaier, G.G., Jakobs, Monken-
busch, Richter, Sottmann, Strey, 2000)

• Polymers & Membranes

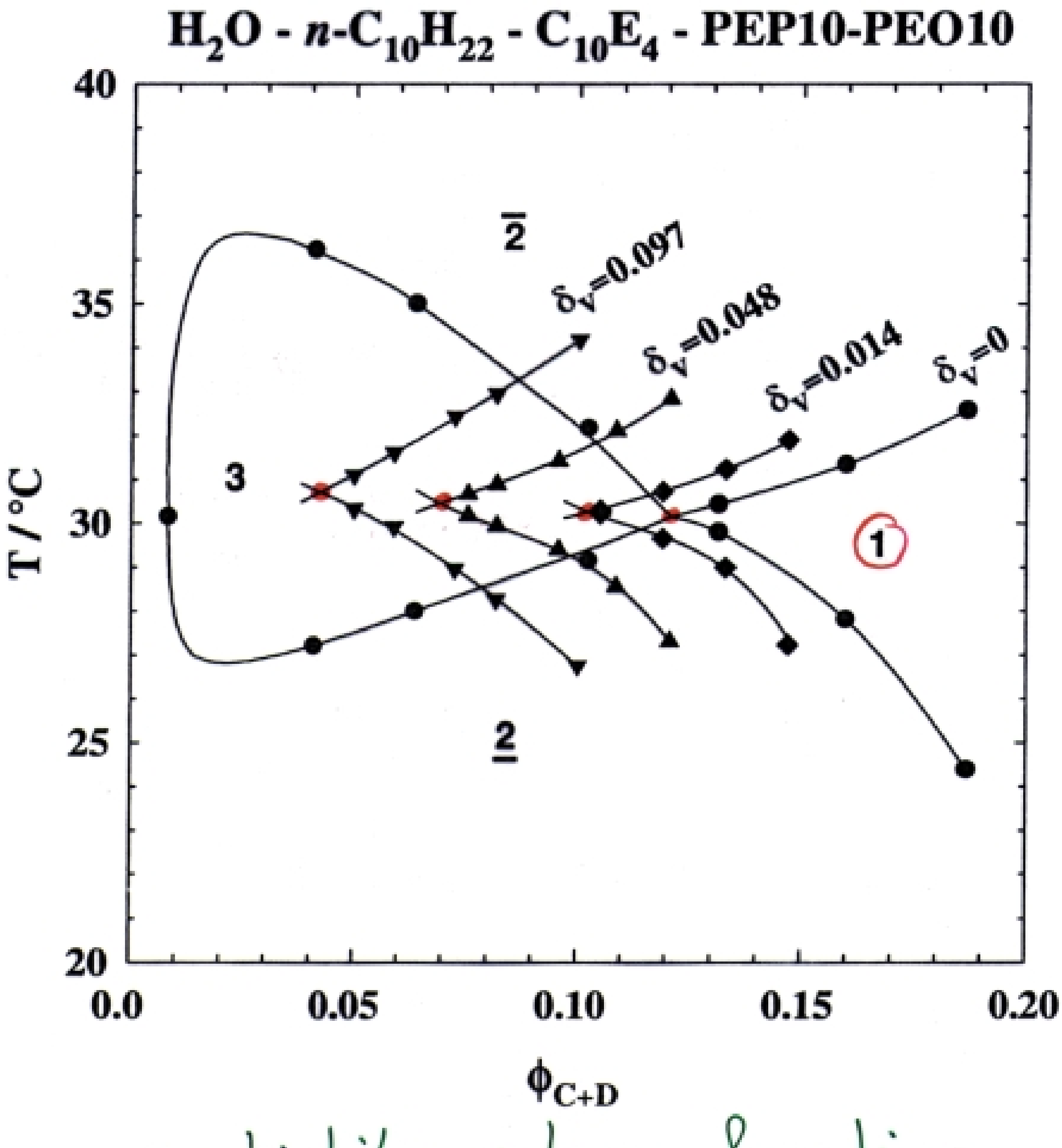


(Endo, Allgaier, GG, Jakobs, Monkenbusch, Richter, Sottmann, Strey; 2000)

Phase Behavior

surfactant

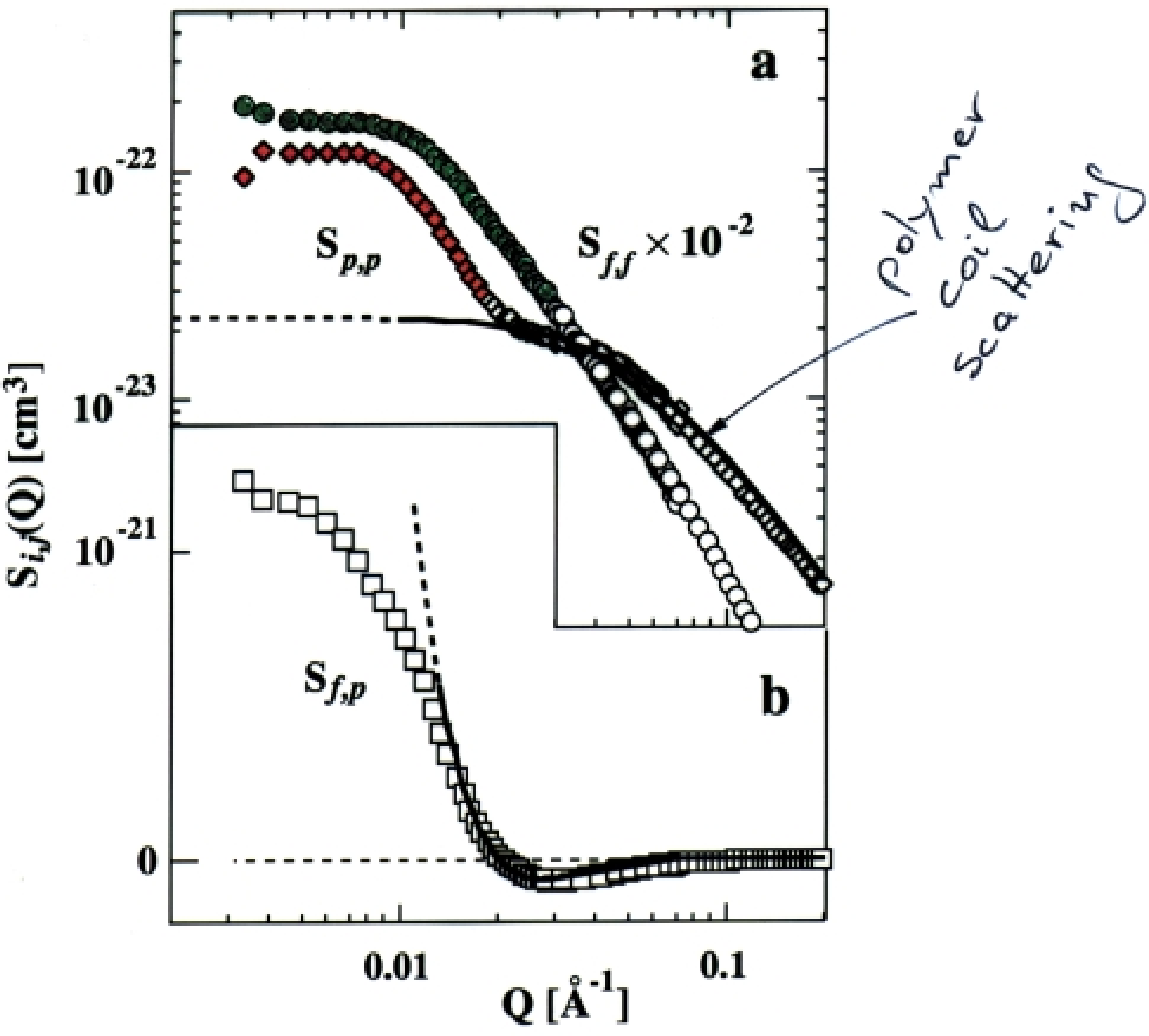
amphiphilic block copolymer



amphiphile volume fraction

(Endo et al., 2000)

Partial Structure Functions



- Polymer scattering S_{pp} follows film scattering S_{ff} for small Q

$\curvearrowright$ polymer decorates membrane

- Prediction for phase boundary:

$$\ln \phi = \frac{2\pi}{\alpha_-} \frac{\bar{\kappa}_{eff}}{k_B T} - \ln \phi_0 - \Xi \, \sigma \left(R_w^2 + R_0^2 \right)$$

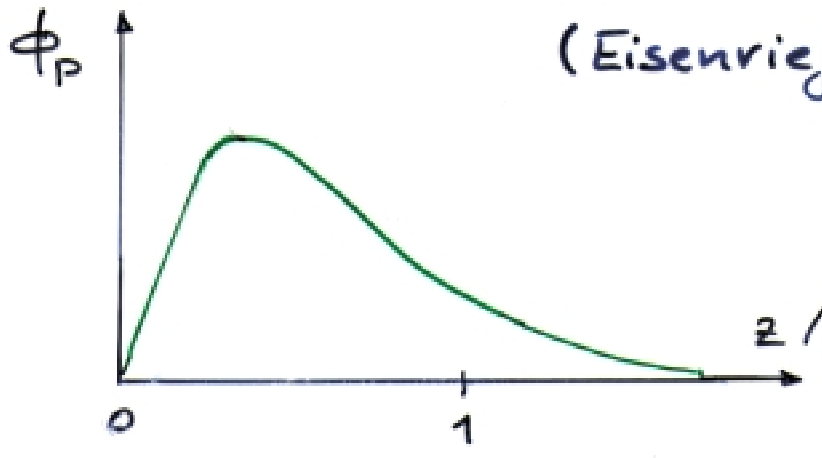
with $\Xi = \frac{\pi}{5} = 0.628\ldots$

(for ideal chains)

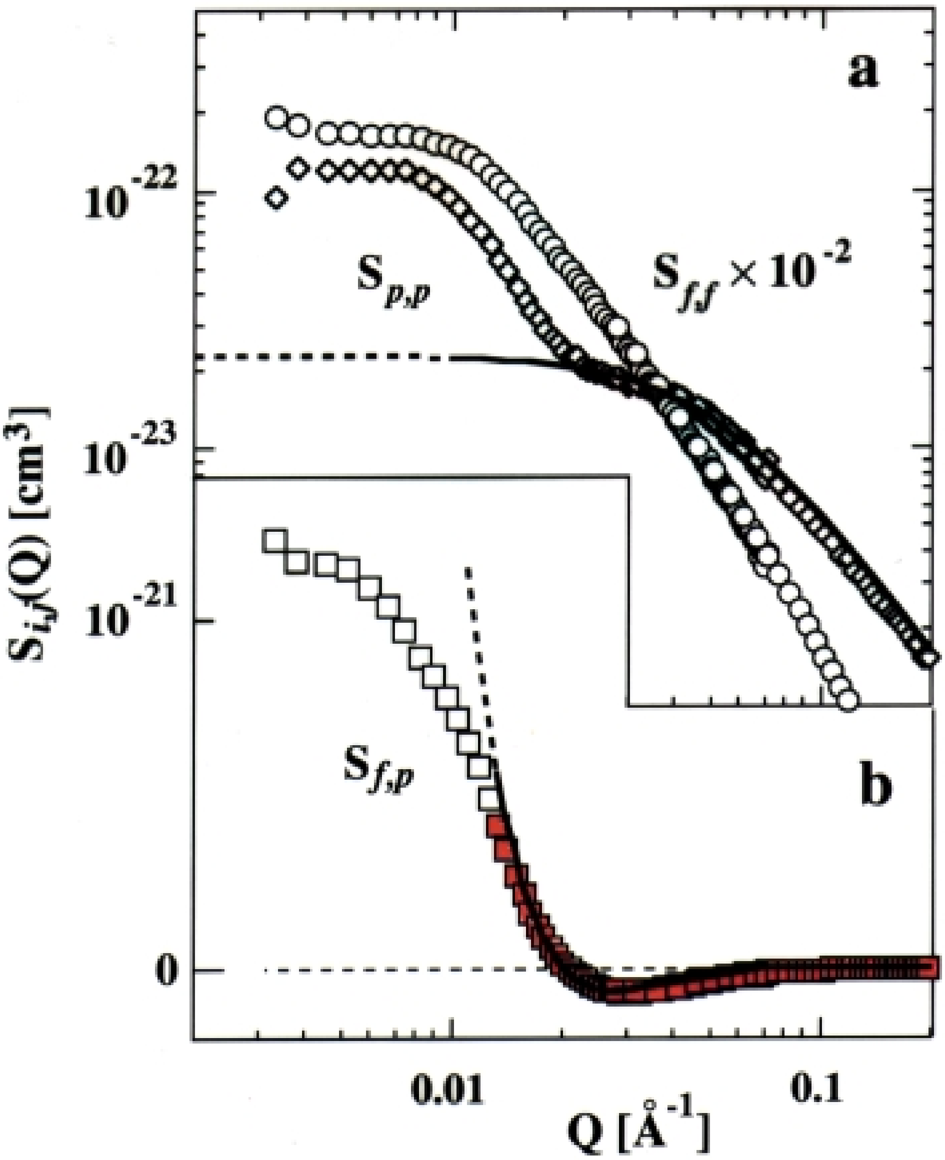
- Monomer density of polymers attached to planar wall:

$$\phi_p(z) = \frac{\sqrt{6\pi}}{R_e} \left[\mathrm{erfc}\left(\frac{\sqrt{6}}{2} \frac{z}{R_e} \right) - \mathrm{erfc}\left(\sqrt{6} \frac{z}{R_e} \right) \right]$$

(Eisenriegler et al, '82)



- Polymer - film scattering



Fit to theoretical result

$\curvearrowright$ $R_e^{PEO} \simeq 140$ Å

Compare free chains: 150 Å

$\curvearrowright$ mushroom conformations

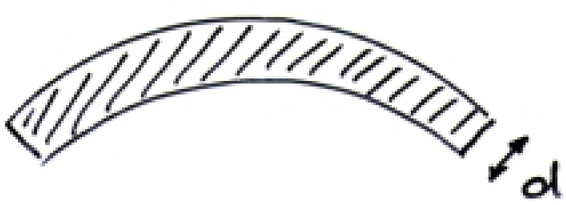
- Polymers attached to membranes affect elastic moduli:

(Hiergeist & Lipowsky '96
Eisenriegler et al. '96)

$$\boxed{\begin{aligned} \varkappa_{\mathrm{eff}} &= \varkappa + \frac{k_B T}{12}\left(1+\frac{\pi}{2}\right)\sigma\left(R_W^2 + R_0^2\right) \\ \bar{\varkappa}_{\mathrm{eff}} &= \bar{\varkappa} - \frac{k_B T}{6}\sigma\left(R_W^2 + R_0^2\right) \end{aligned}}$$

σ: surface density of polymer

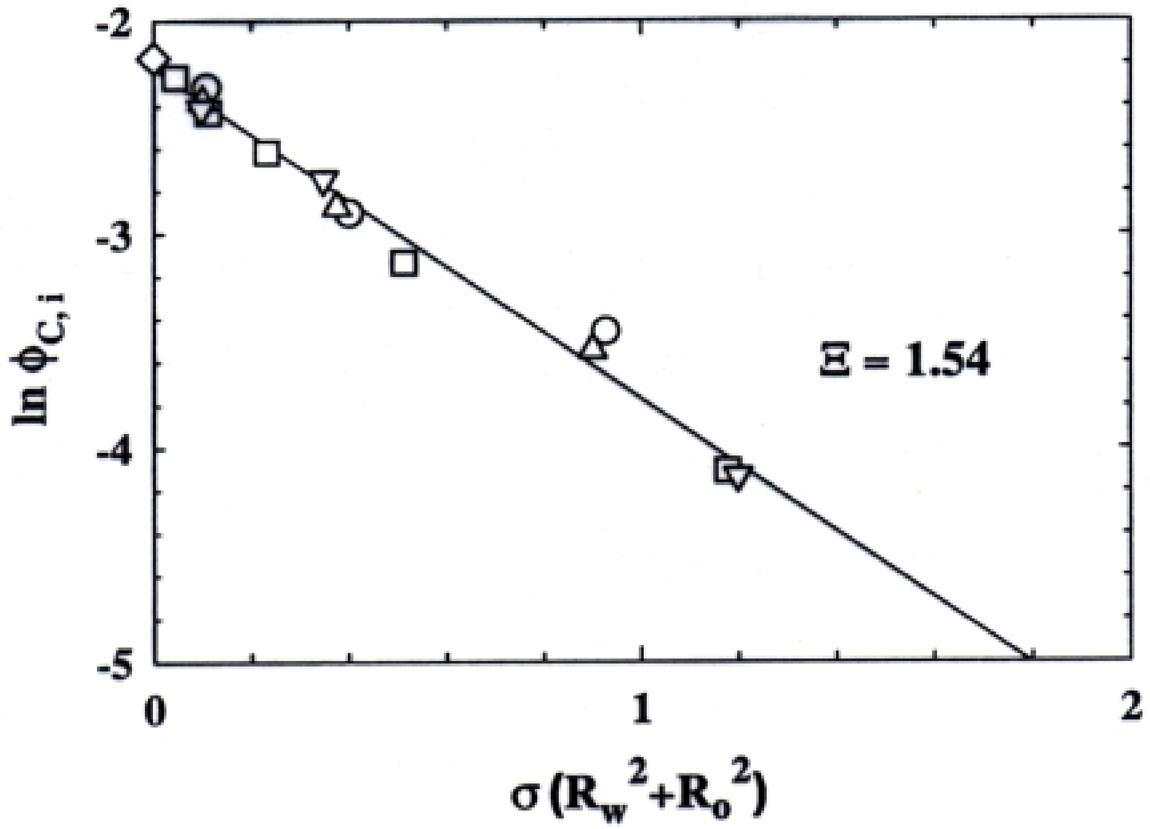
Compare: Elastic sheets



$\varkappa \sim d^3$

- Scaling behavior of optimal point:

universal law



Chain lengths:

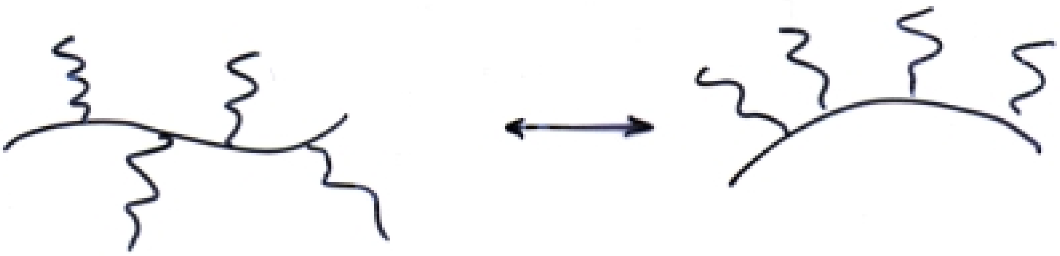
▽	PEPS	PEOS
△	10	10
□	22	22
○	5	15

Some comments ...

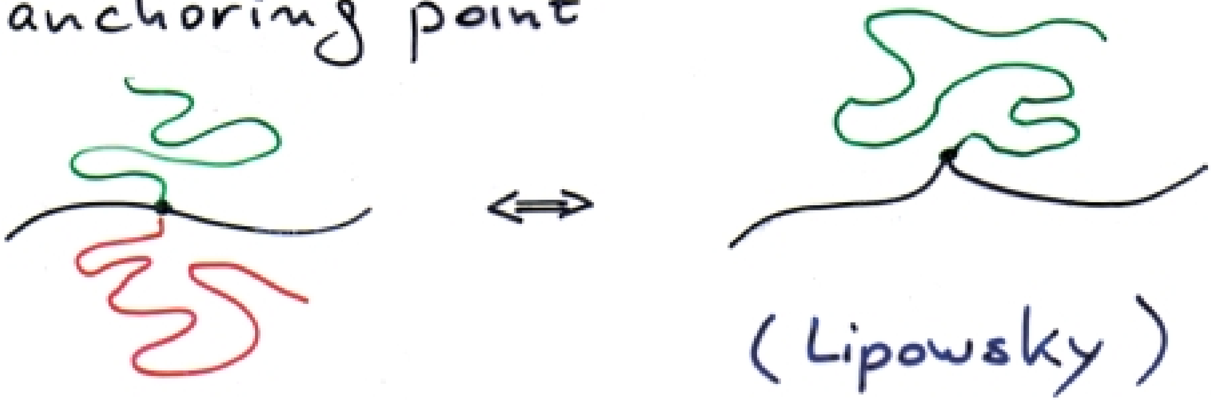
- <u>One</u>-component surfactant membrane

  ↝ no segregation effects at anchoring points

- No symmetry breaking between sides of membrane



- No membrane deformation at anchoring point



(Lipowsky)

quantitative understanding of polymer-membrane interactions

Collaborators:

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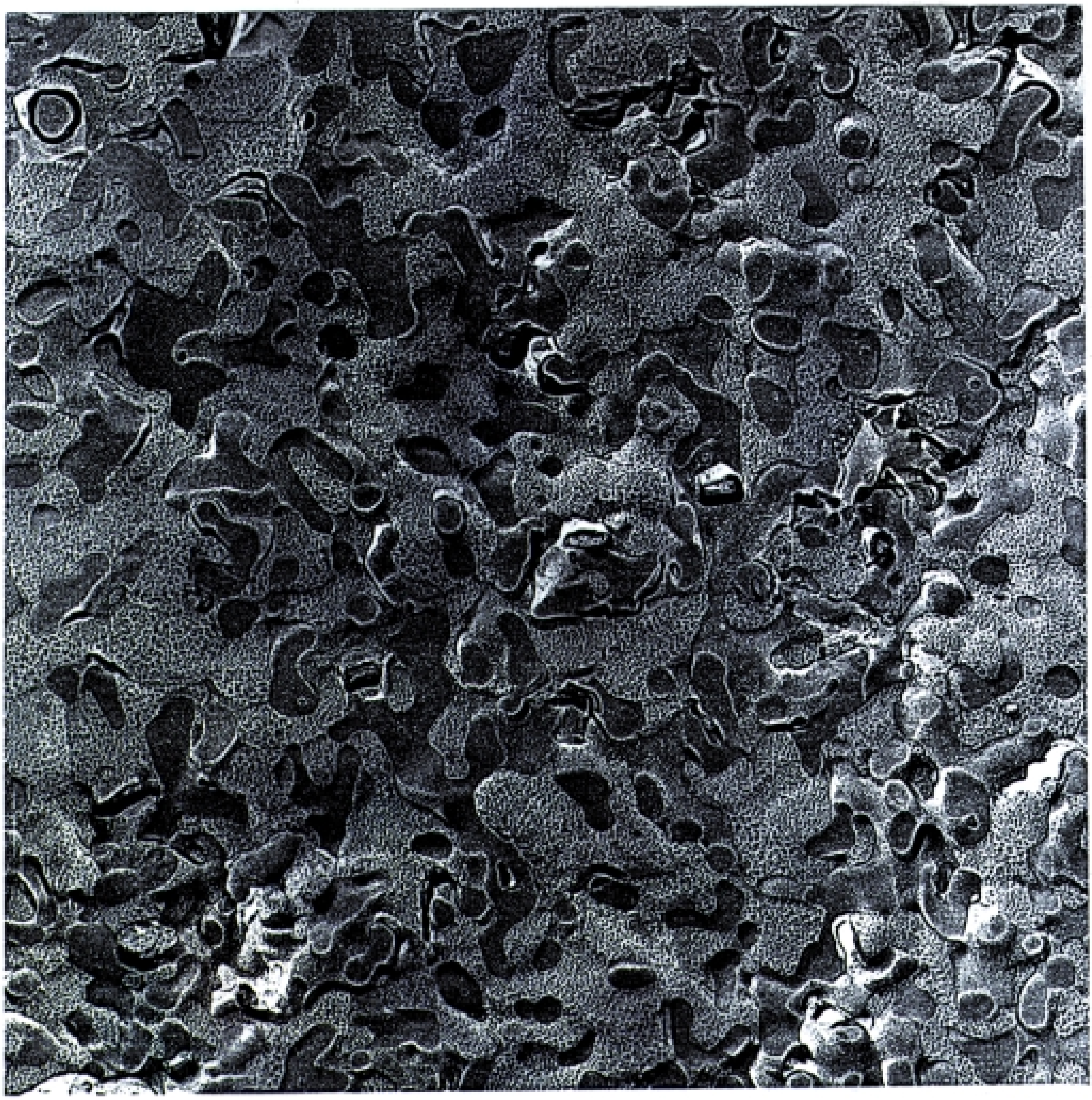
B. Jakobs T. Sottmann R. Strey	Physical Chemistry Univ. Köln
D.M. Kroll	Minnesota Supercomputer Inst.

Freeze-fracture microscopy:



$H_2O - C_8 - C_{12}E_5$
$\alpha = 41,2 \quad \gamma = 5,5$
59000x $\vdash\!\dashv$ 100nm

Jahn & Strey (1988)