Topological Fluctuations in Membranes (Dedicated to I.M.Khalatnikov)

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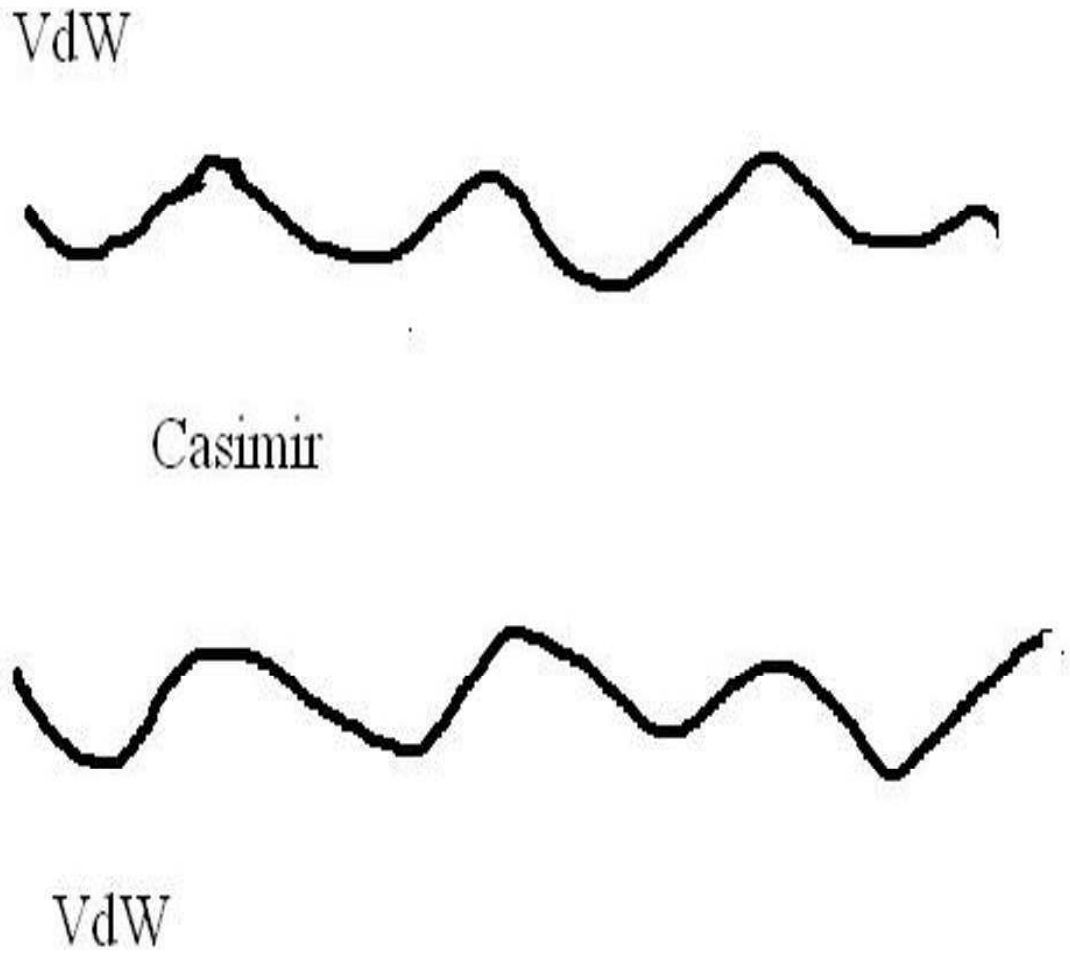
My major Discovery:

- If dominating fluctuations are ”inside” - corresponding forces can be termed ”Van der Waals forces”;
- If fluctuations ”outside” are dominating, one has to deal with ”Casimir effect”.



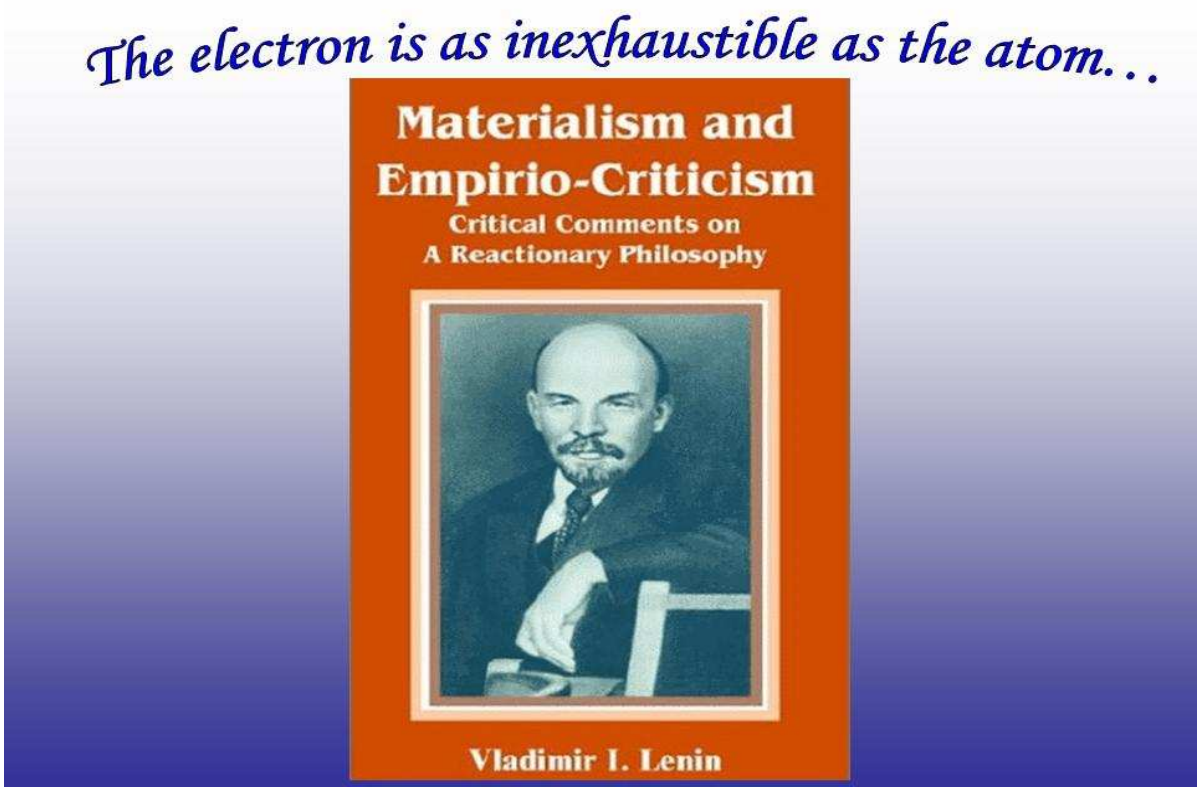


Figure: Casimir and VdW phenomena are also inexhaustible.

Conceptional outline:

Manifolds embedded in a correlated medium can impose boundary, or modify material parameters. this usually gives rise

- to mean field forces, which are due to the deformation of the medium and
- to Casimir-VdW forces which are due to modification of its thermal fluctuations.
- **Such interactions are generally non pairwise additive.**

Membrane self organization:

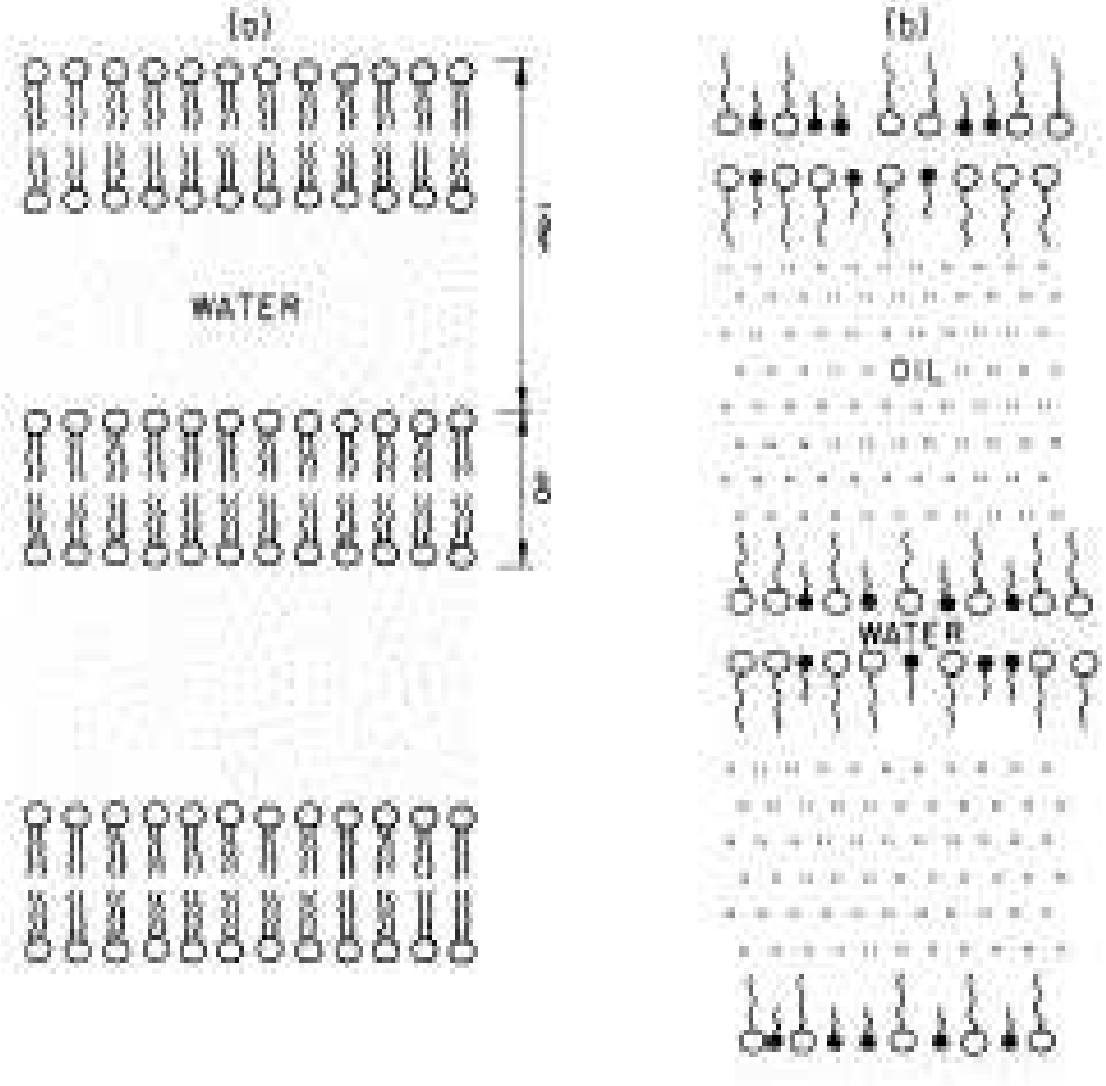


Figure: Self-aggregation of amphiphilic molecules

Membranes:

Amphiphilic molecules spontaneously self-assemble into membranes, vesicles and other structures.

- A suitable thermodynamic potential is $\Omega(T, \mu, v)$ since these quantities are continuous through the interface (while, e.g., mass density is discontinuous).
- The interface Ω

$$\Omega_s = \int dA \omega_s$$

-

$$\omega_s = \sigma - \beta \left(\frac{1}{R_1} + \frac{1}{R_2} \right) + \frac{\kappa}{2} \left(\frac{1}{R_1} + \frac{1}{R_2} \right)^2 + \bar{\kappa} \frac{1}{R_1 R_2}$$

Here R_1 and R_2 are local curvature radii (combined in mean and Gaussian curvatures).

Possible membrane configurations:

- One big spherical vesicle (or one infinite membrane):

$$E_1 = 4\pi(2\kappa + \bar{\kappa})$$

- Many small vesicles $E = N_{ves}E_1$, and also translational entropy

$$-TN_{ves}\left[\ln\left(\frac{N_{site}}{N_{ves}}\right) + \ln\left(\frac{N_{tot}}{N_{ves}}\right)\right]$$

(N_{tot} is the total number of molecules, N_{site} number of in-plane sites available for vesicles).

- Gauss-Bonnet theorem

$$\int dA \frac{1}{R_1 R_2} \equiv -4\pi(g-1)$$

(g is genus, or the number of topological handles). Lattice of passages

$$E = -N_{pas}4\pi\bar{\kappa}$$

(translational entropy of passages is similar to that of vesicles).

Schematic phase diagram of membranes:

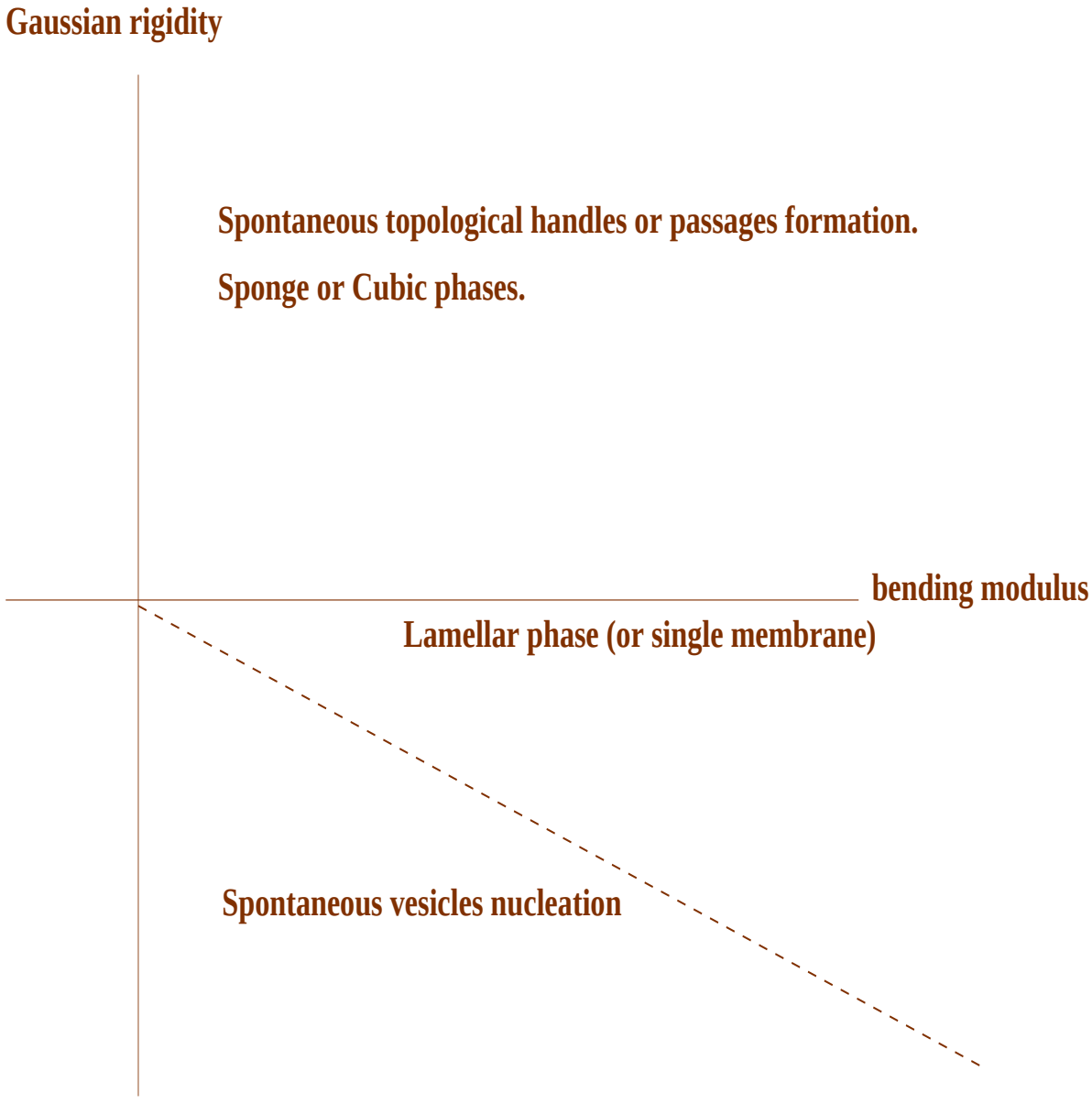


Figure: Various membrane phases

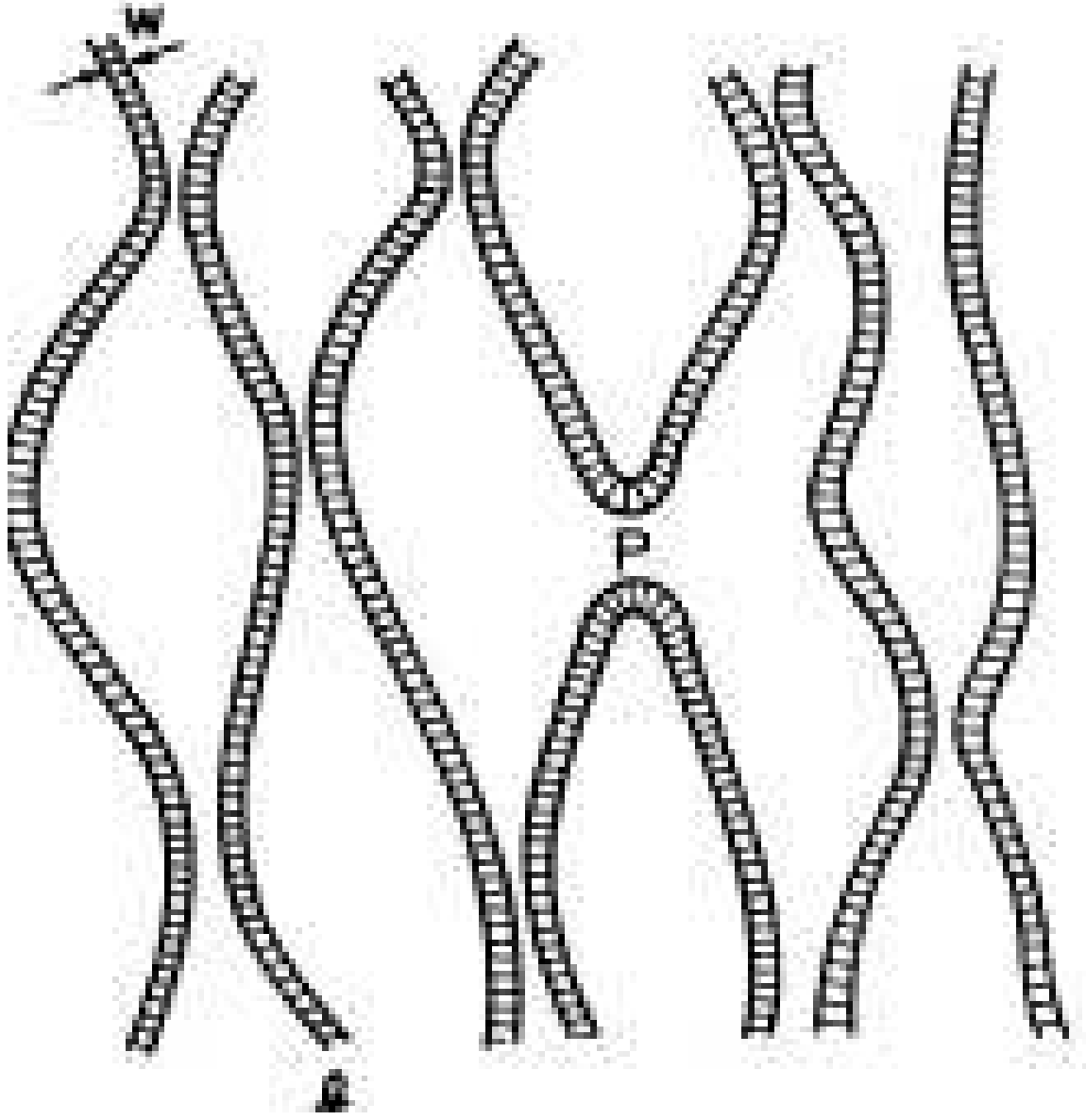


Figure: Fluctuations of a stack of membranes stabilized by self-avoiding ”Casimir” interactions

Casimir-like Undulation repulsion:

- Membranes undergo fluctuations about some average flat (on a scale $\xi_{||}$) configuration;
- The height fluctuations in the normal direction z

$$\langle h^2 \rangle \propto \frac{T\xi_{||}^2}{\kappa}$$

- Collisions between membranes occur when height fluctuations become of order of the interlayer spacing l. Thus h can be identified with l and $\xi_{||}$ with the mean distance between collisions in the plane;
- The free energy per collision is estimated as T, and therefore the membrane free energy per unit area

$$F_{st} \simeq \frac{T}{\xi_{||}^2}$$

and in terms of d it reads as

$$F_{st} \simeq \frac{T^2}{\kappa l^2}$$

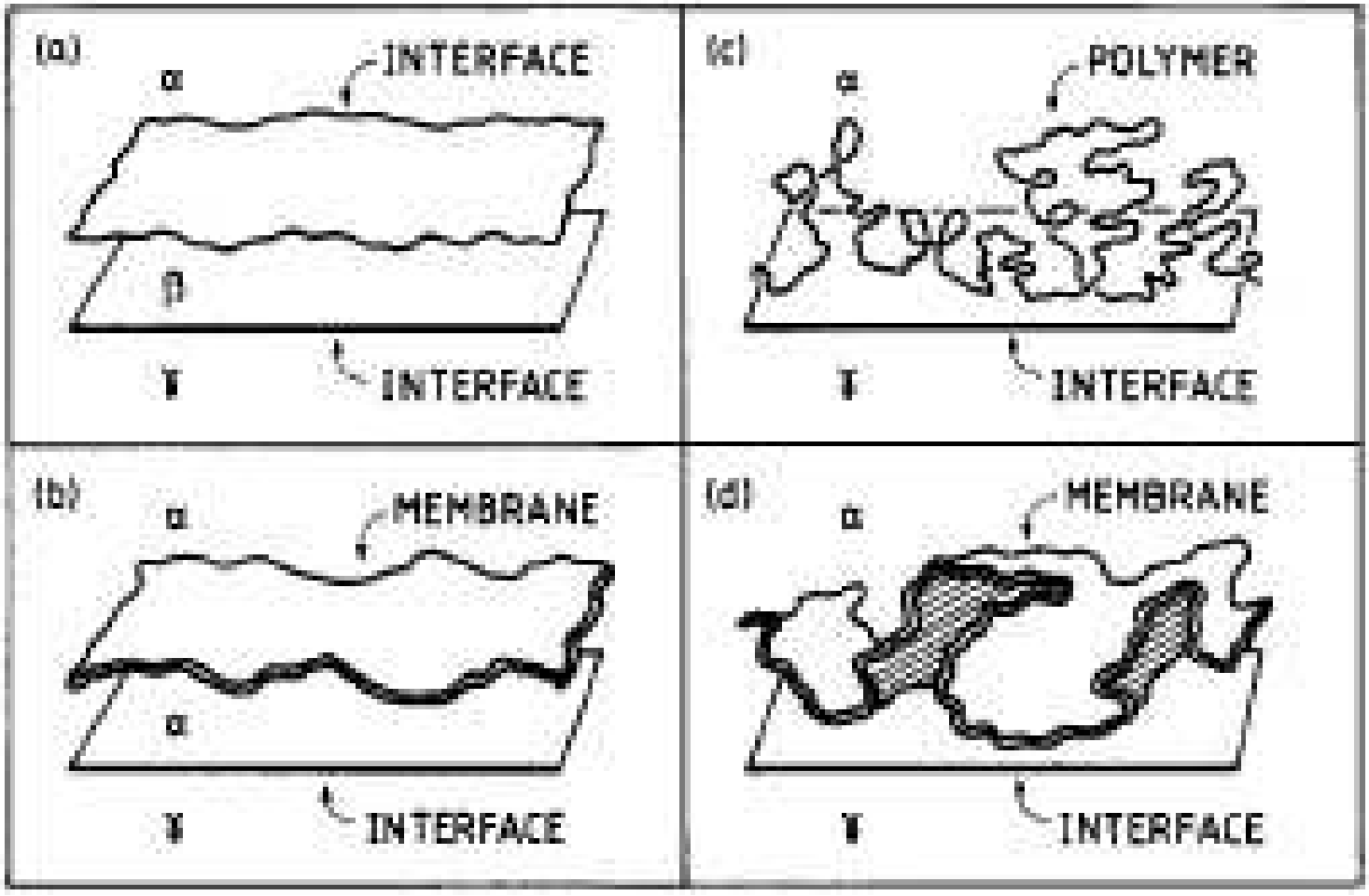


Figure: Oriented versus crumpled manifolds

Orientationally ordered manifolds:

- Each manifold can be characterized by its persistence length ξ_p and can be considered as orientationally ordered at linear size $L < \xi_p$.
- Oriented manifold can be viewed as an ensemble of humps with a longitudinal extension set by the correlation length $\xi_{||}$, and typical roughness $\xi_\perp \propto \xi_{||}^\zeta$. One usually has $\zeta = 1/2$ for interfaces in $d = 1 + 1$ and $\zeta = 1$ for fluid membranes in $d = 2 + 1$.
- Since $\xi_{||}$ is the correlation length, different humps are essentially uncorrelated. Thus a manifold with projected area $L_{||}^{d_{||}}$ may be viewed as $(L_{||}/\xi_{||})^{d_{||}}$ independent humps. The thermal fluctuation free energy

$$F_{fl} \propto T \left(\frac{L_{||}}{\xi_{||}} \right)^{d_{||}}$$

Casimir like repulsion (per unit projected area) between two oriented manifolds:

$$V_{fl} = \frac{F_{fl}}{L_{||}^{d_{||}}} \propto \frac{T}{\xi_{||}^{d_{||}}} \propto \frac{T}{\xi_{\perp}^{d_{||}/\zeta}}$$

The mean distance $l \simeq \xi_{\perp}$ between two interacting manifolds

$$V_{fl} = \frac{T}{l^{\tau}} \; ; \; \tau \equiv \frac{d_{||}}{\zeta}$$

Crumpled manifolds:

- Large scale configuration consists of blobs of linear size X_b. Each blob contains a manifold with total area $(N_b a)^{d_{||}}$ (a is a small distance cutoff).
- For each blob

$$X_b \propto a\, N_b^{\nu}$$

  The exponent ν depends on $d_\perp$ and internal manifold structure (e.g., for linear polymers in $d = 1 + 2$, $\nu = 3/5$).
- It is again plausible to assume that correlations between different blobs can be neglected. Then a crumpled manifold consists of $(N/N_b)^{d_{||}}$ independent blobs and

$$F_{fl} \propto T \left(\frac{N}{N_b} \right)^{d_{||}}$$

and

$$V_{fl} \propto \frac{F_{fl}}{(aN)^{d_{||}}} \propto \frac{T}{I^{\tau_b}} \; ; \; \tau_b \equiv \frac{d_{||}}{\nu}$$

Two persistence lengths:

- $$\xi_\kappa \propto w \exp\left(\frac{4\pi\kappa}{3T}\right)$$

  where w is molecular scale (membrane thickness), and on scales smaller than ξ_κ the membrane is flat with respect to bending fluctuations.

- $$\xi_{\bar{\kappa}} \propto w \exp\left(-\frac{6\pi\bar{\kappa}}{5T}\right)$$

Two regimes:

- Passage regime

$$0 < -\bar{\kappa} < \frac{10}{9}\kappa$$

For low temperatures, and intermembrane distances $l \simeq l_{max} \simeq \xi_{\bar{\kappa}} \ll \xi_{\kappa}$ there are numerous passages connecting membranes. In this regime such a lamellar phase melts into a sponge phase.

- Droplet regime

$$-\bar{\kappa} > \frac{10}{9}\kappa$$

For low temperatures, and intermembrane scales $l_{max} \simeq \xi_{drop} \simeq \xi_{\kappa}(\xi_{\kappa}/\xi_{\bar{\kappa}})^{10/9} \ll \xi_{\kappa} \ll \xi_{\bar{\kappa}}$ there are numerous droplets between lamellas (i.e., melting into a droplet phase).

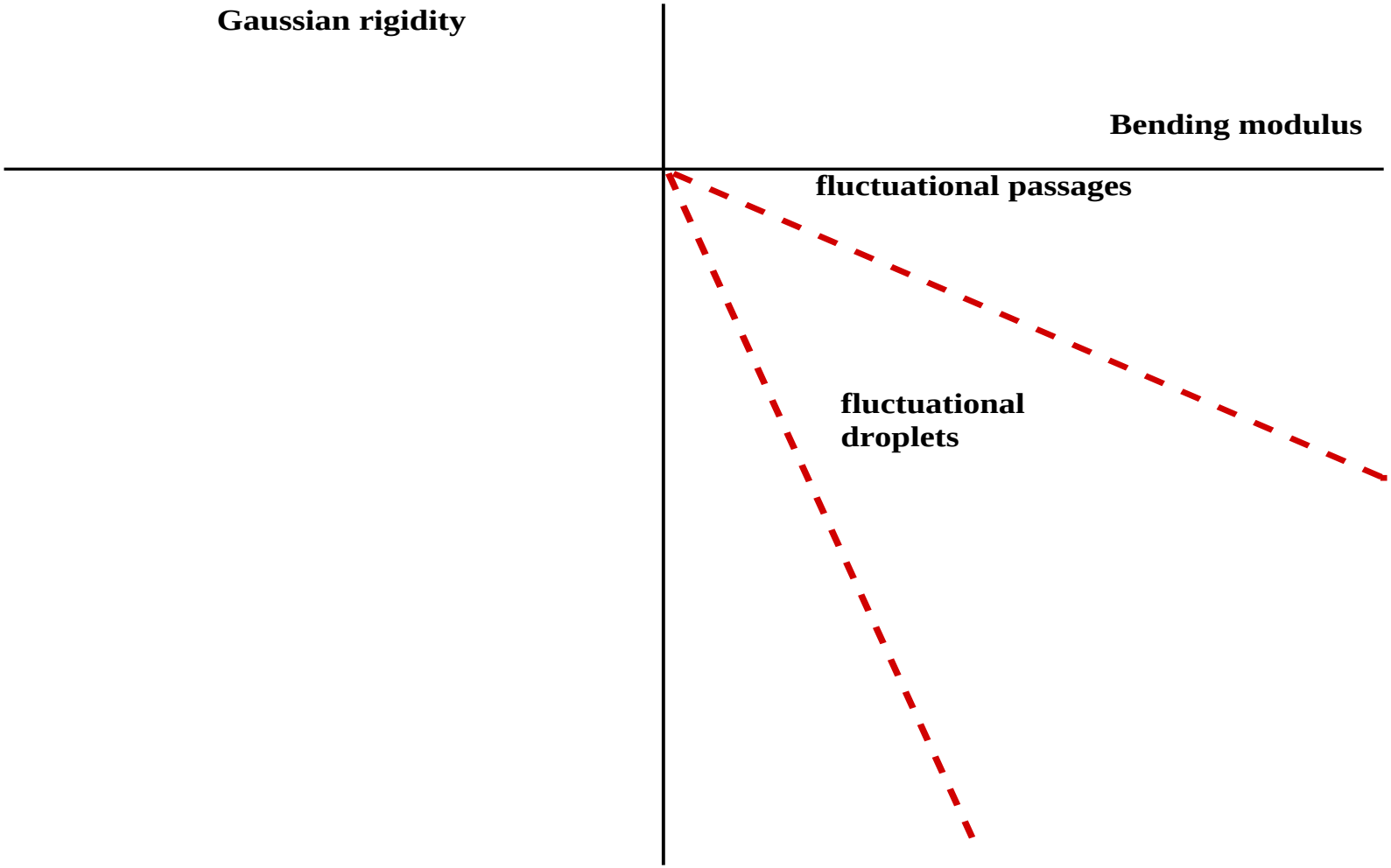


Figure: Passage and droplet fluctuations.

Renormalization of the curvature moduli:

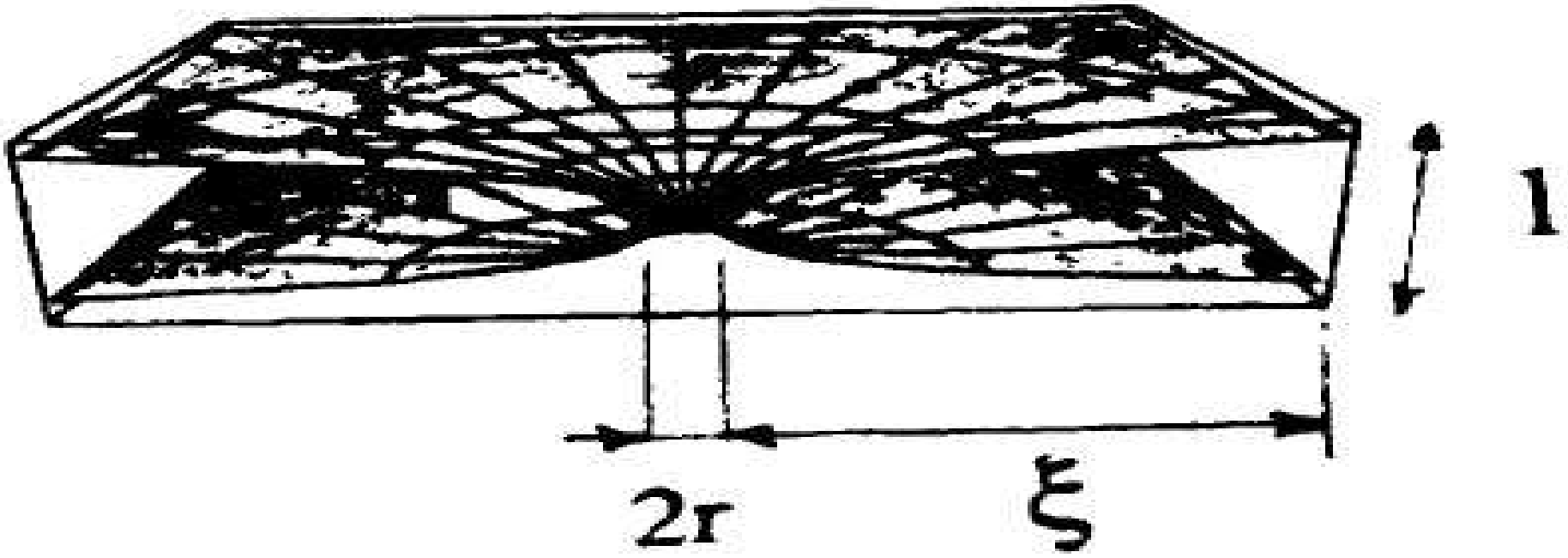
- $$\kappa(l) \propto \frac{3T}{4\pi} \ln\left(\frac{\xi_\kappa}{l}\right)$$
- $$\bar{\kappa}(l) \propto \frac{5T}{6\pi} \ln\left(\frac{l}{\xi_{\bar{\kappa}}}\right)$$

One passage connecting two lamellas:

Its curvature energy is estimated as

$$E_{pas} \propto \kappa(\xi) \left(\frac{r}{\xi}\right)^2 - 4\pi\bar{\kappa}(r)$$

where r is the size of the passage neck, and ξ is the size of the passage deformation region. At distances from the neck smaller than ξ, the presence of a passage curves the membrane (1-st term in E_{pas}).



If there are no overhangs:

For almost planar membrane, minimization of the bending energy gives the biharmonic Euler-Lagrange equation

$$\Delta^2 h(\mathbf{r}) = 0$$

In cylindrical coordinates the general solution is

$$h(r) = \frac{1}{4} r^2 (2C_2 - C_3) + C_4 + \left(C_1 + \frac{1}{2} r^2 C_3 \right) \ln r$$

For a single passage in an infinite planar membrane the bending energy vanishes and the membrane deformation is catenoid-like

$$h(r) \propto r_{eq} \ln \left(\frac{r}{r_{eq}} \right)$$

Catenoid as a trial passage shape:

We approximate the passage as a catenoid (trial surface) and it gives the condition $l \simeq 2r\ln(\xi/r)$ relating ξ and r.

- A catenoid is a 3D shape made by rotating a catenary curve $y = a\cosh(x/a)$ around the x axis.
- A catenoid is one of several types of minimal surfaces. One can bend a catenoid into a helicoid without stretching:

$$x(u,v) = \cos\theta \sinh v \sin u + \sin\theta \cosh v \cos u$$

$$y(u,v) = -\cos\theta \sinh v \cos u + \sin\theta \cosh v \sin u$$

$$z(u,v) = u\cos\theta + v\sin\theta$$

where for u, v in $(-\pi\ \pi]$, x in $(-\infty\ \infty)$, and the deformation parameter $-\pi < \theta \leq \pi$

Minimizing energy we find the passage energy

$$E_{pas} \simeq -\frac{10}{3} T \ln \frac{l}{\xi_{\bar{\kappa}}}$$

and size

$$\xi_{eq} \propto l \frac{\sqrt{(\kappa(l)/T)}}{\ln(\kappa(l)/T)} \; ; \; r_{eq} \propto \frac{l}{\ln(\kappa(l)/T)}$$

Next we consider 2 passages at distance R. They interact via the repulsive potential

$$U_{pp}(R) \propto \kappa(R) \left(\frac{r_{eq}}{R}\right)^2$$

- for $R > \xi_{eq}$, $U_{pp} < T$, and the interaction can be ignored; for $R < \xi_{eq}$, $U_{pp} > T$.
- The passage repulsion can be viewed as a hard core repulsion with its core size $\simeq \xi_{eq}$.

Fluid of passages:

Mixing entropy plays a role of hard core particle free energy per unit area

$$F_{pas} \simeq T n_p \ln \frac{n_p}{n_0(l)} - T \ln(1 - n_p \xi_{eq}^2)$$

where

$$n_p \propto \frac{1}{\xi_{eq}^2}$$

and $n_0(l)$ is passage density in a dilute limit: $n_0(l) \propto l^{4/3}$.
Minimizing over n_p we end up

$$F_{pas} \simeq -\frac{T}{\xi_{eq}^2} \ln(1 + n_0(l)\xi_{eq}^2) \simeq -\frac{T^2}{\kappa(l) l^2} \ln\left(1 + \left(\frac{l}{l^*}\right)^{10/3}\right)$$

where $l^* \propto \xi_{\bar{\kappa}}$.

Passage induced attraction:

Tending to keep the membranes at a preferred distance

$l \simeq l^* \simeq \xi_{\bar{\kappa}}$

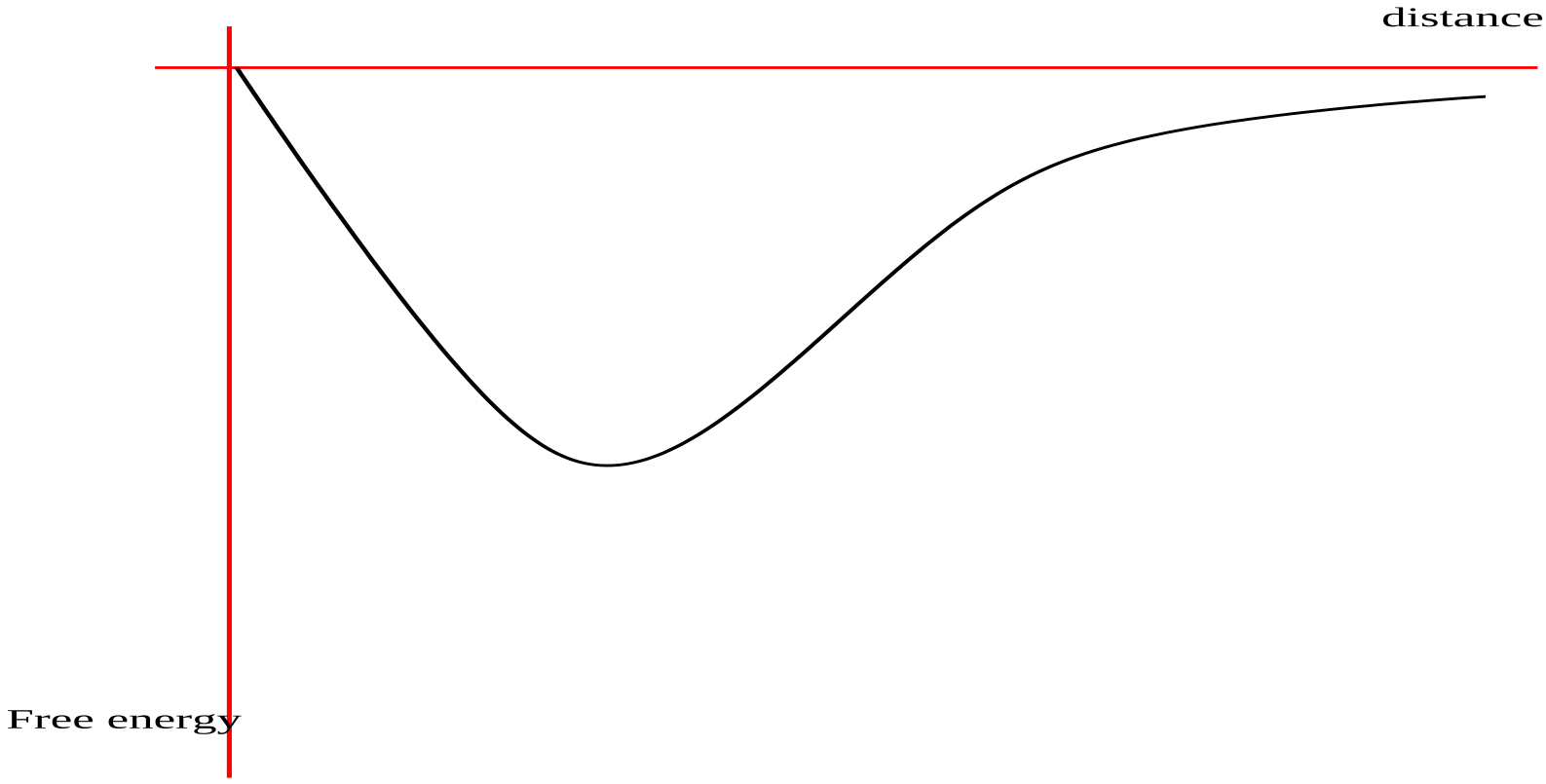


Figure: Passage mediated attraction between membranes

Membrane in nematic solvent:

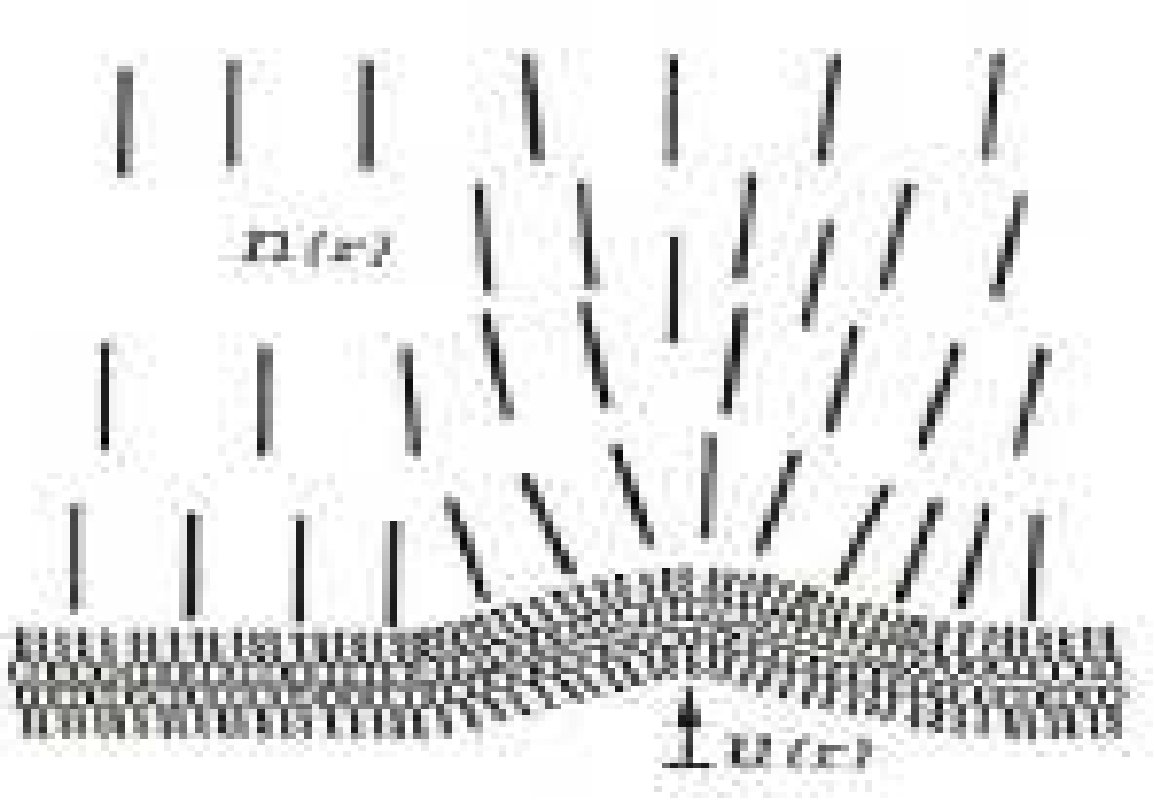


Figure: Nematic strong anchoring on a membrane.

- Strong homeotropic anchoring

$$\delta n(r_\perp, z = 0) = -\nabla_\perp u(r_\perp)$$

and since bulk nematic solvent minimizes the bulk orientational energy

$$F_n = \frac{1}{2} K \int d^3 r (\nabla n)^2$$

-

$$\delta n(r_\perp, z) = \int \frac{d^2 q_\perp}{(2\pi)^2} i q_\perp u(q_\perp) \exp(-i q_\perp r_\perp - |q_\perp| z)$$

with the limits between $2\pi/a$ and $2\pi/L_\perp$ ($L_\perp$ is the membrane size).

- Substituting δn into F_n and integrating over z

$$F_n = \frac{1}{2} K \int \frac{d^2 q_\perp}{(2\pi)^2} |q_\perp|^3 (1 - \exp(-|q_\perp| L_z)) |u(q_\perp)|^2$$

- Convenient interpolation formula which handles properly large and small q limits

$$F_n = \frac{1}{2} K \int \frac{d^2 q_\perp}{(2\pi)^2} \frac{q_\perp^4 L_z}{1 + |q_\perp| L_z} |u(q_\perp)|^2$$

- To this one has to add

$$F_b = \frac{1}{2} \kappa \int d^2 r_\perp (\nabla_\perp^2 u)^2$$

- Single-membrane ($L_z = \infty$):

$$< |\delta n(r) - \delta n(0)|^2 >= 2T \int \frac{d^2 q_\perp}{(2\pi)^3} \frac{1 - \cos(q_\perp r)}{K|q_\perp| + \kappa q_\perp^2} =$$

$$\frac{T}{\pi\kappa} \ln \left| \frac{K + 2\pi\kappa/a}{K + 2\pi\kappa/r} \right|$$

- Correlation length ξ_0 for which n fluctuations are of order unity

$$\frac{\xi_0}{a} \simeq \frac{\exp(4\pi\kappa/3T)}{1 - Ka/(2\pi\kappa)[\exp(4\pi\kappa/3T) - 1]}$$

For $K = 0$ the membrane in isotropic solvent is crumpled at distances larger than ξ_0. For $K \neq 0$ ξ_0 increases rapidly with K and reaches the system size (∞) for

$$\frac{Ka}{2\pi\kappa} = [\exp(4\pi\kappa/3T) - 1]^{-1}$$

- Typical parameters:

$$\kappa \simeq 5 \cdot 10^{-13}\, erg\,;\; K \simeq 10^{-6}\, erg/cm\,;\; a \simeq 1\, nm$$

Membrane roughness:

- Correlation length ξ_0 for which n fluctuations are of order unity

$$< u^2(r) >= T \int \frac{d^2 q_\perp}{(2\pi)^2} \frac{1}{\kappa q_\perp^4 + K|q_\perp|^3} =$$

$$\frac{T}{2\pi K^2} \left(K \frac{L_\perp}{2\pi} + \kappa \ln \frac{2\pi\kappa + aK}{2\pi\kappa + L_\perp K} \right)$$

- For $K = 0$ we recover the known for a membrane in isotropic solvent behavior $< u^2 > \propto L_\perp^2$, and in a strong nematic solvent $< u^2 > \propto L_\perp$.

Renormalization of κ:

- By non-linear terms in the bending energy

$$\kappa_R^{anh} = \kappa - \frac{T}{4\pi} \ln \frac{\kappa q_{max} + K}{\kappa q_{min} + K}$$

- By nematic Casimir effect

$$\kappa_R^{Cas} = \kappa + \frac{3T}{128\pi} \ln \frac{L_\perp}{a}$$

The same in words:

- In the limit $K \to 0$ (almost isotropic solvent):

$$\kappa_R^{anh} \simeq \kappa - \frac{T}{\pi} \ln \frac{L_\perp}{a}$$

- When $K \neq 0$, divergent ln is replaced by a constant factor

$$\ln(1 + \kappa\pi/(aK))$$

- In addition there is also increase of κ due to Casimir effect in a nematic solvent.

Stack of membranes ($L_z = d$):

- Strong nematic solvent condition $Kd \gg \kappa$ (might be weaker condition than $Ka \gg \kappa$)

$$< u^2(r) >= \frac{T}{4\pi\kappa q_0^2} \frac{1 + Kd(1 + 2q_0 d)/\kappa}{1 + (Kd/\kappa)^2}$$

  where q_0 is the low-q cutoff in the membrane plane should be determined self-consistently.

- Membrane stack to be sterically stabilized

$$< u^2 > \simeq d^2$$

This determines q_0:

- for a weak nematic solvent

$$q_0 d \simeq \sqrt{\frac{T}{\kappa}}$$

- for a strong nematic solvent $Kd \gg \kappa$

$$(q_0 d)^2 = \frac{T}{4\pi K d}(1 + 2q_0 d)$$

since typically $\kappa > T$ and $Kd > T$

$$q_0 \simeq \left(\frac{T}{4\pi K}\right)^{1/2} d^{-3/2}$$

- This defines a new in-plane correlation length $\xi = q_0^{-1}$ (mean distance between membrane collisions), and it yields

$$P \simeq \frac{T}{d\xi^2}$$

Casimir energy for a membrane stack in nematic solvent:

- because $F/A = Pd$ we arrive at

$$\frac{F}{A} = \frac{T^2}{4\pi K d^3}$$

- should be compared with the d^{-2} behavior for a stack in isotropic solvent and with d^{-1} law for electrostatic stabilization.

Elastic energy for a membrane stack in nematic solvent:

- $$F_{sm} = \frac{1}{2}\int \frac{d^3q}{(2\pi)^3}\left(\overline{B}q_z^2 + \left(\frac{\kappa}{d} + K\right)q_\perp^4\right)|u(q)^2|$$
- B scales as $d^{-\alpha}$ with $\alpha = 2\,,\,3\,,\,4$ for electrostatic, Casimir-like in isotropic solvent, and Casimir-like in nematic solvent, stabilizations.
- According to the Landau - Peierls theorem, a membrane stack structure factor has power law behavior (instead of Bragg peaks):

$$S(0, q_z) \propto (q_z - 2\pi/d)^{-2+\eta}$$

- $$\eta = \frac{\pi}{2d^2}\frac{T}{\sqrt{\overline{B}(\kappa/d + K)}}$$

Miscellaneous:

- Because $K > \kappa/d$ in a strong nematic solvent η decreases when the solvent undergoes nematic transition.
- In smectic solvent

$$\kappa_R \to \kappa + 2\sqrt{\kappa_s B} d$$

- Magnetic field along the normal to a membrane

$$|q_\perp|^3 \to q_\perp^2 \sqrt{q_\perp^2 + \xi_H^{-2}}$$

where $\xi_H = (K/\chi_a H^2)^{1/2}$.

- Magnetic field further reduces the height fluctuations of the membrane and correspondingly yields to very weak pseudo-Casimir repulsion, and suppresses the Landau - Peierls instability in favor of Bragg peaks at $q = 2\pi/d$.

CREDITS:

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