Vanishing tension of fluctuating membranes

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Abstract. — The statistical behavior of fluctuating, flexible membranes or films can be governed by their (surface) tension or by their curvature energy, depending on imposed boundary conditions We present here simple thermodynamic arguments which enable us to classify the different physical situations. In particular, we clarify the notion of vanishing tension, and the (or some of the) conditions under which it can occur Then, in view of this classification, we reconsider the effects of thermal fluctuations on tension and rigidity, and briefly discuss the experimental systems in which renormalization effects should be expected and could be observed

1. Introduction.

When amphiphilic molecules are brought into contact with water they can assemble to form bilayers so as to orient their polar parts towards water and their oily hydrophobic tails away from it These amphiphilic membranes have many interesting properties from the point of view of statistical mechanics they are (quasi-) two-dimensional objects, assembled through weak, nonspecific interactions [1] Morover, recent experiments, such as quantitative studies of the shapes and undulations of bilayer vesicles [2, 3], and of the entropic interactions between membranes [4, 5], have demonstrated that these flexible sheets are often governed by their *rigidity* [6] This means that membranes are dominated by their curvature energy rather than by their surface tension, as is the case for usual fluid/fluid interfaces This is often summarized by the claim that the membranes have *vanishing surface tension*

There exists, however, quite a lot of confusion as for the precise meaning of such a statement What does one really call the surface tension of a membrane ? Is it strictly zero or just very small ? If the tension indeed vanishes, then in which situations does this occur ? And finally, how can one measure membrane tensions and show that they can vanish ? In particular, do the measured tensions depend on the lengthscales involved in experiments ? It seems to us that although these questions are really essential for many recent theoretical and experimental developments it is difficult to find in literature clear answers to them. The aim of this paper is therefore to try to clarify some of these issues

Amphiphilic membranes are not the only systems governed by curvature effects Thin plates, or shells, are also objects for which the dominating energy is bending [7]. By

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introducing constraints (e.g by appropriate boundary conditions) on a free shell one can introduce an internal tension (pressure). For small strains such a tension will be equilibrated by cohesive forces, or compressibility There is an important difference, however, between such a mechanical plate and a membrane : the rigidity modulus for the later is of order $k_B T$. Therefore, a membrane fluctuates due to thermal excitations and one has to consider the tension from a statistical — mechanical rather than a mechanical point of view

For a fluctuating membrane there are two *independent* thermodynamic variables the total area, A, which can be modified through for example compressibility effects or exchange of molecules with a reservoir, and the projected area, A_p, which can be modified through the constraints imposed on the system or can vary due to thermal undulations ([1]) We discuss this important point in chapter 2, where we also argue that the (surface) tension, τ, of the membrane is an intensive thermodynamical variable corresponding to A_p, whereas the variable r corresponding to A is related to the chemical potential of the amphiphilic molecules Although there is no reason in general for r to be equal zero (contrary to what is often claimed in literature) in some physical situations τ can indeed vanish.

Having defined thermodynamic ensembles corresponding to different physical situations we reconsider in chapter 3 an example of a theoretical calculation for which the issue of vanishing or nonvanishing surface tension is crucial Namely, we discuss the problem of the effect of thermal fluctuations on the rigidity constant of fluid membranes [10, 11] We try to point out which lenght scales are important in different situations, and in which situations one can expect to observe the subtle logarithmic renormalization effects to be present. This seems to be a relevant issue in view of recent experiments claiming to observe such effects [12, 13].

The experimental problems are also discussed in the last chapter 4 We try there to clarify what is indeed measured in reflection — type experiments [14, 15] and what are the relevant lengthscales for such experiments.

2. Elementary thermodynamics of fluctuating membranes.

Consider a fluctuating membrane made from amphiphilic molecules Let us suppose, for simplicity, that it spans a planar frame of a total area A_p (Fig. 1). If the number of molecules forming the membrane is $2N$ and the equilibrium area per molecule a_m then the total area of the membrane is $A = a_m N$ We shall suppose for the moment that the compressibility of the monolayers is very low, and thus the total area A can vary only through changes in the number of molecules N (exchange with a reservoir). The quantities A and A_p can be
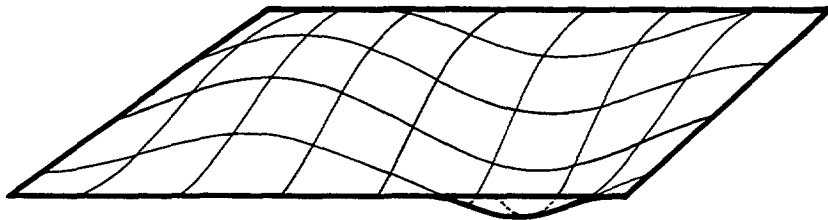

Fig. 1 — A fluctuating membrane spanning a rectangular planar frame of area A_p.

([1]) The distinction between A and A_p is already present in reference [6] but we disagree on their conclusions The need for these two independent variables was previously introduced for lyotropic systems in reference [8] and reference [9]

considered as *independent* thermodynamical variables [6] Indeed, in real systems they can be made to vary independently For instance, for black lipid films or monolayers films on air-water interface the projected area A_p is fixed by the geometry of the experiment, whereas the total area A (directly proportional to N) can fluctuate due to the exchange of the amphiphiles with a reservoir On the contrary, in lipid vesicles, for which the exchange times are long, the total area does not vary, whereas the projected one does fluctuates.

From the thermodynamical point of view, the area A and the projected area A_p are extensive variables. It is important to realize that the corresponding intensive variables represent *distinct* physical quantities The *area coefficient* conjugate to the total area A, which we denote r, is for incompressible films directly proportional to the chemical potential μ, of amphiphilic molecules The *film tension* conjugate to the projected area A_p, which we denote τ, corresponds to the physical « surface tension ». As we shall show below, the situation of « vanishing surface tension » considered by many authors [6, 16, 11] does *not,* in fact, correspond to vanishing r but rather to vanishing τ

With two independent extensive variables one can define four different thermodynamical ensembles

(ı) (A, A_p)-ensemble. We call the membranes belonging to this ensemble *isolated, framed* systems

(ıı) (A, τ)-ensemble. We call the membranes belonging to this ensemble *isolated, unframed* systems.

(ııı) (r, A_p)-ensemble We call the membranes belonging to this ensemble *open, framed* systems.

(ıv) (r, τ)-ensemble. We call the membranes belonging to this ensemble *open, unframed* systems.

In particular two of these four ensembles are important for experimental systems and we shall discuss them now :

Open, framed systems.

In this ensemble the projected area A_p is fixed, for instance by imposing proper boundary conditions on a frame, and the total area A fluctuates. The fluctuations are governed by a Hamiltonian of the form

$$H = rA + H_{el} \tag{1}$$

where H_{el} contains the contribution of elastic internal forces (bending energy, shear modulus, etc.) The partition function is written as the sum over all film configurations $\mathcal{C}$ with fixed A_p

$$Z_0 = \sum_{\mathcal{C}} e^{-\beta H(\mathcal{C})}, \quad \beta = \frac{1}{k_B T}. \tag{2}$$

The free energy in this ensemble is

$$G_0(A_p, r) = -k_B T \ln Z_0(A_p, r) \tag{3}$$

and the film tension is simply defined as free energy per unit area

$$\tau_0 = \lim_{A_p \to \infty} \frac{G_0(A_p, r)}{A_p}. \tag{4}$$

Isolated, unframed systems.

In this ensemble the total area A is fixed while the projected area may fluctuate. The thermodynamical potential is obtained from G_0 by first going to the intermediate (A, A_p) ensemble where *both A and A_p are fixed*, and the thermodynamical potential is obtained by a Legendre transform

$$F_i(A_p, A) = G_0(A_p, r) - rA, \quad A = \left. \frac{\partial G_0}{\partial r} \right|_{A_p} \tag{5}$$

Then one goes to the isolated, unframed film ensemble by a second Legendre transform which defines the associated thermodynamical potential

$$G_i(\tau, A) = F_i(A_p, A) - \tau A_p \tag{6}$$

where the surface tension τ is defined by

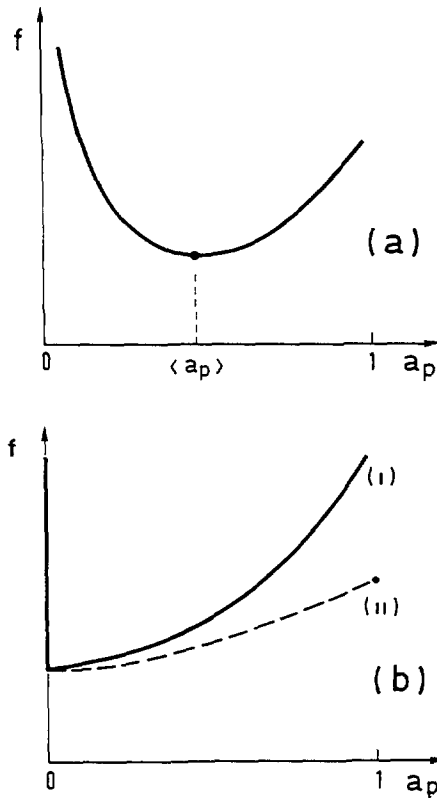$$\tau = \left. \frac{\partial F_i}{\partial A_p} \right|_A = \left. \frac{\partial G_0}{\partial A_p} \right|_r. \tag{7}$$

Fig. 2. — The free energy density f as a function of the area ratio a_p (a) f has a minimum for $a_p > 0$ and the tension τ vanishes (b) f has its minimum at $a_p = 0$ and the tension τ may be positive (i) or zero (ii)

It is clear that *in the thermodynamical limit*, $A \to \infty$, the surface tension defined in this ensemble by (7) coincides with the surface tension defined for the open, framed systems by (4)

We can now analyse the meaning of the tension τ for isolated, unframed systems with fixed total area A. Let us assume that the projected area fluctuates around its mean value $\langle A_p \rangle$. This mean value can be obtained by minimizing $F_t(A_p, A)$ (given by (5)) with respects to A_p, while A is fixed. In the thermodynamical limit, $A \to \infty$, it is better to consider the free energy density

$$f = \frac{F_t}{A} \tag{8}$$

as a function of the area ratio

$$a_p = \frac{A_p}{A} \tag{9}$$

Two situations are then in general possible, as depicted in figure 2

(i) $f(a_p)$ has its minimum for a non zero ratio $0 < a_p < 1$ (Fig 2a) The membrane is then said to be *flat*, since although shrunk due to thermal fluctuations, it still keeps the global structure of a two dimensional object. In such a case, we conclude from (7) that the surface tension vanishes

$$\tau = \frac{\partial f}{\partial a_p}\bigg|_A (\langle a_p \rangle) = 0 \tag{10}$$

(ii) $f(a_p)$ has its minimum at $\langle a_p \rangle = 0$ (Fig 2b) The membrane is then said to be *crumpled*, since it is so shrunk by thermal fluctuations so that its extension in space does not scale linearly with its internal extension ([2]). In this case it is obvious from figure 2b that the tension τ is positive, but has in general no reason to vanish

$$\tau = \frac{\partial f}{\partial a_p}\bigg|_A (\langle a_p \rangle = 0) > 0 \tag{11}$$

One should also include in this case (ii) a marginal situation in which although the minimum of $f(a_p)$ is at $\langle a_p \rangle = 0$, its slope at this point does vanish, and therefore $\tau = 0$.

Each of these cases can in fact be encountered for isolated, unframed systems, at least in idealized theoretical situations Indeed, at low temperatures *polymerized* membranes are in a flat phase, where $\langle a_p \rangle$ is non zero [17] Therefore their tension τ vanishes, except if they are submitted to an external stress. An isolated, unframed *fluid* membrane with fixed topology, on the other hand, is in principle crumpled [11], with $\langle a_p \rangle = 0$, and has therefore a non zero tension [18, 19], as we shall discuss in next section We shall also see that τ is in fact related to the persistance length ξ_κ by the relation $\tau \sim k_B T \xi_\kappa^{-2}$ Finally, free *hexatic* sheets [17], characterized by a quasi-long range orientational order are crumpled (« crinkled ») since $\langle a_p \rangle = 0$, but they correspond to the marginal situation where τ is also zero since their persistence lenght is infinite (the slope of $f(a_p)$ at $\langle a_p \rangle = 0$ vanishes) [20].

([2]) One might be worried that in this situation A_p scales with the number of molecules N as N^ν ($\nu < 1$) and is therefore not an extensive variable However from (7) the tension is then defined by first considering the situation where $a_p = A_p/A > 0$ (in which case A_p is indeed extensive) and **then** taking the limit $a_p \to \langle a_p \rangle = 0$

Free fluid sheets which do not change their topology are hard to realize experimentally However, our argument is much more general and can also be applied for interacting membranes, e g. in a stack of lamellae [4] In the case of a stack of fluid membranes, or in the case of a membrane fluctuating in a confining potential (e.g. of a adsorbing wall), no topology changes will take place as long as the average distance d between membranes (or between the membrane and the wall) is small compared with the persistence length, $(d \ll \xi_\kappa)$. Then the interactions force $\langle a_p \rangle$ to be non zero, while A_p still can fluctuate freely In these situations the tension τ of each membrane vanishes (as described in the case (1) above)

It is important to stress that the argument presented here to explain why τ can vanish for fluctuating membranes is very different from usual arguments leading to the so-called « Schulman » condition [21]. This term is used to describe situations in which the area per molecule, a_m, of a non-fluctuating film, can vary The area $\langle a_m \rangle$ chosen by the system corresponds then to the minimum of the free energy, $\phi(a_m, N)$, and at this minimum

$$\frac{\partial \phi}{\partial a_m} \bigg|_N (\langle a_m \rangle) = 0 \qquad (12)$$

However, this quantity does *not* coincide with the tension, τ, of the film defined in (10). Indeed, the above argument is purely mechanical, since it considers only the internal elastic forces associated to the finite compressibility of the membrane, and since it does not take into account the thermal fluctuations. On the contrary, the argument presented here takes into account the thermal fluctuations, and does not depend on the compressibility.

3. Effective rigidity and tension of fluctuating membranes.

In this section we shall discuss the case of fluid membranes subjected to thermal undulations A phenomenological Hamiltonian for such membranes which is often used is [2, 3]

$$H_{el} = \int dS \left(\frac{\kappa}{2} H^2 + \bar{\kappa} K \right) \qquad (13)$$

where dS is the element of surface.

$$H = \left(\frac{1}{R_1} + \frac{1}{R_2} \right), \quad K = \frac{1}{R_1 R_2} \qquad (14)$$

are respectively the mean curvature and the Gaussian curvature (R_1 and R_2 are the principal radii of curvature), and κ and $\bar{\kappa}$ are respectively the mean and the Gaussian bending rigidity. We assume that the membrane is symmetric so that there is no spontaneous curvature term, linear in H. For flexible fluid membranes, with κ not too large, thermal undulations renormalize the effective bending rigidity and the tension at large distances. Our purpose is not to rederive this well known result in detail, but rather to discuss the meaning of this renormalization for the tension, and its domain of validity, in the light of the discussion of section 2

Most of the calculations of the effect of the renormalization of the rigidity and tension have been done in the « constrained ensemble » where the projected area, A_p, is kept fixed, while the total area, A, fluctuates. Indeed, if one neglects the effect of $\bar{\kappa}$, which is not important as long as no topology changes occur, one can start from the Hamiltonian (1)

$$H_0 = \int dS \left(r_0 + \frac{\kappa_0}{2} H^2 \right) \qquad (15)$$

and then integrate out thermal fluctuations with wavelength larger than a microscopic cutoff $a = \pi/\Lambda$ (which corresponds typically to the width of the membrane, or to the equilibrium extent of a amphiphilic molecule) In doing so one usually assumes that the amplitude of the undulations above the equilibrium plane of the membrane vanishes at infinity (or is periodic) and thus neglects contributions coming from the boundary. This is in fact strictly equivalent to the choice of the constrained ensemble described above.

When integrating out thermal fluctuations one can define two types of effective quantities

Effective potential .

The so called effective potential Γ_{eff} is obtained in the standard way by adding a source term $- \int dS\, \mathbf{X}\mathbf{J}$ to the Hamiltonian H_0 ($\mathbf{X}$ denotes the position of the membrane in 3 dimensional bulk space), computing the free energy (3), and taking its Legendre transform with respect to $\mathbf{J}$ (a precise definition must take into account the reparametrization invariance of (15) by some gauge fixing) The resulting effective potential $\Gamma_{\text{eff}}(\mathbf{X})$ may be expanded in powers of the curvature

$$\Gamma_{\text{eff}} = \int dS \left(r_{\text{eff}} + \frac{\kappa_{\text{eff}}}{2} H^2 + \cdots \right) \tag{16}$$

Γ_{eff} is the generating functional for all static correlations functions for the membrane at thermal equilibrium. In particular its minimization gives the mean equilibrium configuration of the membrane. If this equilibrium configuration is flat (which is not obvious, since this depends on the sign of κ_{eff} and on the sign of the neglected higher order terms) all curvature terms vanish at the minimum in (16) so that

$$\Gamma_{\text{eff/min}} = G_0(A_{\text{p}}, r_0) = A_{\text{p}}\, r_{\text{eff}} . \tag{17}$$

Thus from (4) we obtain again, under the assumption that the equilibrium configuration is flat, an important equality between the effective surface term and the surface tension

$$i_{\text{eff}} = \tau . \tag{18}$$

Renormalized Hamiltonian

An effective Wilson Hamiltonian [22] $H_{\text{eff},\, S}$ is obtained after integrating out all fluctuations with wave vector k in a shell

$$\Lambda_S = \Lambda S^{-1} < |k| < \Lambda \tag{19}$$

where $S > 1$. This nonlocal effective Hamiltonian can again be expanded as

$$H_{\text{eff},\, S} = \int dS \left(r_{\text{eff}}(S) + \frac{\kappa_{\text{eff}}(S)}{2} H^2 + \cdots \right) \tag{20}$$

and it governs the fluctuations of the membrane at wave vectors $|k| < \Lambda_S$. One can then rescale back the distances and momenta

$$\mathbf{X} \to S\mathbf{X}, \quad k \to S^{-1}k \tag{21}$$

in order to obtain the renormalized Hamiltonian

$$H_S = \int dS \left(r_S + \frac{\kappa_S}{2} H^2 + \cdots \right) \tag{22}$$

with the initial cutoff Λ, and the renormalized couplings given by

$$r_S = S^2 r_{\text{eff}}(S) , \quad \kappa_S = \kappa_{\text{eff}}(S) \tag{23}$$

The operation which transforms the initial Hamiltonian H_0 into H_S is the Renormalization Group transformation $\mathcal{R}_S$

In practice, however, the renormalized Hamiltonian H_S is not calculated directly. One performs rather an « infinitesimal R.G. transformation » for an infinitesimal shell, $S = 1 + \varepsilon$,

$$\mathcal{R}_{1 + \varepsilon} = 1 + \varepsilon S \frac{\partial}{\partial S} \mathcal{R}_S \bigg|_{S = 1} = 1 + \varepsilon \mathcal{L} \tag{24}$$

Then one integrates out the corresponding differential equation

$$S \frac{\partial}{\partial S} H_S = H_S , \qquad H_{(S = 1)} = H_0 \tag{25}$$

from 1 to S in order to obtain H_S

From the definition of the intermediate effective Hamiltonian $H_{\text{eff}, S}$ (18, 20), it is clear that in the limit $S \to \infty$ it becomes equal to the effective potential (16)

$$\lim_{S \to \infty} H_{\text{eff}, S} = \Gamma_{\text{eff}} . \tag{26}$$

Therefore the relation with the renormalized couplings (23) and the effective couplings in Γ_{eff} is

$$\kappa_{\text{eff}} = \lim_{S \to \infty} \kappa_S , \qquad r_{\text{eff}} = \lim_{S \to \infty} (r_S/S^2) . \tag{27}$$

The R.G analysis performed for fluid membranes consists now in studying the dependence in the scale factor S of the renormalized rigidity modulus κ_S and the renormalized surface term r_S In order to apply these results to physical situations in which the total area A of the membrane does not fluctuate and the membrane is subjected to a physical tension τ, one has then to use (18). Hence when performing the R G calculation one should start from a Hamiltonian H_0 with microscopic rigidity κ_0 (corresponding to the elastic properties of the membrane at microscopic scales) and with a microscopic surface coefficient r_0 adjusted in such a way that the effective surface term r_{eff}, obtained from the R G calculation by (27), coincides with the physical tension τ (we still assume that the equilibrium configuration is flat)

The R G. calculation at one loop is recalled in Appendix. Its final result (Λ being the sharp regulator in momentum space) is

$$S \frac{\partial}{\partial S} \kappa_S = - \frac{3}{4 \pi} \frac{k_B T}{\left(1 + \dfrac{r_S}{\kappa_S \Lambda^2} \right)} \tag{28}$$

$$S \frac{\partial}{\partial S} r_S = 2 r_S + \frac{k_B T \Lambda^2}{4 \pi} \ln \left(1 + \frac{r_S}{\kappa_S \Lambda^2} \right) . \tag{29}$$

In order to understand the meaning of (28) and (29) it is important to define the domain of

their validity. The calculation is a one loop approximation, therefore it is valid if the terms of order $k_B T$ are small. This implies

$$\kappa > k_B T \quad \text{or} \quad r > k_B T \Lambda^2 \tag{30}$$

depending whether at wave vectors $|q| \sim \Lambda$ it is the curvature energy or the surface term which dominates The phase diagram in the (κ^{-1}, r) plane (for positive r) is depicted in figure 3. It can be separated into three distinct domains .
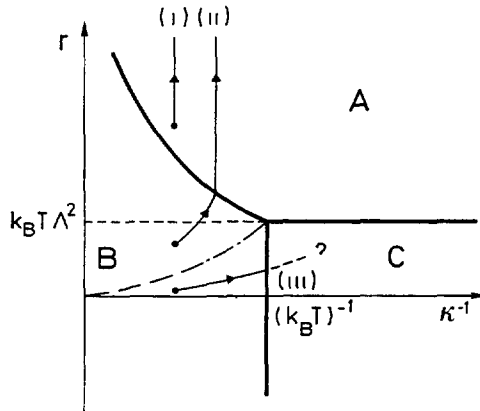

Fig 3 — Phase diagram for fluid membrane and Renormalization Group flows κ^{-1} is the inverse of the bending rigidity and r is the surface term A is the tension dominated region, B the rigidity dominated region and C the thermal fluctuations dominated region The three differents kind of R G trajectories (I), (II) and (III) corresponding to systems with the same microscopic rigidity κ_0 but different microscopic surface term r_0 are depicted as thin lines

A. *Tension dominated region*

$$r > \kappa \Lambda^2 \quad \text{and} \quad r > k_B T \Lambda^2 \tag{31}$$

In this domain fluctuations are small and tension dominates over curvature energy The properties of the model can be described by a simple interface model (drumhead model) characterized by a tension τ. The R G. flow corresponds to a naive scaling

$$\kappa_S = \text{constant}, \quad r_S = s^2 \tau \tag{32}$$

B. *Rigidity dominated region*

$$\kappa > k_B T \quad \text{and} \quad r < \kappa \Lambda^2 \tag{33}$$

In this region fluctuations are small and rigidity dominates over tension energy The renormalization group flow corresponds to the perturbative result of [11, 18]

$$S \frac{\partial}{\partial S} \kappa_S = - \frac{3 k_B T}{4 \pi} \tag{34}$$

$$S \frac{\partial}{\partial S} r_S = \left(2 + \frac{k_B T}{4 \pi \kappa_S} \right) r_S . \tag{35}$$

The renormalization of the surface term can be simply attributed to the increase of the ratio *total area/projected area* due to thermal undulations Indeed, at leading order in $k_B T$ (i.e. in the Gaussian approximation), the contribution of undulations with wave vector k in the shell (20) to this ratio is equal to

$$\delta \langle A \rangle / A_p = \frac{1}{2} \int_{A_S}^{\Lambda} \frac{d^2k}{(2\pi)^2} \frac{k_B T k^2}{\kappa k^4} = \frac{k_B T}{4\pi\kappa} \ln (S) \qquad (36)$$

(35) follows from the fact that r is the conjugate parameter to the total area A.

C Thermal fluctuations dominated region

$$\kappa < k_B T \quad \text{and} \quad r < k_B T \Lambda^2 \qquad (37)$$

In this domain thermal fluctuations are so important that perturbation theory breaks down. One expects that wild fluctuations of the membrane will take place, and that changes of topology and steric interactions will be very important

The properties of the membrane at a length scale ℓ are simply obtained by considering the R G. flows and deciding in which region of phase diagram one finds the values of the renormalized couplings κ_S and r_S at this scale i e. with $S = \ell/a = \ell\Lambda/\pi$ For a membrane with microscopic bending rigidity κ_0 (for obvious reasons κ_0 has to be larger or of the order of $k_B T$, but cannot be much smaller than $k_B T$, otherwise the membrane will not have any internal stability) three different kind of R G trajectories may be encountered depending on the value of the microscopic surface term r_0 These three cases are depicted in figure 3.

(i) If r_0 is large enough one start from domain **A**. Tension dominates and at all scales $\pi/\Lambda = a < \ell < \infty$ the membrane may be described by a simple interface model with physical tension $\tau = r_0$ (and rigidity κ_0)

(ii) If r_0 is small enough, one starts from domain **B**, but one then flows towards domain **A**. This means that there exists a crossover length ℓ_c, larger than the microscopic cut off $a = \pi/\Lambda$, which separates two regimes :

(a) At scales $\ell > \ell_c$ one is in regime **A**, the physics is described by the Hamiltonian (15) with an effective rigidity $\kappa_{eff} > k_B T$ and an effective surface term $r_{eff} = \tau$, small but nonzero. From (31) and (32) the crossover length ℓ_c is given in terms of the physical parameters τ and κ_{eff} by

$$\ell_c = \sqrt{\frac{\kappa_{eff}}{\tau}} \qquad (38)$$

(b) At scales $\ell < \ell_c$ one is in regime **B**. Tension effects may be neglected and the physics is described by the elastic Hamiltonian (13), but with an effective rigidity $\kappa(\ell)$ which decreases logarithmically as ℓ increases according to (34)

$$\dot{\kappa}(\ell) = \kappa_0 - \frac{3 k_B T}{4\pi} \ln (\ell/a) \qquad (39)$$

until $\ell = \ell_c$, where the tension takes over the rigidity

Note that in case (i) one can also define ℓ_c by (38) but it is then smaller than the cut off a

(iii) If r_0 is still smaller, one start from domain **B** but one flows into domain **C** before tension becomes important This occurs at a crossover length ℓ_c such that $\kappa(\ell)$ (as given by

(39)) is of order $k_B T$ Therefore this length is nothing but the *persistence length* [21] (usually denoted ξ_κ), and from (39) we see that it depends exponentially of the microscopic bending rigidity

$$\ell_c = \xi_\kappa \simeq a \exp \left(\frac{4 \pi \kappa_0}{3 k_B T} \right) . \qquad (40)$$

At scales larger than ξ_κ one enters therefore the nonperturbative regime where thermal fluctuations are very large and where both rigidity and tension are ineffective The membrane will be crumpled, with a correlation length for its normals of order ξ_κ At this scale $(S = \xi_\kappa/a)$ the effective surface term $r_{\text{eff}}(\ell_c) = S^{-2} r_S$ is of order [23]

$$r_{\text{eff}}(\ell_c) \propto \frac{k_B T}{\xi_\kappa^2} \qquad (41)$$

In this regime C the physics of the membrane is not adequately described by the Hamiltonians (13) or (15), and effects such as topology changes (partially governed by the Gaussian bending rigidity $\bar{\kappa}$) or strong steric repulsion between distant parts of the membrane have to be taken into account Phenomenological models which describe this phase are for instance the lattice models [24] of non-rigid self avoiding surfaces with ξ_κ playing the role of the lattice spacing and $\xi_\kappa^2 r_{\text{eff}}(\ell_c)$ that of the chemical potential of plaquettes Therefore $r_{\text{eff}}(\ell_c)$ may be considered as the effective surface tension τ at that scale. Indeed, if there is coexistence between this membrane-rich phase (where space is filled with membranes) and another surface-poor phase (see below), those models predict that the tension of the interface between those two phases will be of order $\tau = r_{\text{eff}}(\ell_c)$ This provides a justification of the commonly adopted relation

$$\tau \propto k_B T \xi_\kappa^{-2} \qquad (42)$$

between the tension τ and the persistence length ξ_κ in microemulsions

As we shall discuss in more details in the next section, it is possible to encounter these three situations in experimental systems In figure 4 we have schematically depicted the idealized example of a ternary (water + oil + surfactant) system forming a microemulsion (sponge) phase At scales of ~ 10 Å the surfactant film can be described by a membrane model with moderate rigidity and small tension (regime **B**) At scales larger than the average distance, d, between the films in the sponge phase (d being identified with the persistence length ξ_κ) one is in regime C and one is looking at the properties of the sponge phase Finally at much larger scales the interface between the sponge phase and the water-or-oil-rich phase can also be described by a model of interface with a small tension ($\tau \sim k_B T d^{-2}$) but one is now in regime A.

Let us also stress that we have discussed in this section the situation where the transverse undulations of a membrane are only limited at large scales by the effect of the tension. Other effects may limit those undulations and act as an effective « infrared cutoff ». For instance if one considers a monolayer at the interface between two fluids with different densities, gravity supresses undulations at wave-lengths larger that the capillary length ℓ_{cap} [25] For a membrane between two walls, or in a stack of membranes, steric repulsion will also suppress undulations with amplitude larger than the average distance between the membrane and the wall (or between neighbouring membranes) [4]. In those situations the R.G. equations (28), (29) are valid up to this I R cut off scale ℓ_{IR} [23, 9] In particular, in the case of a stack of fluid membranes already discussed at the end of section 2, we are in the situation where the tension
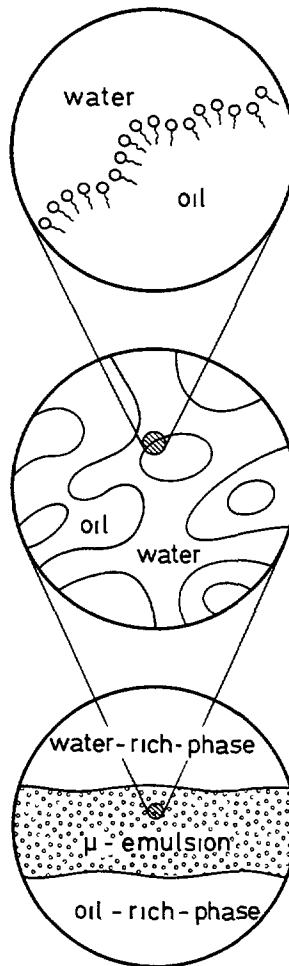
Fig. 4 — Schematic description of a microemulsion at three different scales The description of the surfactant film at short scales corresponds to regime **B.** The description of the sponge phase at intermediate scales corresponds to regime **C.** The description of the interface between the different thermodynamical phases corresponds to regime **A.**

τ vanish (as long as the average distance between membranes, d, is small compared to the persistence length ξ_κ (as given by (40)) It follows that at all scales $a < \ell < \ell_{\mathrm{IR}} \sim d$ one is in regime **B** and that the renormalised tension r_S vanishes

4. Possible experimental consequences.

It is interesting to reconsider, from the point of view described in the last Chapter, different measurements done in the past in order to study the role of thermal fluctuations on the rigidity of films and membranes.

The existence of three distinct regimes for the thermodynamical behavior of the membranes can be explored directly by inspecting the mesoscopic structure of different phases The progress made in freeze — fracture microscopy [26] allows for instance the direct visualization of various structures made of membranes, such as lamellar crystals, bicontinuous

fluid phases (e.g a fascinating L_3 « sponge » phase [27]) or ensembles of closed vesicles. With the help of careful studies of different « cuts » through a bicontinuous phase one can for instance establish the existence of highly curved regions of complicated topology (corresponding to regime **C**) at large length scales. One could in principle obtain in this way *quantitative* information about curvature distributions, dependence of the curvature on the length scales, fluctuations in topology etc.

In the meantime, however, one relies mainly on diffraction experiments to obtain information about the structure and fluctuations of membrane phases. This information is mainly contained in the structure factor $S(q)$, the Fourier transform of the position correlation function Two types of experiments give access to $S(q)$:

(i) *Specular reflexion experiments* [28, 14] In these experiments one measures

$$I(q_z) = \left\langle \int d^2x \int d^2y \exp(iq_z(u(x) - u(y))) \right\rangle \qquad (43)$$

where q_z is the wave vector perpendicular to the reflexion plane of the membrane $u(x)$ is the perpendicular displacement of the membrane above the plane of the membrane (x and y are coordinates of the plane) In harmonic approximation this can be replaced by

$$I(q_z) = \int d^2x \int d^2y \exp\left(-\frac{q_z^2}{2} \langle (u(x) - u(y))^2 \rangle \right) \qquad (44)$$

in which

$$\langle (u(x) - u(y))^2 \rangle = 2 \int \frac{d^2q}{(2\pi)^2} (1 - e^{-iq(x-y)}) S(q) . \qquad (45)$$

(ii) *Ellipsometry* [14, 15] This powerful technique allows one to measure

$$\sum_q qS(q) \qquad (46)$$

and therefore check whether $S(q)$ has an assumed form

These methods, in which one integrates over a whole range of wave vectors, can be useful in practice only if one puts together the results obtained in the different regimes described above. For instance, if we make an ellipsometric measurements for a membrane which at small q is in regime **A** while for large q in regime **B** it would be useful to have a consistent form for $S(q)$ which we could then substitute in (46) We can do this in the following way · for $q < q_R = \sqrt{\frac{\tau}{\kappa}}$ one takes

$$S(q) = \frac{k_B T}{\tau q^2 + \kappa q^4}, \qquad (47)$$

while for $q_R < q < \frac{\pi}{a} = \Lambda$ one takes

$$S(q) = \frac{k_B T}{\kappa(q) q^4}, \qquad (48)$$

where $\kappa(q)$ is given by

$$\kappa(q) = \kappa_0 + \frac{3}{4\pi} k_B T \ln (q/\Lambda) \qquad (49)$$

One can then make $S(q)$ continuous at q_R by adjusting the value of κ_0, which corresponds to the « microscopic » bending rigidity at momentum $q = \Lambda$

A third type of experiment, which has already started to explore the interesting renormalization effects of the regime **B** are the measurements of area fluctuations. In these experiments one measures how the ratio *projected area/number of molecules* varies with external parameters. For instance, in reference [13] by varying the pressure acting on a fluctuating vesicle one measures the functional dependence of the projected area on the tension τ. In this way the logarithmic corrections due to thermal fluctuations in regime **B** were indeed observed. Similarly by varying the distance between the membranes in a lamellar phase, and therefore modifying the effective IR cutoff ℓ_{IR} (as discussed at the end of last section), the authors of reference [12] were able to show the existence of such corrections for multimembrane systems. Note, however, that these logarithmic corrections to the ratio A/A_p

$$\frac{A}{A_p} = 1 + \frac{1}{4\pi} \frac{k_B T}{\kappa} \ln (\Lambda \ell_{IR}) \tag{50}$$

are already present in the Gaussian approximation, while the logarithmic corrections to the rigidity described above are higher order perturbation effects. It would be therefore interesting to try to measure directly the scale dependence of the effective rigidity in the regime **B**. In principle this could be also done through a careful analysis of fluctuations of a single free vesicle [29] This important case is not discussed here

In real systems the simple picture presented in section 2 can in principle be altered by a finite compressibility of the membrane However, as we shall show now, the argument explaining why the tension τ can vanish stays valid Indeed, although the total area A is no longer exactly proportional to the total number of molecules N, one can replace A by N in the definition of the different ensembles without modifying the arguments of section 2. In particular (7), which defines the surface tension τ, is simply replaced by

$$\tau = \left.\frac{\partial F}{\partial A_p}\right|_N = \left.\frac{\partial G_c}{\partial A_p}\right|_r \tag{51}$$

G_c is now the thermodynamical potential in the constrained ensemble where A_p is fixed while the fluctuations of the total number of molecules N is controlled by the chemical potential of the molecules r. F is the potential in the ensemble where both A_p and N are fixed It follows that the surface tension vanishes as soon as the equilibrium area ratio a_p, defined as

$$a_p = \frac{\langle A_p \rangle}{\langle A \rangle} \tag{52}$$

is nonzero. The effects of a finite compressibility will be felt only in fluctuations around the equilibrium value a_p if a_p approaches 1.

5. Conclusions.

We have tried in this paper to classify possible regimes of the behavior of fluctuating membranes and films. First, by defining various thermodynamic ensembles we have pointed out the differences between several physical situations. In particular, we have given a few examples of systems for which the effective surface tension vanishes These include free polymerized sheets or fluid membranes fluctuating freely in a lamellar crystal. Our arguments leading to the conclusion of vanishing surface tension for a fluctuating membrane are different

from those usually evoked and which, in our opinion, do not apply here Next, we have reconsidered the problem of the effect of thermal fluctuations on the effective rigidity and tension of a flexible film Although the calculations presented here are described in many other places in literature, we have reanalysed them in view of our thermodynamic arguments and the classification of different physical situations. This lead us to define for a generic situation (englobing fluctuating membranes, films and interfaces) three different regimes of behavior (i) tension dominated regime, (ii) rigidity dominated regime and (iii) thermal fluctuations dominated regime A fluctuating film can be found in each of these regimes, depending on the length scales at which we observe it. In particular, interesting logarithmic corrections for the effective rigidity can only be observed in regime (ii) We have discussed some connections between recent experiments and these theoretical predictions.

The simple arguments presented here show that when dealing with fluctuating membranes one has to be cautious and precisely define the boundary conditions (e g. free or constrained), the relevant length and time scales, and the physical quantities allowed to vary Only after that one can define precisely the notion of surface tension and, in particular, argue that this tension vanishes.

Acknowledgements.

Appendix.

In this appendix we recall the derivation of the Renormalization Group flow equations (28), (29) for the surface term r and the bending modulus κ.

We use the « background method » first used in that problem by Förster [18], and further developed in references [30, 19, 31] We start from the Hamiltonian (15)

$$H(\mathbf{X}) = \int dS \left(r + \frac{\kappa}{2} H^2 \right) \tag{A1}$$

and consider small fluctuations $\mathbf{X}$ around a « background configuration » $\mathbf{X}_0$ of the membrane, which can be written as

$$\mathbf{X} = \mathbf{X}_0 + \mathbf{n}_0 h \tag{A2}$$

where $\mathbf{n}_0$ is the normal vector to the background configuration. The basic idea of the calculation consists in computing, at leading order in $k_B T$, the effective potential $\Gamma(\mathbf{X}_0)$ for the background configuration This is done by expanding H to second order in h and by using the Gaussian approximation In this way one obtains

$$\Gamma(\mathbf{X}_0) = H(\mathbf{X}_0) + \frac{k_B T}{2} \text{Tr} \ln \left\{ \frac{1}{k_B T \Lambda^4} \frac{\partial^2 H}{\partial h \, \partial h} \right\} \tag{A3}$$

In deriving (A3) we have used the fact that, for the parametrization (A2) of the fluctuations around the background configuration, the contribution of the Fadeev Popov determinant is zero (at leading order in $k_B T$) This determinant has to be introduced in order to be sure that the fluctuations are treated in a *local* way in the sum over configurations. The factor Λ^{-4} inside the bracket { } in (A3) makes the argument of the Tr ln term dimensionless

This is a consequence of the fact that when summing over configurations one has to integrate over h. A natural dimensionless measure of integration is

$$\mathcal{D}[h] = \prod_x \mathrm{d}(h(x)/\Lambda) \tag{A4}$$

since the cut-off Λ is the only momentum scale at our disposal. Losely speaking, the product over points x in (A4) is made over points separated by $a = \pi/\Lambda$. Since r is proportional to the chemical potential for elements of the membranes, each of typical size a^2, another choice of the measure is equivalent to a redefinition of the surface term r in the Hamiltonian.

All we need in the one-loop calculation (i.e. at first order in $k_B T$) is thus a general expression of the second derivative of $H(\mathbf{X})$ with respect to h. The explicit calculation (see for instance [18, 30, 31] gives for the term of order 2, $H^{(2)}$, in the h expansion of $H(\mathbf{X})$ around the background configuration $\mathbf{X}_0$

$$H^{(2)} = \int \mathrm{d}S\, h \left\{ \kappa \left[\Delta^2 + \frac{(H^2 - 4K)}{2}\, \Delta + 2\, HH^{ij} D_i\, D_j + \cdots \right] + r[-\Delta + 2K] \right\} h \tag{A5}$$

where D_i and $\Delta = D^i D_i$ are the covariant derivative and the Laplacian with respect to the background metric on the background configuration $g_{ij} = \partial_i \mathbf{X}_0\, \partial_j \mathbf{X}_0$. Here H and K are the mean and Gaussian curvatures for the background configuration, and H^{ij} is the extrinsic curvature tensor $H^{ij} = \mathbf{n} D^i D^j \mathbf{X}_0$. The dots .. in (A5) denote terms proportional to H^4, $H^2 K$, K^2, or to derivatives of H^2 and K, which are not important in the present approximation

In the sharp cut-off approximation, one integrates out fluctuations $h_{\mathbf{k}}$ with wavevectors $\mathbf{k}$ in the « shell »

$$\Lambda/S < |\mathbf{k}| < \Lambda \tag{A6}$$

Since k^2 corresponds to eigenvalues of (minus) the Laplacian $(-\Delta h_{\mathbf{k}} = k^2 h_{\mathbf{k}})$ we may replace in (A3) the Tr ln term by $\int \mathrm{d}S \int \mathrm{d}^2\mathbf{k}(2\pi)^{-2}$ and the operator $-\Delta$ by k^2. In this way for an infinitesimal shell

$$S = 1 + \varepsilon \tag{A7}$$

we obtain the following expression for the effective Hamiltonian (at leading order in $k_B T$)

$$H_{\mathrm{eff},S} = H_0 + \frac{k_B T}{2} \int \mathrm{d}^2 S \frac{\Lambda^2 \varepsilon}{2\pi} \ln \left\{ \frac{1}{k_B T \Lambda^4} \left[\kappa \Lambda^4 + r\Lambda^2 - \frac{3}{2} \kappa H^2 \Lambda^2 + \cdots \right] \right\} \tag{A8}$$

where neglected terms contain contributions proportional to the Gaussian curvature K (neglected here as being total derivatives, one has to consider these terms if one studies the effects of the renormalization of $\bar{\kappa}$) and higher order powers of the curvatures or of their derivatives. Expanding (A8) in power of H as done for (20) we obtain

$$r_{\mathrm{eff}}(S) = r + \varepsilon \Lambda^2 \frac{k_B T}{4\pi} \ln \left(\frac{\kappa}{k_B T} + \frac{r}{k_B T \Lambda^2} \right) \tag{A9}$$

$$\kappa_{\mathrm{eff}}(S) = \kappa - \varepsilon \frac{3 k_B T}{4\pi} \frac{1}{\left(1 + \dfrac{r}{\kappa \Lambda^2} \right)} \tag{A10}$$

By rescaling back **X** and **k**, as explained in section 3, we obtain the renormalized couplings r_S and κ_S, which obey the R.G flow equations

$$S \frac{\partial \kappa}{\partial S} = -\frac{3}{4\pi} \frac{k_B T}{\left(1 + \dfrac{r}{\kappa \Lambda^2}\right)} \tag{A11}$$

$$S \frac{\partial r}{\partial S} = 2r + \frac{\Lambda^2}{4\pi} k_B T \ln \left(\frac{\kappa}{k_B T} + \frac{r}{k_B T \Lambda^2}\right) \tag{A12}$$

The equation for r differs from (29) by a factor $k_B T \Lambda^2 / 4\pi \ln (\kappa/k_B T)$ However, if we redefine the surface term r as

$$r \to r' = r - \frac{\Lambda^2}{4\pi} k_B T \ln \left(\frac{\kappa}{k_B T}\right) \tag{A13}$$

which is equivalent to a change in the measure (A4), then (A12) coincides with (29), up to subleading terms of order $(k_B T)^2 \ln (k_B T)$ Such terms are neglected in the one-loop approximation

Finally, let us compare our results with those of reference [25]. One can go from the renormalized couplings κ_S, r_S, to the momentum dependent effective couplings $\kappa(q)$ and $r(q)$, by the simple relation

$$\kappa(q) = \kappa_S, \quad r(q) = S^{-2} r_S, \quad S = \Lambda/q \tag{A14}$$

Then the R G. equations can be written as

$$q \frac{\partial \kappa}{\partial q} = \frac{3}{4\pi} \frac{k_B T}{\left(1 + \dfrac{r}{\kappa q^2}\right)} \tag{A15}$$

$$q \frac{\partial r}{\partial q} = -q^2 \frac{k_B T}{4\pi} \ln \left(1 + \frac{r}{\kappa q^2}\right). \tag{A16}$$

Equation (A15) coincides with the one obtained in reference [25] for the effective bending rigidity $\kappa(q)$ However, our result (A16) for the effective tension differs from the one of reference [25], namely

$$q \frac{\partial r}{\partial q} = q^2 \frac{3}{4\pi} k_B T. \tag{A17}$$

Although equations (A15) and (A17) are equivalent in the regime **A**, in which $q \frac{\partial r}{\partial q} \simeq 0$, they differ in an important way in regime **B**, where the effects of the renormalization of κ are nontrivial It is also important to stress that one cannot in any case apply (A15) in the regime **C** (nor (A17), as is done in Ref. [25] for critical interfaces), since in this regime we expect the perturbative results to be invalid In fact, equation (A15) obtained here is equivalent to the perturbation results of reference [11], in which only small fluctuations around a planar membrane where taken into account As we have already discussed in section 3 a membrane in regime **C** cannot definitely be described in such approximation.

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