

Chapter 4

Thermal fluctuations of surfaces and membranes

marc.durand@univ-paris-diderot.fr

• Outline :

- I- Interface between bulk phases (liquids or solids)
 - Thermal fluctuations
 - Roughening transition

- II- Membranes
 - Helfrich energy
 - Surface tensions of a membrane
 - entropic elasticity
 - entropic interactions

• Bibliography for this lesson :

- S. Safran, “Statistical thermodynamics of surfaces, interfaces and membranes”
- Chaikin and Lubensky, “Principles of Condensed Matter Physics”
- D. Nelson, T. Piran, S. Weiberg, “Statistical mechanics of membranes and surfaces”

1 Thermal fluctuations of an interface

- Up to now, we assumed the idealized interface to be flat. However, the interface might be crumpled due to thermal fluctuations.

- This description makes sense only if the height fluctuations are larger than the typical thickness of the *real* interface.

- The goal of this paragraph is to develop the formalism that allows to characterize these thermal fluctuations.

- From amplitude of fluctuations we can measure extremely low values of surface tensions.

1.1 Coarse-grained description

- Strictly, a microstate λ of the system is given by the values of all the degrees of freedom of its constituents : e.g., the position and momentum of every molecule of both phases in a classical description. However, such a fined-grained description is too cumbersome.

- Instead, we use a coarse grained description in which a (coarse-grained) microstate L is given by the configuration $\mathbf{r}(s)$ of the interface shape.

- The coarse-grained Hamiltonian \mathcal{H}_L is formally defined as :

$$Z_L = e^{-\beta\mathcal{H}_L} \equiv \sum_{\{\lambda \rightarrow L\}} e^{-\beta E_\lambda},$$

where the sum is carried over all the microstates λ that correspond to the same interface shape L .

In a classic description, the sum is carried over all $\mathbf{q}_i, \mathbf{p}_i$ of the molecules of the two phases, i.e. \mathbf{p}_i is integrated over $] -\infty, +\infty[$, and \mathbf{q}_i is integrated over the half-space of the corresponding phase.

Note : actually, \mathcal{H}_L is a partial free energy, not an energy : \mathcal{H}_L depends on T .

- Such coarse-grained description introduces some mathematical difficulties yet :

- We replace a large but finite number of **degrees of freedom** (dof) with a continuum of dof : the points that describe the interface contour.

- How to enumerate properly the different configurations of the interface ?

Note : in a quantum description, each dof takes discrete values. However, quasi classic approximation tells us that the right measure in the classic description (in which the dof have continuous values) is $\frac{1}{N!} \prod_{\alpha=1}^N \frac{d^3\mathbf{q}_\alpha d^3\mathbf{p}_\alpha}{h^3}$.

1.2 Expression for \mathcal{H}_L

- For short-range interactions between molecules, the (partial) surface free energy (or surface grand-potential) of an element of area dA must be $\propto dA$. Thus :

$$\mathcal{H}_L = \iint_{A_L} \gamma dA,$$

where A_L is the surface area of the interface in configuration L .

- γ , the surface tension, is not exactly the same that the one introduced before when we studied the surface from a macroscopic point-of-view. At this scale, the interface is smooth and flat (far from any boundary). Let us note γ_p and A_p the corresponding surface tension and surface area of the flat, projected, area. The surface free energy is then $\gamma_p A_p$. Thus, the two surface tensions are related through :

$$e^{-\beta\gamma_p A_p} = \sum_L e^{-\beta\gamma A_L}$$

- In addition to short-range interactions, molecules are submitted to long-range interactions with external fields, in particular with gravity, which must be included.

1.3 Monge parametrization

- To make statistics on the interface configurations, we need to define first a parametrization of the interface. The most natural one is the *Monge parametrization* : each point is located by its height $h(x, y)$ from the Oxy plane, which coincides with the average interface height.
 - By definition, $\langle h \rangle = 0$ (but $\langle h^2 \rangle \neq 0$).
 - Monge parametrization cannot describe contours with “overhangs”. Therefore, it works for not too high temperature only.

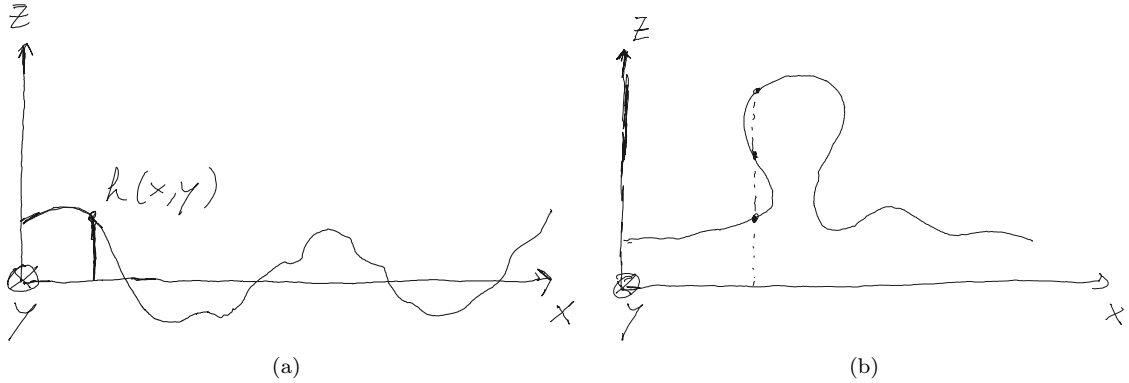


FIGURE 1 – Monge parametrization. (a) Position of every point of the interface given by $(x, y, z = h(x, y))$. (b) Such a parametrization cannot describe configurations with overhangs (several values of h for given (x, y)).

- Expression of \mathcal{H}_L :

– $A_L = \iint_{A_p} \|\mathbf{du} \times \mathbf{dv}\|$ with $\mathbf{du} = (dx, 0, \frac{\partial h}{\partial x} dx)$ and $\mathbf{dv} = (0, dy, \frac{\partial h}{\partial y} dy)$ ¹. It comes :

$$A_L = \iint_{A_p} \sqrt{1 + \left(\frac{\partial h}{\partial x}\right)^2 + \left(\frac{\partial h}{\partial y}\right)^2} dx dy.$$

And for small gradients :

$$A_L = A_p + \frac{1}{2} \iint_{A_p} (\nabla h)^2 dx dy + \mathcal{O}(\nabla h)^4.$$

– Adding gravity energy $\iint_{A_p} \int_0^{h(x,y)} \rho g z dx dy$ (where ρ is the difference of density of the two fluids), the coarse-grained Hamiltonian writes :

$$\mathcal{H}_L \equiv \mathcal{H}[h] = \gamma A_p + \frac{\gamma}{2} \iint_{A_p} (\nabla h)^2 dx dy + \frac{\rho g}{2} \iint_{A_p} h^2 dx dy. \quad (1)$$

– The 2 phases and their interface lie in a box with fixed dimensions. The first term is a constant then, and it does not play any role in the statistics of configurations and hence can be dropped out.

– note : since we assume thermal equilibrium, time average and ensemble average are equivalent, and we forget temporal dependence of the quantities.

¹. Incidentally, we can easily calculate the coordinates of normal unit vector $\mathbf{n} = (1 + (\nabla h)^2)^{-1/2} \left(-\frac{\partial h}{\partial x}, -\frac{\partial h}{\partial y}, 1 \right)$. It will be useful for Section 1.7.

- To get statistics on interface configurations, one needs to calculate the partition function $Z = \sum_{\{L\}} e^{-\beta\mathcal{H}_L}$. We extend the notion of integration over variables to integration over functions (functional integration) :

$$Z = \int e^{-\beta\mathcal{H}[h]} \mathcal{D}\left[\frac{h}{\delta}\right],$$

where the *measure* $\mathcal{D}\left[\frac{h}{\delta}\right]$ is an element of “volume” in the space of h functions.

- Z is a dimensionless quantity. We introduced a quantum of height fluctuations δ to satisfy this requirement. Probably δ is $\sim \lambda_T$ (thermal de Broglie length) but its value is not important.
- How to enumerate properly the different interface configurations? That is, how to define properly the measure $\mathcal{D}[h/\delta]$?
- \Rightarrow we must start from a discretized interface.

1.4 Discretized interface

- In a first step, we approximate the real interface with an interface made of N^2 square patches connecting N^2 mathematical points lying in the real interface.
 - One assumes $N^2 \ll \mathcal{N}$, the number of molecules (or more exactly, the number of dof) of both phases. In the thermodynamic limit, \mathcal{N} , and so N , become very large.
 - Therefore, a large number of fine-grained microstates λ corresponds to a same coarse-grained microstate L , given by the location of the N^2 points.
 - Let choose the point location such that they keep uniform distance a in the x and y directions. This will allow to work in the reciprocal (Fourier) space. We can always introduce an ad-hoc function $\mathcal{H}^*(\{h_{mn}\})$ and write :

$$Z_N = \int \dots \int e^{-\beta\mathcal{H}^*(\{h_{mn}\})} \prod_{m,n=0}^{N-1} \left(\frac{dh_{mn}}{\delta} \right).$$

where $h_{mn} = h(x = ma, y = na)$.

- In the limit $N \rightarrow \infty$ ($a \rightarrow 0$), we may be inclined to identify $\mathcal{H}[h]$ (Eq. 1) with $\mathcal{H}^*(\{h_{mn}\})$ and $\mathcal{D}[h/\delta]$ with $\prod_{m,n=0}^{N-1} (dh_{mn}/\delta)$. However, this is not the only possible choice : we could introduce *any* function $f(\{h_{mn}\})$ and make the identification $\mathcal{D}[h/\delta] \equiv f(\{h_{mn}\}) \prod_{m,n=0}^{N-1} (dh_{mn}/\delta)$, $\mathcal{H}[h] \equiv \mathcal{H}^*(\{h_{mn}\}) + k_B T \ln f(\{h_{mn}\})$. In the following we will assume $f = 1$ and will come back on the validity of this guess in Sect. 1.7 :

$$Z = \int e^{-\beta\mathcal{H}[h]} \mathcal{D}\left[\frac{h}{\delta}\right], \quad \text{with} \quad \mathcal{D}\left[\frac{h}{\delta}\right] = \lim_{N \rightarrow \infty} \prod_{m,n=0}^{N-1} \left(\frac{dh_{mn}}{\delta} \right) \quad (2)$$

and $\mathcal{H}[h]$ given by Eq. 1. Note that we wrote that N can goes up to infinity. However, this is not true, as emphasized before : it cannot exceed the number of dof of the system, which is very large, but finite.

- To calculate Z , it is convenient to work in the reciprocal space. However, one must be careful on what is the corresponding measure in reciprocal space. Here again, it is useful to define it first for the discretized interface (note that we could also calculate Z in the real space, using discretized interface).

– One defines the *Discrete Fourier Transform* as follows : we can always write (this is just a linear change of variables) :

$$h_{mn} = \sum_{k_x, k_y} \tilde{h}(k_x, k_y) e^{i\mathbf{k}\cdot\mathbf{r}},$$

where both k_x and k_y must take N distinct values.

– We use periodic boundary conditions : $h_{m,n} = h_{m+N,n} = h_{m,n+N}$. Thus $e^{ik_x Na} = e^{ik_y Na} = 1$, i.e. $k_x = n_x 2\pi/Na$, $k_y = n_y 2\pi/Na$.

– Both n_x, n_y must take N different values, e.g. within $[0, N-1]$ or within $]-N/2, +N/2]$ (assuming

N is even for simplicity). With this second choice, \mathbf{k} is defined over the first Brillouin zone $]-\pi/a, \pi/a] \times]-\pi/a, \pi/a]$:

$$h_{mn} = \sum_{n_x, n_y = -N/2+1}^{N/2} \tilde{h}_{n_x, n_y} e^{i \frac{2\pi}{N} (mn_x + nn_y)}.$$

– This relation can be inverted easily. One shows that (just calculate RHS and it gives you LHS) :

$$\tilde{h}_{n_x, n_y} = \frac{1}{N^2} \sum_{m, n=0}^{N-1} h_{mn} e^{-i \frac{2\pi}{N} (mn_x + nn_y)}. \quad (3)$$

– Note that since the points are allowed to move only in the z direction, the projected area $A_p = L^2$ with $L = (N-1)a$ is the same for all configurations.

– In the limit $N \rightarrow \infty$, $a \rightarrow 0$ (but $Na = L = \text{cst}$), one recovers the expression of the coefficients of the Fourier series :

$$\tilde{h}(\mathbf{k}) = \frac{1}{L^2} \iint_{A_p} h(\mathbf{r}) e^{-i\mathbf{k}\cdot\mathbf{r}} dxdy.$$

– Equation 3 allows to calculate the elements of the Jacobian matrix associated with the change of variables $J_{ij} = \frac{\partial \tilde{h}_i}{\partial h_j}$.

– N^2 real variables $\{h_{mn}\}$ in the real space.

– Also N^2 real variables $\{\tilde{h}_{n_x, n_y}^{\mathcal{R}}, \tilde{h}_{n_x, n_y}^{\mathcal{I}}\}$ in the reciprocal space too : since $h_{mn} \in \mathbb{R}$, $\tilde{h}_{n_x, n_y}^* = \tilde{h}_{-n_x, -n_y}$, so the functions $\tilde{h}_{n_x, n_y}^{\mathcal{R}}, \tilde{h}_{n_x, n_y}^{\mathcal{I}}$ constitute a set of independent variables only if we restrict the values of n_x, n_y over the half-plane, e.g. $n_x \in]-N/2, N/2]$ and $n_y \in]0, N/2]$.

– The Jacobian determinant is $|J_N| = 2^{N^2/2-1}$, and the measure in the reciprocal space is :

$$D\left[\frac{\tilde{h}}{\delta}\right] = \lim_{N \rightarrow \infty} |J_N| \prod_{n_x = -N/2+1}^{N/2} \prod_{n_y = 1}^{N/2} \frac{d\tilde{h}_{n_x, n_y}^{\mathcal{R}} d\tilde{h}_{n_x, n_y}^{\mathcal{I}}}{\delta^2}. \quad (4)$$

– In fact, the exact value of $|J_N|$ is not important for our purpose. The important point for us is that $|J_N|$ is a constant. This is due to the fact that the change of variables is linear².

1.5 Partition function

• Expression of \mathcal{H} using Fourier expansion :

– Using the Fourier expansion $h(x, y) = \sum_{k_x, k_y} \tilde{h}(k_x, k_y) e^{i\mathbf{k}\cdot\mathbf{r}}$, Eq. 1 becomes :

$$\mathcal{H}[h] = -\frac{\gamma}{2} \iint_{A_p} \sum_{\mathbf{k}, \mathbf{k}'} \mathbf{k} \cdot \mathbf{k}' \tilde{h}(\mathbf{k}) \tilde{h}(\mathbf{k}') e^{i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{r}} dxdy + \frac{\rho g}{2} \iint_{A_p} \sum_{\mathbf{k}, \mathbf{k}'} \tilde{h}(\mathbf{k}) \tilde{h}(\mathbf{k}') e^{i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{r}} dxdy.$$

– Using the fact that $\tilde{h}^*(k_x, k_y) = \tilde{h}(-k_x, -k_y)$ and $\iint_{A_p} e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} dxdy = L^2 \delta_{\mathbf{k}, \mathbf{k}'}$, we obtain :

$$\mathcal{H}[h] = \frac{\gamma L^2}{2} \sum_{\mathbf{k}} (k^2 + \ell_c^{-2}) |\tilde{h}(\mathbf{k})|^2, \quad (5)$$

where $\ell_c = \sqrt{\gamma/\rho g}$ is the capillary length.

– The partition function is :

$$Z = \int e^{-\frac{\beta \gamma L^2}{2} \sum_{\mathbf{k}} (k^2 + \ell_c^{-2}) |\tilde{h}(\mathbf{k})|^2} \mathcal{D}\left[\frac{\tilde{h}}{\delta}\right],$$

2. Personal side-note : Morse et Millner trouvent que *delta* dépend en fait de a . Le Jacobien dépend alors aussi de a mais de sorte que finalement ces 2 dépendances se compensent !

with $\mathcal{D}[\tilde{h}]$ given by Eq. 4.

– Using the fact that $\int_{-\infty}^{+\infty} e^{-\alpha x^2} = \sqrt{\pi/\alpha}$, it comes :

$$Z = \lim_{N \rightarrow \infty} \left(\frac{J_N}{\delta^{N^2}} \prod_{k_x = (-\frac{N}{2} + 1) \frac{2\pi}{L}}^{\frac{N}{2} \frac{2\pi}{L}} \prod_{k_y = \frac{2\pi}{L}}^{\frac{N}{2} \frac{2\pi}{L}} \sqrt{\frac{\pi}{\beta \gamma L^2 (k_x^2 + k_y^2 + \ell_c^{-2})}} \right).$$

1.6 Thermal roughness of the interface, and correlation function

- One can now calculate average quantities such as the roughness $\sqrt{\langle h^2 \rangle}$ of the interface :
 - For a homogeneous and isotropic interface (invariance by translation and rotation), $\langle h^2(x, y) \rangle$ is independent of x and y , i.e. $\langle h^2(x, y) \rangle = \overline{\langle h^2(x, y) \rangle} = \langle \overline{h^2(x, y)} \rangle$, where $\overline{}$ denotes spatial average, and $\langle \rangle$ the statistical average.
 - We already established, when calculating the gravitational energy of a configuration (Eq. 5) that :

$$\overline{h^2} = \sum_{\mathbf{k}} |\tilde{h}(\mathbf{k})|^2.$$

Therefore,

$$\langle h^2 \rangle = \sum_{\mathbf{k}} \left(\langle |\tilde{h}^{\mathcal{R}}(\mathbf{k})|^2 \rangle + \langle |\tilde{h}^{\mathcal{I}}(\mathbf{k})|^2 \rangle \right).$$

– Using the expression of Z , it comes :

$$\langle |\tilde{h}^{\mathcal{R}}(\mathbf{k})|^2 \rangle = \langle |\tilde{h}^{\mathcal{I}}(\mathbf{k})|^2 \rangle = -\frac{\partial \ln Z}{\partial \beta (\gamma L^2 (k^2 + \ell_c^{-2}))} = \frac{1}{\gamma L^2 (k^2 + \ell_c^{-2})} \frac{k_B T}{2}$$

(this is Equipartition theorem!). Thus :

$$\langle h^2 \rangle = \sum_{\mathbf{k}} \frac{k_B T}{\gamma L^2 (k^2 + \ell_c^{-2})}.$$

We remind that for the discrete interface with $N \times N$ points, $k_x = n_x 2\pi/Na$, $k_y = n_y 2\pi/Na$ with $-N/2 < n_x, n_y \leq N/2$. The mode $n_x = n_y = 0$ is disregarded of the sum because we imposed $\overline{h} = \tilde{h}(\mathbf{k} = \mathbf{0}) = 0$.

– As we don't know calculate this sum, we will use the continuous approximation : as N is very large (and a very small for that $Na = L = \text{cst}$), we introduce the density of modes $\rho(k)$, defined as follows : the number of modes \mathbf{k} having $|\mathbf{k}| \in [k, k + dk]$ is $\rho(k)dk = 2\pi k dk / (2\pi/L)^2$.

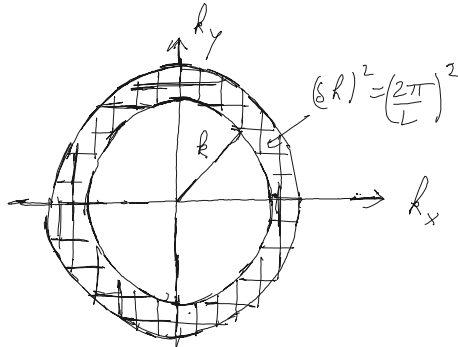


FIGURE 2 – Calculation of the density of modes $\rho(k)$.

Therefore :

$$\langle h^2 \rangle = \frac{1}{2\pi} \int_{2\pi/L}^{2\pi/L} \frac{k_B T}{\gamma (k^2 + \ell_c^{-2})} k dk.$$

$k_{min} = 2\pi/L$ is the first non-zero mode. $k_{max} = \pi/a = 2\pi/\Lambda$ is the largest mode. Note that if we had taken $N \rightarrow \infty$, $a \rightarrow 0$ (with $Na = L = \text{cst}$), the integral would not converge. This is not surprising : the continuous description fails for wave-length comparable to the interatomic distance. Moreover, as we emphasized in the beginning, N must be smaller than the number of dof of the systems, which is large but finite.

– Integration gives :

$$\langle h^2 \rangle = \frac{k_B T}{4\pi\gamma} \ln \left[\frac{1 + (2\pi\ell_c/\Lambda)^2}{1 + (2\pi\ell_c/L)^2} \right].$$

– Usually, $L \gg \ell_c \gg \Lambda$:

$$\langle h^2 \rangle \simeq \frac{k_B T}{2\pi\gamma} \ln \left(\frac{2\pi\ell_c}{\Lambda} \right).$$

In this limit, $\langle h^2 \rangle$ is independent of L , what is observed experimentally. Note the importance of the gravity term in the Hamiltonian for this result. This is gravity that limits the large deformations of the interface.

– Order of magnitude : the term $2\pi\ell_c/\Lambda$ does not change a lot with the nature of the two fluid phases, so $\langle h^2 \rangle$ is mainly governed by the prefactor $k_B T/2\pi\gamma$.

- For water-air interface at 300 K : $k_B T \simeq 4.10^{-21}$ J, $\gamma \simeq 70$ mN/m, and thus $\sqrt{\langle h^2 \rangle} \simeq 10^{-10}$ m. This is very small, smaller than the typical thickness of the real interface (see previous chapter). This description is certainly not adapted!
- For interface between liquid and gas phases colloids+polymer mixtures, : $\gamma \lesssim 100$ nN/m, and thus $\sqrt{\langle h^2 \rangle} \gtrsim 10^{-7} - 10^{-6}$ m. Fluctuations can be observed with an optical microscope!
- Correlation function $g(\mathbf{r}) = \langle h(\mathbf{0})h(\mathbf{r}) \rangle$. Using the same methodology, we show that :

$$g(\mathbf{r}) = \frac{k_B T}{2\pi\gamma} K_0 \left(\frac{r}{\ell_c} \right),$$

where K_0 is the Modified Bessel function of the second kind at zeroth order. $K_0(z) \sim e^{-z}/z$ when $z \gg 1$.

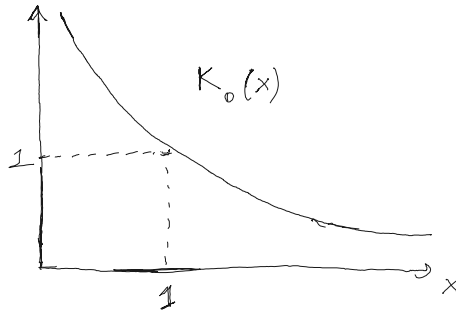


FIGURE 3 – Modified Bessel function of the second kind at zeroth order K_0 .

1.7 Corrections to the measure $\mathcal{D}[h]$

• In Section 1.4 we emphasized that the identification of the coarse-grained Hamiltonian $\mathcal{H}[h]$ and the measure $\mathcal{D}[h/\delta]$ is not unique. The correct identification must be such that both $\mathcal{H}[h]$ and $\mathcal{D}[h/\delta]$ have a physical meaning that is independent of the choice of the reference $h = 0$ and of the system of coordinates (x, y) (they must also be invariant by translation and rotation). The choice we made ($f = 1$) does not satisfy this property :

• First, we can notice that with this choice of measure, a same interface configuration is counted multiple times : when the height of a given point (m, n) is increased of $dh_{m,n}$, this displacement

has a component which is locally tangent to the interface. Such tangential displacement does not modify the shape of the interface at first order (and in the limit $a \rightarrow 0$).

- Therefore we must replace $dh_{m,n}$ by $dh_{m,n} \mathbf{n}_{m,n} \cdot \mathbf{e}_z$ in the measure to weight properly the different configurations.
- Considering only normal displacements also ensures that we do not account for non-realistic configurations with singular points.

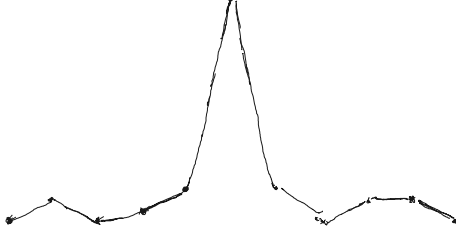


FIGURE 4 – In our naive enumeration of the configurations, such non-realistic configurations with singular points were accounted for.

- From the expression of the local normal vector given in Section 1.3, one has $\mathbf{n} \cdot \mathbf{e}_z = \left(1 + (\nabla h)^2\right)^{-1/2} \simeq 1 - (\nabla h)^2/2$. Then we have the correct measure by multiplying the wrong one (Eq. 2) with $\prod_{m,n=0}^{N-1} \left(1 - (\nabla h)_{m,n}^2/2\right)$. Equivalently, this term can be written :

$$\exp \left[\sum_{m,n=0}^{N-1} \ln \left(1 - (\nabla h)_{m,n}^2/2\right) \right] \simeq \exp \left[-\frac{1}{2a^2} \iint_{A_p} (\nabla h)^2 dx dy \right].$$

- This term can be incorporated in the surface tension term in Eq. 1 by defining a new surface tension : $\gamma^* = \gamma + k_B T/a^2$. N.A. : with $\gamma \sim 4 \cdot 10^{-2} \text{ N/m}$, $k_B T \sim 4 \cdot 10^{-21} \text{ J}$, and $a \sim 10^{-9} \text{ m}$, one has $k_B T/(\gamma a^2) \sim 10^{-1}$, that is, a correction of 10%. The correction becomes more important for lower surface tension values.
- Second, some authors (Cai, Lubensky, Nelson, Powers (J. Phys. II **4**, 1994)) claim that a second corrective term should be added, to take into account the fact that the number of molecules fluctuates with configuration, while the number of points (and their projected distance in the xy plane, a) of the discretized interface is independent of the configurations. This is still debated.
- The inclusion of these corrections ensures that $\mathcal{D}[h/\delta]$ is independent of the choice of reference frame $h = 0$ and of the system of coordinates (x, y) . Unfortunately, these corrections have not been taken into account in textbooks yet !

2 Membranes

2.1 Introduction

- Most of boundaries within the cell and with the cell outside are lipid bilayer membranes (with few proteins).
- lipids are amphiphilic molecules with very low solubility : max concentration of lipids in bulk $\sim 10^{-10} - 10^{-6}$ M. **Here, there is no reservoir of molecules in the bulk.**
- At physiological temperature, biological membranes are usually in the *fluid phase* : molecules freely move and diffuse within the surface. Diffusive coefficient : $D \sim 1 \mu\text{m}^2/\text{s}$.

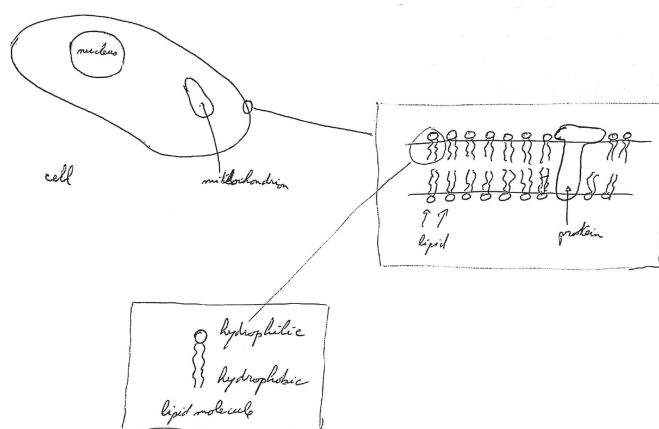


FIGURE 5 – Biological material is surrounded by lipid bilayers.

2.2 Energy of a membrane

Two kinds of deformation : in-plane (stretching+shearing) and out-of-plane (bending).

2.2.1 In-plane strain energy

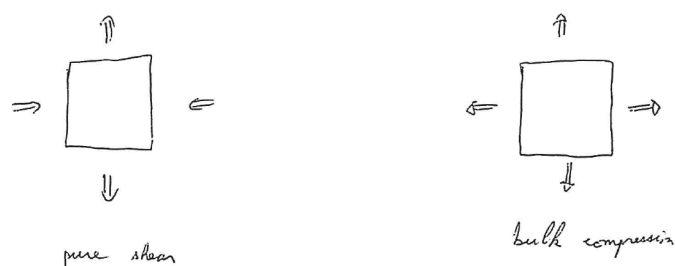


FIGURE 6 – Two independent modes of in-plane deformations.

- Two independent in-plane deformations : stretching+shearing : the first one is associated with a change of area, while the second one preserve the are.
- Shear modulus : we consider here only quasi-static deformation of fluid membranes :strain rate is low compared with relaxation rate associated with the in-plane displacements of the molecules.

Thus, **shear modulus of a fluid membrane is zero.**

- Bulk modulus : when the surface is stretch or compressed, there is no exchange of lipids with the bulk, because of their very low solubility. Thus the surface concentration Γ must vary from its equilibrium value Γ_0 . Let $f_s(\Gamma)$ be the stretching free energy per unit surface area : $f'_s(\Gamma_0) = 0$ and thus :

$$f_s(\Gamma) \simeq f_s(\Gamma_0) + f''_s(\Gamma_0)(\Gamma - \Gamma_0)^2/2,$$

and so the increase of free energy is :

$$\Delta f_s = \frac{\kappa_s}{2} \left(\frac{\Gamma - \Gamma_0}{\Gamma_0} \right)^2.$$

κ_s is the stretching modulus of the membrane. Typically $\kappa_s \sim 100$ mN/m. This is quite high : a membrane will deform preferably through bending rather than stretching mode.

2.2.2 Bending energy

- If the membrane is slightly curved, we can expand the bending free energy per unit surface area f_b in terms of the surfaces curvatures C_1 and C_2 :

$$f_b(C_1, C_2) = f_0 + f_1 C_1 + f_2 C_2 + f_3 C_1^2 + f_4 C_2^2 + f_5 C_1 C_2 + \dots$$

- The free energy is a scalar quantity : its value must be independent of the choice of frame in which it is calculated. Therefore, f_b must be a function of the 2 invariants of the Hessian matrix : $H = C_1 + C_2$ and $G = C_1 C_2$, where C_1 and C_2 now represent the *principal* curvatures. Up to second order terms :

$$f = f_0 + f_1 H + f_2 H^2 + \bar{f}_2 G$$

(these are not the same coefficients as in the previous equation!). This equation can be rewritten :

$$\Delta f_b = \frac{\kappa_b}{2} (C_1 + C_2 - C_1^0 - C_2^0)^2 + \kappa_G C_1 C_2.$$

κ_b : bending rigidity (always > 0)

κ_G : gaussian bending rigidity

C_1^0, C_2^0 : spontaneous curvatures

- *Theorema Egregium* (Gauss) : The gaussian curvature G of a surface is preserved under isometric transformation (*i.e.*: transformation that preserves distances, *e.g.*: plane \rightarrow cylinder).

Consequence : under isometric transformation, only the term associated with mean curvature is modified. Since $\Delta f_b > 0$, it comes : $\kappa_b > 0$.

- Gauss-Bonnet formula : for a closed membrane :

$$\oint\!\!\!\oint G d^2 S = 4\pi(1 - g) = \text{cst.}$$

- Spontaneous curvatures are 0 for membranes with up-down symmetry, but not when considering *e.g.*: one monolayer, or one bilayer with different molecules or concentrations on both sides, or with asymmetric proteins in it.

2.3 Thermal fluctuations of a membrane

- We consider a closed membrane (=vesicle) with zero spontaneous curvatures. Its area/volume ratio is usually larger than for a sphere (flattened ball). We suppose that the large-scale curvature of the vesicle is small compared with the curvatures associated with thermal fluctuations, so the

reference shape is considered flat locally.

- Coarse grained Hamiltonian (this is the partial free energy for a given shape, number of molecules, and temperature) :

$$\mathcal{H} = \frac{\kappa_b}{2} \iint_A (C_1 + C_2 - C_1^0 - C_2^0)^2 dA + \frac{\kappa_s}{2} \iint_A \left(\frac{\Gamma - \Gamma_0}{\Gamma_0} \right)^2 dA$$

(constant term have been dropped).

- Strictly, the number of lipid molecules is fixed : $\iint_A \Gamma dA = \Gamma_0 A = \text{cst}$. Evaluate the statistical weight of every configuration with this constraint is not easy. However, we have seen that stretching modulus is high \Rightarrow we will consider that the surface area of the membrane is fixed, and the surface concentration is $\Gamma = \Gamma_0$. The variable Γ is then eliminated from the coarse-grained Hamiltonian :

$$\mathcal{H} = \frac{\kappa_b}{2} \iint_A (C_1 + C_2 - C_1^0 - C_2^0)^2 dA \quad \text{with constraint} \quad \iint_A dA = \text{cst}.$$

- **Lagrange multiplier technique** : we define $\mathcal{H}' = \mathcal{H} + \sigma A$, where σ is the Lagrange multiplier. Now we can do statistics on any configuration, as if there is no constraint on the area.

- Equivalent interpretation : **change of ensemble** : we consider that the membrane is in contact with a reservoir of area, with fixed ‘‘tension’’ σ (Legendre transformation) \Rightarrow new thermodynamic potential $\mathcal{H}' = \mathcal{H} + \sigma A$.

- σ is often called the *intrinsic surface tension* of the membrane, but this name is misleading : its interpretation as a tension is not clear : its orientation should change with configuration to remain tangent to the interface!

– Its origin is elasticity due to the increase (or decrease) of distance between lipids. It is thus very different from the origin of the surface tension of an interface between to bulk phases (which is due to the cost of energy to create new bonds between the two kinds of molecules). We remind that for lipids there is no reservoir in the bulk.

– σ is better understood as related to the (fixed) chemical potential μ of a reservoir of lipids (rather than reservoir of area). One has $\sigma A = \mu N$ and $N = \Gamma_0 A$. Thus $\sigma = \mu \Gamma_0$.

- σ is not directly measurable. What we measure (numerically or experimentally) is the *mechanical (or frame) tension* τ of a membrane attached to some kind of frame :

$$\tau = \frac{\partial F}{\partial A_p}.$$

- Expansion for small curvatures :

$$\mathcal{H}' = \frac{\kappa_b}{2} \iint_{A_p} (\nabla^2 h)^2 dx dy + \frac{\sigma}{2} \iint_{A_p} (\nabla h)^2 dx dy$$

- Expansion in Fourier Series :

$$h(x, y) = \sum_{\mathbf{k}} \tilde{h}(\mathbf{k}) e^{-i\mathbf{k}\cdot\mathbf{r}}.$$

After lengthy but simple calculations, we obtain :

$$\langle |\tilde{h}(\mathbf{k})|^2 \rangle = \frac{k_B T}{A_p (\sigma k^2 + \kappa_b k^4)}$$

using the naive measure. If we include the corrections to the measure described in Sect. 1.7, σ is replaced with the frame tension τ in the above formula.

- Therefore :

$$\begin{aligned}
\langle h^2 \rangle = \overline{h^2} &= \sum_{\mathbf{k}} |\tilde{h}(\mathbf{k})|^2 \\
&= \sum_{\mathbf{k}} \frac{k_B T}{A_p (\sigma k^2 + \kappa_b k^4)} \\
&= \int_{2\pi/L}^{2\pi/a} \frac{k_B T}{A_p (\sigma k^2 + \kappa_b k^4)} \frac{2\pi k dk}{4\pi^2/A_p}
\end{aligned}$$

Using the dimensionless variable $u = k^2 \lambda_c^2$ where $\lambda_c = \sqrt{\kappa_b/\sigma}$, we obtain without difficulty :

$$\langle h^2 \rangle = \frac{k_B T}{4\pi\sigma} \ln \left(\frac{1 + (a/(2\pi\lambda_c))^2}{1 + (L/(2\pi\lambda_c))^2} \right)$$

Usually, $\lambda_c \gg L \gg a$:

$$\langle h^2 \rangle \simeq \frac{k_B T}{8\pi^3 \kappa_b} L^2.$$

\implies amplitude of fluctuations $\sqrt{\langle h^2 \rangle}$ increases linearly with membrane size L .

- Note : we have considered that the volume of the vesicle is not constrained (permeable membrane). If the volume is constrained, we have to add a new Lagrange multiplier term $-pV$ to the coarse-grained Hamiltonian : $\mathcal{H}'' = \mathcal{H}' - pV$. The Lagrange multiplier p is nothing but the pressure within the vesicle.

Alternative (but equivalent) approach : change of statistical ensemble (Legendre transformation) : the vesicle is in contact with a reservoir of volume with a fixed pressure p .

- **Persistence length** : the change of orientation of the membrane between points $\mathbf{0}$ and \mathbf{r} is measured by $\mathbf{n}(\mathbf{0}) - \mathbf{n}(\mathbf{r})$.

$$- \langle (\mathbf{n}(\mathbf{0}) - \mathbf{n}(\mathbf{r}))^2 \rangle = 2(1 - \langle \mathbf{n}(\mathbf{0}) \cdot \mathbf{n}(\mathbf{r}) \rangle) = 2(1 - \langle \cos \theta(\mathbf{r}) \rangle) \simeq \langle \theta^2(\mathbf{r}) \rangle$$

$$- \text{We remind : } \mathbf{n} = \left(1 + (\nabla h)^2\right)^{-1/2} \left(-\frac{\partial h}{\partial x}, -\frac{\partial h}{\partial x}, 1\right).$$

- Using again Fourier Series analysis, we obtain in the low tension regime ($\lambda_c \gg L \gg a$) :

$$\langle \theta^2(\mathbf{r}) \rangle = \frac{k_B T}{\pi \kappa_b} \ln \frac{r}{a}.$$

- **Persistence length** : typical distance over which $\langle \cos \theta(\mathbf{r}) \rangle \simeq 0$, i.e. : $\langle \theta^2(\mathbf{r}) \rangle \simeq 2$:

$$l_p = a e^{\frac{2\pi \kappa_b}{k_B T}}.$$

