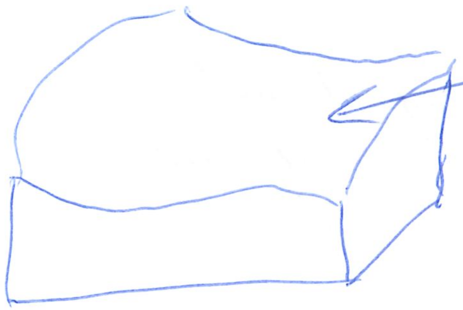
(44)

2.2.7) Surfaces and Membranes

Shape and fluctuations of a surface between two coexisting phases are controlled through the surface tension σ.



~~surface~~ area A

Energy: $E = \sigma A$

(case flat surface)

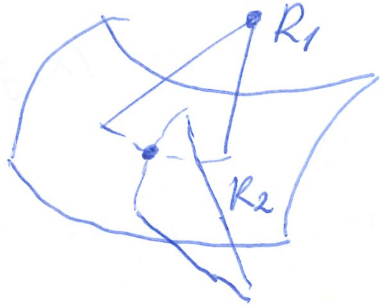
Example: Surface tension minimizes the area having a fixed volume.

(case)

$\Rightarrow$ droplet shape is spherical

(45)

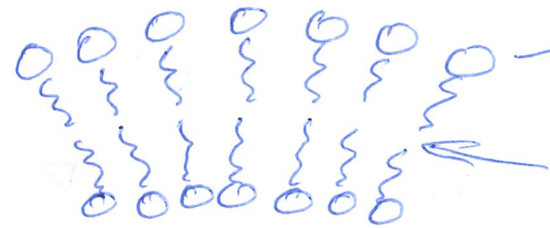
Shape and fluctuations of amphiphile surfaces (membranes) are controlled through the bending rigidity κ



Energy: $E = \frac{\kappa}{2} \int dA \left(\frac{1}{R_1} + \frac{1}{R_2} \right)^2$

Amphiphile membrane:

H_2O



polar head

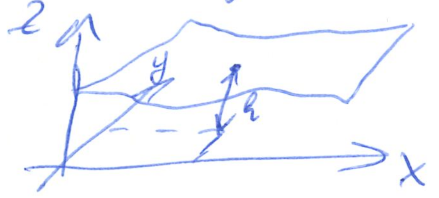
hydrocarbon tail

H_2O

Hydrophobic effect: Polar & unpolar fluids do not mix.

Small fluctuations:

Describe configuration of a surface or membrane through a "height variable" $h(\underline{r})$:



$\underline{r} = (x, y)$

"Monge representation"

<u>Assumption</u>: Small deformations, so the configuration will be described by simple function $h(\underline{r})$

<u>Then</u>:

Area $A = \int d^2r \sqrt{1+(\nabla h)^2}$

For small fluctuations: $|\nabla h| \ll 1$

$\Rightarrow A = A_0 + \frac{1}{2} \int d^2r (\nabla h)^2$

~~Average~~ Mean curvature:

$$\frac{1}{R_1} + \frac{1}{R_2} = \nabla \cdot \frac{\nabla h}{\sqrt{1+(\nabla h)^2}}$$

For small fluctuations:

$$\int dA \left(\frac{1}{R_1} + \frac{1}{R_2}\right)^2 = \int d^2x (\nabla^2 h)^2$$

<u>Hence</u>: Energy functional for surfaces and membranes

$$\mathcal{H} = \frac{\gamma}{2} \int d^2x (\nabla^n h)^2$$

with $\gamma = \sigma$, $n = 1$ surfaces

$\gamma = \kappa$, $n = 2$ membranes

Monte-Carlo simulation:

(i) Select initial configuration $h=0$.

(ii) choose a lattice space $\underline{r}$

(iii) Choose a height increment (ask)

$\delta h \in [-s, s]$ - uniformly distributed

(iv) Calculate energy difference for the proposed deformation

$$h(\underline{r}) \to h(\underline{r}) + \delta h$$

Discretized energy:

(a) Surfaces

$$\int d^2x\, (\nabla h)^2 \to \sum_{\langle i,j \rangle} (h_i - h_j)^2$$

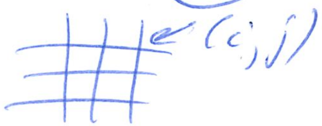
(show how)

(b) Membranes

$$\int d^2x\, (\nabla^2 h)^2 \to \sum_i \Big[\sum_{j(i)} (h_j - h_i) \Big]^2$$

change in energy:

(a) Surfaces



$$\delta\mathcal{L}(\ldots, h_{ij}, \ldots) - \delta\mathcal{L}(\ldots, h_{ij} + \delta h, \ldots) =$$

$$= (h_{i+1,j} - h_{ij})^2 + (h_{i-1,j} - h_{ij})^2 +$$

$$+ (h_{i,j+1} - h_{ij})^2 + (h_{i,j-1} - h_{ij})^2 -$$

$$- (h_{i+1,j} - h_{ij} - \delta h)^2 - (h_{i-1,j} - h_{ij} - \delta h)^2 -$$

$$- (h_{i,j+1} - h_{ij} - \delta h)^2 - (h_{i,j-1} - h_{ij} - \delta h)^2 =$$

$$= 2\delta h \,[h_{i+1,j} + h_{i-1,j} + h_{i,j+1} + h_{i,j-1} - 4h_{ij}] -$$

$$- 4(\delta h)^2 =$$

$$= 2\delta h (\nabla^2 h - 2\delta h)$$

full analog to Ising model

(b) Membranes

More complicated due to long range interactions.

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Analytical calculation of fluctuations of a surface or a membrane.

<u>Fourier transform</u>:

$$h(\underline{r}) = \int \frac{d^2q}{(2\pi)^2}\, h(\underline{q})\, e^{i\underline{q}\underline{r}}$$

Energy:

$$\int d^2r \left(\nabla^n h(\underline{r})\right)^2 =$$

$$= \int \frac{d^2q}{(2\pi)^2} \int \frac{d^2q'}{(2\pi)^2}\, h(\underline{q})\, h(\underline{q}') \cdot$$

$$\cdot \int d^2r \big(\underbrace{\nabla^n e^{i\underline{q}\underline{r}}}_{(i\underline{q})^n e^{i\underline{q}\underline{r}}}\big)\left(\nabla^n e^{i\underline{q}'\underline{r}}\right) =$$

$$= \int \frac{d^2q}{(2\pi)^2} \int \frac{d^2q'}{(2\pi)^2}\, h(\underline{q})\, h(\underline{q}')\, (i\underline{q})^n (i\underline{q}')^n \cdot$$

$$\cdot \underbrace{\int d^2r\, e^{i(\underline{q}+\underline{q}')\underline{r}}}_{(2\pi)^2\,\delta(\underline{q}+\underline{q}')} =$$

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$$= \int \frac{d^2q}{(2\pi)^2}\, q^{2n} |h(q)|^2$$

where $h(\underline{q}) = h^*(-\underline{q})$

and $h(\underline{r})$ is real!

<u>Finally</u>: $\boxed{\mathcal{H} = \frac{\gamma}{2} \int \frac{d^2q}{(2\pi)^2}\, q^{2n} |h(q)|^2}$

<u>Equilibrium assumption</u>:

Each independent degree of freedom has on average energy $\frac{1}{2} k_B T \Rightarrow$

$$\langle |h_q|^2 \rangle \sim \frac{k_B T}{\gamma q^{2n}}$$

<u>More exact</u>:

$$\boxed{\langle h(\underline{q})\, h(\underline{q}') \rangle = \frac{k_B T}{\gamma q^{2n}} (2\pi)^2 \delta(\underline{q}+\underline{q}')}$$

Then, the ~~...~~ calculation of average values ~~like~~ $\langle h^2(\underline{r})\rangle$, $\langle(\nabla h(\underline{r}))^2\rangle$ becomes rather easy.

<u>Surfaces:</u>

$$\langle h^2(\underline{r})\rangle = \int\frac{d^2q}{(2\pi)^2}\int\frac{d^2q'}{(2\pi)^2}\langle h(\underline{q})h(\underline{q}')\rangle\cdot e^{i(\underline{q}+\underline{q}')\underline{r}} =$$

$$= \int\frac{d^2q}{(2\pi)^2}\frac{k_BT}{\gamma q^2}$$

with integral limits:

L – system size

a – microscopic length

$$\Rightarrow \langle h^2(\underline{r})\rangle = \frac{1}{\cancel{2\pi}}\frac{k_BT}{\gamma}\int_{1/L}^{1/a}dq\,\frac{1}{q}$$

$$\boxed{\langle h^2(\underline{r})\rangle = \frac{k_BT}{\cancel{2\pi}\gamma}\ln\frac{L}{a}}$$

Similarly:

$$\langle(\nabla h)^2\rangle = \int\frac{d^2q}{(2\pi)^2}\int\frac{d^2q'}{(2\pi)^2}(i\underline{q})(i\underline{q}')\cdot\langle h(\underline{q})h(\underline{q}')\rangle e^{i(\underline{q}+\underline{q}')\underline{r}} =$$

$$= \int\frac{d^2q}{(2\pi)^2}q^2\frac{k_BT}{\gamma q^2} =$$

$$= \approx\frac{k_BT}{\cancel{2\pi}\gamma a^2} \text{ - independent of } L.$$

<u>Main result:</u>

– Surfaces have a well defined orientation.

– Surfaces are not local for $L \gg a$!

Normal vector: $n_z = \frac{1}{\sqrt{1+(\nabla h)^2}} = \cos\theta$

$$\Rightarrow \langle\theta^2\rangle = \langle(\nabla h)^2\rangle$$

Membranes:

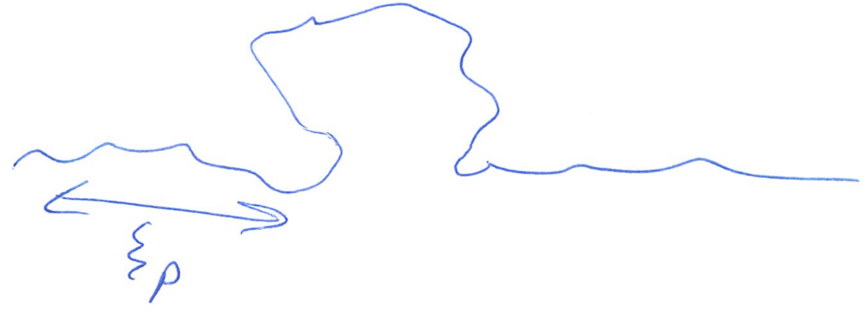
Similar to the derivation for surfaces:

$$\langle (\nabla h)^2 \rangle = \int \frac{d^2q}{(2\pi)^2} q^2 \frac{k_B T}{K q^4}$$

$$\boxed{\langle (\nabla h)^2 \rangle = \frac{k_B T}{K} \ln \frac{L}{a}}$$

Results:

- Membrane have no defined orientation for $L \gg a$
- critical size (= persistence length ξ_p) depends on the bending rigidity K: $\xi_p \sim a\, e^{K/k_B T}$
- approximation of small fluctuations breaks down when $|\nabla h| \simeq 1$



3.) Molecular Dynamics Simulations

3.1) Equations of motion

Kinetic energy E_{kin} } for N-particle
Potential energy Φ } system

(i) Lagrangian:

Lagrange operator:

$$L(\underline{q}_i, \dot{\underline{q}}_i) = E_{kin}(\dot{\underline{q}}_i) - \Phi(\underline{q}_i)$$

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{\underline{q}}_k} - \frac{\partial L}{\partial \underline{q}_k} = 0$$

$$\Rightarrow \frac{d}{dt}\frac{\partial}{\partial \dot{\underline{q}}_k} E_{kin}(\dot{\underline{q}}_k) + \frac{\partial}{\partial \underline{q}_k}\Phi(\underline{q}_k) = 0$$

$$E_{kin}(\dot{\underline{q}}_i) = \sum_i \frac{1}{2} m_i \dot{\underline{q}}_i^2$$

$$\Rightarrow \boxed{m_k \ddot{\underline{q}}_k = -\nabla_k \Phi} \quad k = 1, \dots, N$$