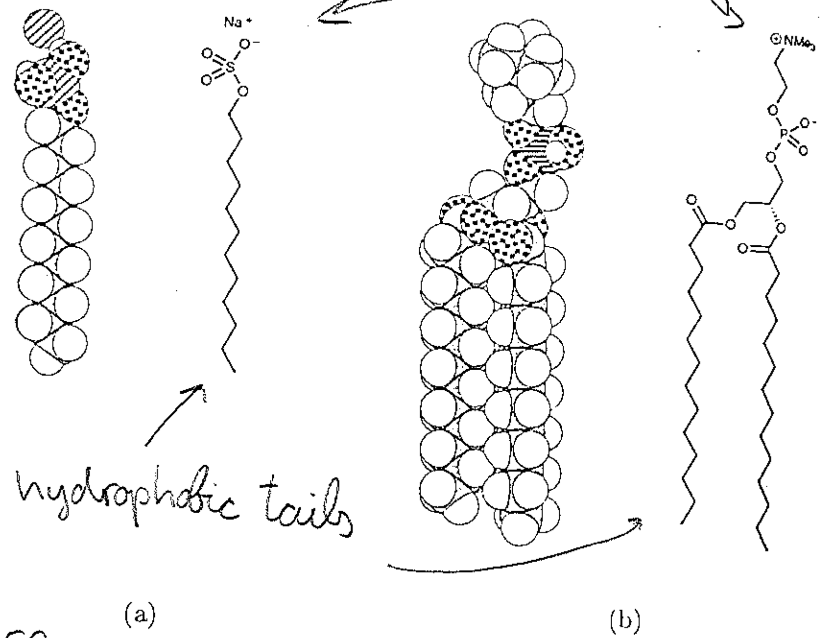
Lecture 13 Membranes

(1)

hydrophilic heads

Lipids →

amphiphilic molecules



hydrophobic tails

hydrophobic parts are shielded from water

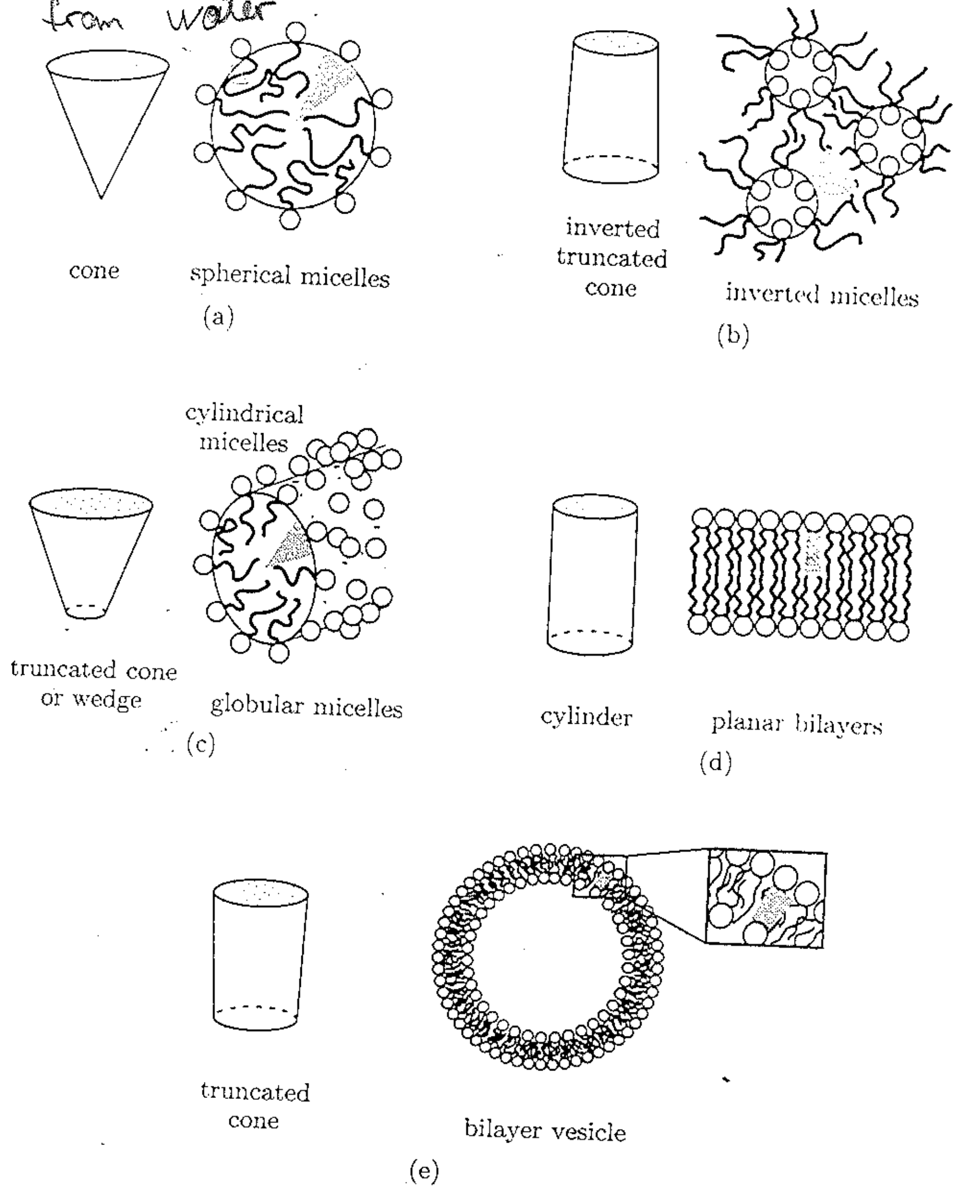


Fig. 2.7.13. Different local structures formed by lipids: (a) micelle, (b) inverted micelle, (c) cylindrical micelle, (d) flat bilayer, and (e) closed vesicle. Average shapes of the lipid molecules favoring the various structures are also shown. Note that asymmetric shapes favor nonzero curvature. [Adapted from J.N. Israelachvili, ...

Surface area

For an arbitrary parametrization $\vec{r}(\xi_1, \xi_2)$

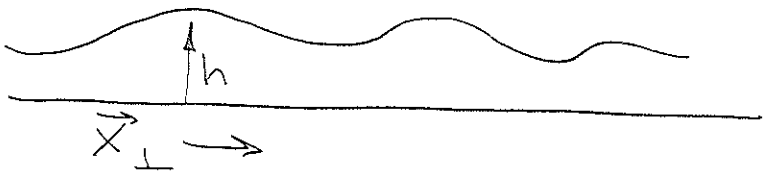
$$S = \int \sqrt{|g|}\, d^2\xi \quad , \text{where} \quad g = \operatorname{Det} g_{ij}$$

and g_{ij} - the metric tensor

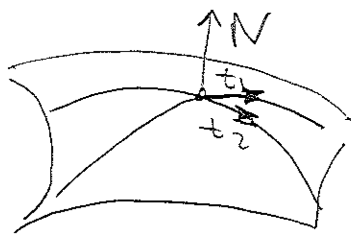
$$g_{ij} = \frac{\partial \vec{r}}{\partial \xi^i} \frac{\partial \vec{r}}{\partial \xi^j} \Rightarrow (d\vec{r})^2 = g_{ij}\, d\xi^i d\xi^j$$

Different parametrization $\Longleftrightarrow$ different gauge in electrodynamics

Monge gauge $\quad \vec{r}(x_\perp) = (x_\perp, h(x_\perp))$



In this gauge $\quad dS = \sqrt{1 + (\nabla_\perp h)^2}\, dx_1 dx_2$



Normal $\quad \vec{N} = \frac{\vec{t}_1 \times \vec{t}_2}{|\vec{t}_1 \times \vec{t}_2|} = \frac{(-\vec{\nabla}_\perp h, 1)}{\sqrt{1 + (\nabla_\perp h)^2}}$

$$\vec{t}_1 = \frac{\partial \vec{r}}{\partial x_1}$$

$$\vec{t}_2 = \frac{\partial \vec{r}}{\partial x_2}$$

$$dS = \left| \frac{\partial \vec{r}}{\partial x_1} \times \frac{\partial \vec{r}}{\partial x_2} \right| dx_1 dx_2 =$$

$$= \sqrt{\left(\frac{\partial \vec{r}}{\partial x_1} \cdot \frac{\partial \vec{r}}{\partial x_1}\right)\left(\frac{\partial \vec{r}}{\partial x_2} \cdot \frac{\partial \vec{r}}{\partial x_2}\right) - \left(\frac{\partial \vec{r}}{\partial x_1} \cdot \frac{\partial \vec{r}}{\partial x_2}\right)^2}\; dx_1 dx_2 =$$

$$= \sqrt{g}\; dx_1 dx_2$$

Curvature

If x_1 and x_2 are ortogonal coordinates in the tangent plane $\Rightarrow$ $h(x_\perp) = \frac{1}{2} K_{ij} \, x_i x_j$

K_{ij} has 2 real eigenvalues:

$$h = \frac{1}{2} \frac{(\vec{x}_\perp \cdot \vec{e}_1)^2}{R_1} + \frac{1}{2} \frac{(\vec{x}_\perp \cdot \vec{e}_2)^2}{R_2}$$

, R_1 and R_2 are the radii of curvature

positive $R_i > 0$ negative $R_i < 0$ sadle $R_1 \cdot R_2 < 0$

One can construct 2 invariants from K_{ij}

$$\mathrm{Tr}\, K = \frac{1}{R_1} + \frac{1}{R_2} = 2 \cdot \text{mean curvature}$$

$$\mathrm{Det}\, K = \frac{1}{R_1 R_2} \equiv \text{Gaussian curvature}$$

In the Monge gauge $\mathrm{Tr}\, K = -\nabla_\perp \cdot N$ (up to $O(x^2)$)

Indeed if the base plane is tangent $\Rightarrow$ $N = (-K_{ij} x_j, 1) \Rightarrow$

$\mathrm{Tr}\, K = -\nabla_\perp \cdot N$. For arbitrary plane $\rightarrow$ rotation $\Rightarrow$

$$\frac{1}{R_1} + \frac{1}{R_2} = -\nabla_\perp \cdot \frac{(-\nabla_\perp h, 1)}{\sqrt{1 + (\nabla_\perp h)^2}} = \frac{\nabla_\perp^2 h}{(1 + (\nabla_\perp h)^2)^{3/2}}$$

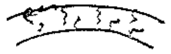
Energy of a surface

$$H = H_\sigma + H_c + H_G$$

$$H_\sigma = \int dS\, \sigma \quad \text{— surface tension}$$

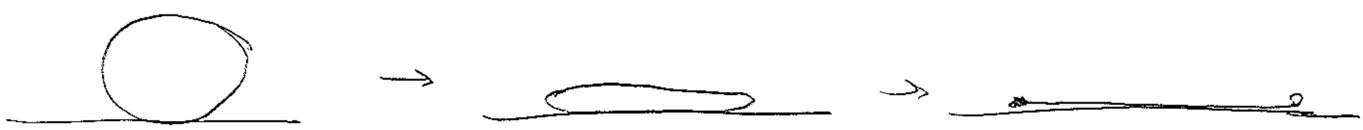
$$H_c = \frac{1}{2}K \int dS \left(\frac{1}{R_1} + \frac{1}{R_2} - \frac{2}{R_0}\right)^2 \quad \text{— bending}$$

$$H_G = -K_G \int dS\, \frac{1}{R_1 R_2}$$

R_0 — spontaneous curvature (if lipid layers are asymetric , for symmetric $R_0 = \infty$)

Usually liquid membrane have no surface tension — only bending energy.

For sphere $E = 4\pi(2K + K_G)$ is independent on radius. For flat membrane  we loose energy of the edges $\propto R$ $\Rightarrow$ large membrane wants to make closed surfaces — sphere. However — adhesion



Since attraction energy $\propto R^2$ it wins over the energy of the edges which is $\propto R$

Integral of Gaussian curvature is topological invariant

$$\int ds \, \frac{1}{R_1 R_2} = 4\pi(1-g) \qquad \text{Gauss - Bonnet theorem}$$

g - number of handles

In the Monge gauge $N = (-K_{ij} x_j, 1) \Rightarrow$

$N_1 = -K_{11}x_1 - K_{12}x_2$, $N_2 = -K_{21}x_1 - K_{22}x_2$, $N_3 = 1$

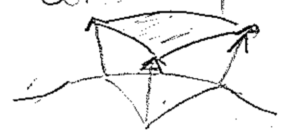
Then $\frac{1}{R_1 R_2} = \mathrm{Det}\,K = K_{11}K_{22} - K_{21}K_{12} = \frac{\partial N_1}{\partial x_1}\frac{\partial N_2}{\partial x_2} - \frac{\partial N_2}{\partial x_1}\frac{\partial N_1}{\partial x_2}$

We can rewrite it in the invariant form

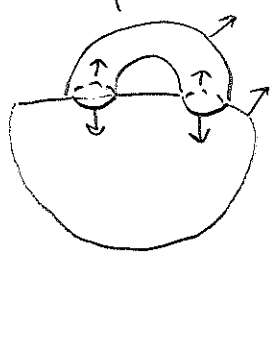
$$\mathrm{Det}\,K = \vec{N}\cdot\left[\frac{\partial \vec{N}}{\partial x_1}\times\frac{\partial \vec{N}}{\partial x_2}\right] = \frac{1}{2}\, N\cdot\left[\frac{\partial \vec{N}}{\partial x_\mu}\times\frac{\partial \vec{N}}{\partial x_\nu}\right]\varepsilon_{\mu\nu}$$

Thus $\int \mathrm{Det}\,K \, dS = \int \vec{N}\cdot\left[\frac{\partial \vec{N}}{\partial x_1}\times\frac{\partial \vec{N}}{\partial x_2}\right] dS$

The last integral is 4π times degree of mapping of the vector field of the normal to the surface of the unit sphere. Indeed, $\vec{N}\cdot\left[\frac{\partial \vec{N}}{\partial x_1}\times\frac{\partial \vec{N}}{\partial x_2}\right] ds$ is how much angle of the unit sphere does the vector $\vec{N}$ covers within the area dS



It is clear that the degree of mapping is topological charge. For mapping sphere on sphere it is 1. For torus $\to$ sphere it is 0. Each handle = - sphere = = -1



$$\Rightarrow \int \frac{dS}{R_1 R_2} = 4\pi(1-g)$$

Applications

Gaussian curvature is not important for change of shape at fixed topology but determines topology of the surface

For sphere $E = 4\pi\,(2\kappa + \kappa_G)$

For $\kappa_G > -2\kappa$ two free vesicles after collision fuse into 1

For $\kappa_G > 0$ it is favourable to make as much handles as possible — sponge phase (disordered) or plumber nightmare (ordered)

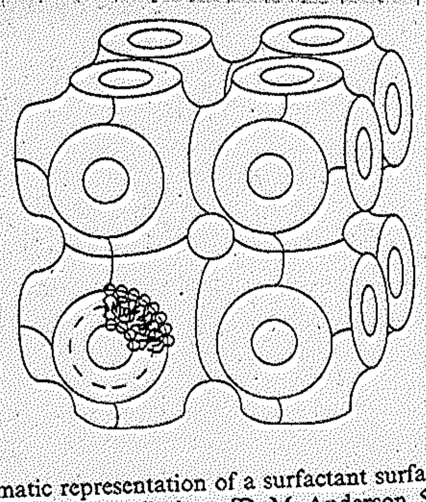


Fig. 2.7.15. Schematic representation of a surfactant surface in the trip periodic "plumber's nightmare" phase [D. M. Anderson, S. M. Gruner, S. Leibler, *Proc. Acad. Sci. USA* 85, 5364 (1988)]. This phase has the symmetry of a periodic crystal.

Fluctuations

in harmonic approximation

$$H = \frac{1}{2}\int d^2x_\perp \left[\sigma \underbrace{(\nabla_\perp h)^2}_{\text{surface tension}} + \kappa \underbrace{(\nabla_\perp^2 h)^2}_{\text{curvature}} \right]$$

If $\sigma \neq 0 \Rightarrow$

$$\langle (h(x) - h(0))^2 \rangle = 2\int \frac{d^2q}{(2\pi)^2} \frac{T}{\sigma q^2}\left(1 - e^{iq\cdot x_\perp}\right) = \frac{T}{\pi\sigma} \ln\left|\frac{x_\perp}{a}\right|$$

$\Rightarrow$ no long range order but orientational order

$$\langle |\delta N|^2 \rangle \sim (\nabla_\perp h)^2 = \int \frac{d^2q}{(2\pi)^2} \frac{T}{\sigma} \sim \frac{T}{\sigma a^2} = \text{const}$$

If $\sigma = 0 \Rightarrow \langle h^2(x_\perp) \rangle = \frac{T}{2\pi\kappa} x_\perp^2$ - strongly divergent and orientational order diverges as well

$$|\delta N|^2 = \frac{T}{2\pi\kappa} \ln\left|\frac{x_\perp}{a}\right|$$ This defines

$\xi_p = a\, e^{\frac{2\pi\kappa}{T}}$ - persistence length or De Gennes Taupin length

for $x > \xi_p$ there are overhangs and surface is crumpled

Nonlinearities strongly effect fluctuations and suppress the bend rigidity

$$H_c = \frac{1}{2} \kappa \int dS \, (\vec{\nabla}_\perp \cdot \vec{N})^2 = \frac{1}{2} \kappa \int d^2x \, \frac{(\nabla_\perp^2 h)^2}{(1+(\nabla_\perp h)^2)^{5/2}}$$

$$H_c = \frac{1}{2} \kappa \int d^2x \, (\nabla_\perp^2 h)^2 \left[1 - \frac{5}{2} (\nabla_\perp h)^2 \right]$$

We can calculate corrections to κ estimating

$$\langle \kappa (\nabla_\perp^2 h)^2 (\nabla_\perp h)^2 \rangle \sim \kappa (\nabla_\perp^2 h)^2 \langle (\nabla_\perp h)^2 \rangle$$

since $\langle h_q^2 \rangle \sim \frac{T}{\kappa q^4} \Rightarrow \langle (\nabla_\perp h)^2 \rangle \sim \frac{T}{\kappa} \ln \frac{x}{a} \Rightarrow$

$\kappa \approx \kappa_0 - T \ln \frac{x}{a}$ — cut off

more precise, we first integrate short distances

$h = \overset{<}{h} + \overset{>}{h}$ ($\overset{>}{h}$ has Fourier componentst $> \Lambda$)
$\phantom{h = \overset{<}{h} + \overset{>}{h}}$ ($\overset{<}{h}$ ———— " ———— $< \Lambda$)

Then $H_c^{\Lambda'} = -T \ln \int \mathcal{D} \overset{>}{h}(x) \, e^{-H(\Lambda)/T}$

and as a result — similar to nonlinear σ model Heisenberg

$$\kappa(\Lambda') = \kappa(\Lambda) - \frac{3T}{4\pi} \ln \frac{\Lambda}{\Lambda'} \Rightarrow$$ (RG)

$$\frac{d\kappa}{d \ln(\Lambda')} = -\frac{3T}{4\pi} \Rightarrow \frac{d \frac{1}{\kappa}}{d \ln(\frac{\Lambda}{\Lambda'})} = \frac{3T}{4\pi \kappa^2}$$ (Peliti Leibler) (1985)

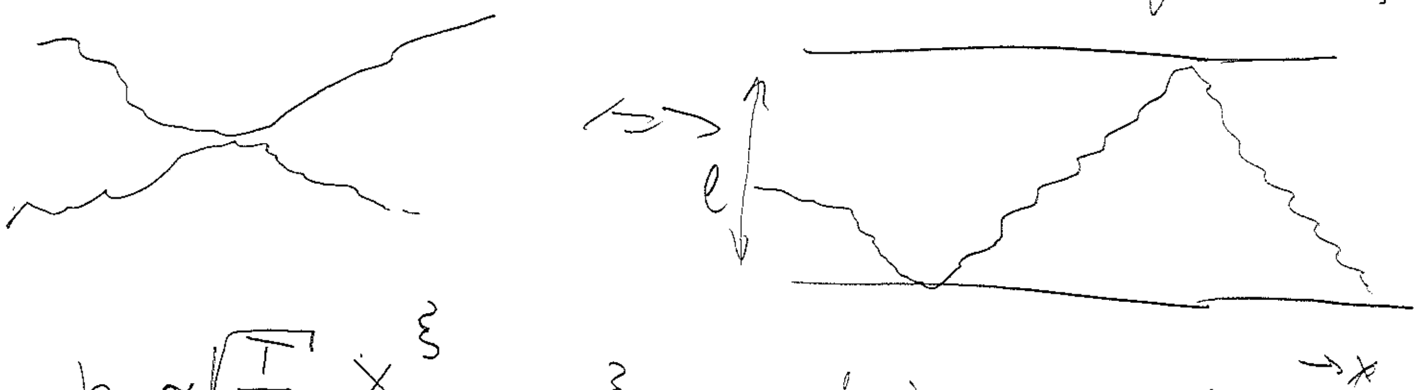
$\frac{1}{\kappa}$ - coupling constant diverges $\frac{1}{\kappa} = \frac{1}{\kappa_0 - \frac{3T}{4\pi} \ln \frac{\ell}{a}} \Rightarrow$

correlation length $\xi \approx a e^{\frac{4\pi \kappa_0}{3T}}$

at $l > \xi$ angle corr function $\sim e^{-\frac{\ell}{\xi}}$

Steric repulsion of membranes

(Helfrich 79)



$h \sim \sqrt{\frac{T}{K}}\, x^{\xi}$, ξ - wondering exponent

$\xi = \frac{5-d}{2} = 1$ for $d=3$

Average distance between collisions $\sim \ell^{\frac{1}{\xi}}$

$x_c \sim \sqrt{\frac{K}{T}}\, \ell$

Entropic contribution to the free energy $\sim \frac{T}{x_c^2} \sim \ell^{-\frac{2}{\xi}}$

$\Delta F \sim \frac{T^2}{K \ell^2}$, more precisely $\Delta F = \frac{3\pi^2}{128} \frac{T^2}{K\ell^2}$ (1)

Thus we have compression modulus $B = \ell^2 \frac{\partial^2 \Delta F}{\partial \ell^2}$

and $H = \frac{1}{2} \int \left(B q_z^2 + K q_\perp^4\right) h_q^2 \, (dq)$ - smectic order

$\langle h(r)^2 \rangle \sim \int \frac{T \, dq_z \, d^2 q}{B q_z^2 + K q_\perp^4} \sim \frac{T}{\sqrt{BK}} \ln(r)$

Bragg peak $S(q) \sim (q_z - q_0)^{-(2-\nu)}$ with $\nu = \frac{q_0^2 T}{8\pi\sqrt{BK}}$

taking B from (1) we obtain $\underline{\nu = \frac{4}{3}}$ in agreement with experiment