Effects of Thermal Fluctuations on Systems with Small Surface Tension

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We consider the influence of thermal fluctuations on systems with negligible surface tension ("membranes"), whose behavior is determined by curvature effects. Fluctuations change the effective rigidity and other relevant parameters. Two-dimensional membranes appear rigid at short distances and crumpled at long distances. For more than two-dimensional membranes (or in presence of long-range forces) a crumpling transition separates a rigid low-temperature phase from a crumpled high-temperature one.

Several interesting systems may be described as interfaces with small or even vanishing surface tension. This is the case of certain closed lipidic membranes and of bicontinuous microemulsions. Closed lipidic bilayers, such as red blood cells or artificial liposomes, can have an unswollen shape. They then minimize at equilibrium their free energy with respect to both volume and surface independently,[1] yielding a vanishing surface tension. As shown by Helfrich and co-workers,[2] the size and shape of the vesicles is then determined solely by the curvature free energy, which is in turn a function of only one relevant elastic modulus, called the *rigidity* κ. Vanishing surface tension entails the flicker phenomenon, namely the enhancement of shape fluctuations of vesicles, investigated a few years ago by Brochard and Lennon,[3] and by other theoretical[1] and experimental[4] groups. In microemulsions, the introduction of a surfactant reduces the surface tension of oil-water interfaces to very small values.[5] The structure of the interface is then governed by curvature effects. De Gennes and Taupin[6] have investigated the role of κ in microemulsions and introduced the notion of the persistence length ξ, such that the interface appears rigid at scales smaller than ξ, but flexible and crumpled (losing its orientational coherence) at distances longer than ξ. This length is of the order of a typical "droplet" size in the microemulsion. Helfrich and Servuss[7] have pointed out that rigidity also controls the reduction in base (projected) area of an interface (a membrane) with respect to its true area, due to thermal fluctuations. From now on we shall call "membranes" all physical systems with small or vanishing surface tension.

Helfrich[8] has recently suggested that fluctuations should also reduce the "effective" rigidity of a macroscopic membrane with respect to its "bare" or microscopic value. We have checked this suggestion within a systematic theoretical approach, computing to one-loop order the renormalization-group equations which describe the renormalization of the rigidity κ, as well as of the surface tension r, the true area S, and the spontaneous curvature H^s. The results confirm the main qualitative predictions of Helfrich,[8] and allow us to give a sound definition of the persistence length ξ and to compute its scaling behavior as a function of κ. They also show that for membranes whose dimensionality d exceeds two, one should observe a "crumpling" transition between a low-temperature phase, where the membrane is rigid and flat, and a high-temperature phase, where the effective rigidity decreases with increasing membrane size and the surface appears crumpled. This transition might be observable in real, two-dimensional systems in the presence of long-range forces. We give here a short account of the results. Full calculations will be reported elsewhere.

We start from the usual expression of the curvature elastic free energy density $\mathscr{F}$ per unit area of a fluid membrane[10]:

$$\mathscr{F} = r_0 + \tfrac{1}{2}\kappa_0(H - H_0^s)^2 + \bar{\kappa}_0 K. \tag{1}$$

Here H is the mean curvature of the membrane, i.e., the sum of its inverse curvature radii, whereas K is its Gaussian curvature, i.e., the corresponding product. It is well known[10] that the last term need not be taken into account if one only considers fluctuations of the membrane shape which do not change its topology. The coefficient κ_0 is the bare rigidity, and H_0^s is the bare spontaneous curvature. The bare surface tension is r_0. We are considering systems whose *effective* (macroscopic) surface tension r is negligible. If F is the total free energy and S is the membrane area, we have

$$r = [\partial F/\partial S]_{\text{eq}} \approx 0. \tag{2}$$

This does not necessarily imply $r_0 = 0$, since thermal fluctuations renormalize the surface tension from its bare value to its effective value r.[11] Neglecting asymmetry effects for the moment (and therefore setting $H_0^s = 0$), we allow for the possibility of large deviations of the membrane shape from planar, always assuming large values of the curvature radii, and thus always keeping within the range of validity of Eq. (1). We have, therefore, for any configuration S of the membrane,

$$F[S] = \int dS (r_0 + \tfrac{1}{2}\kappa_0 H^2), \tag{3}$$

and the probability of any configuration is proportional to the Boltzmann factor $\exp(-F[S]/T)$. The integral

runs over the whole area of the membrane and dS is its area element. We parametrize membrane shapes by giving the value of the coordinate z as a function of the coordinates x and y.

$$S: z = u(x,y), \quad (x,y) \in S_0, \tag{4}$$

where S_0 is the base (the projection of S on the $z = 0$ plane). In terms of the vector field $\phi = \mathrm{grad}\, u$, one then has[12]

$$dS = (1 + \phi^2)^{1/2} dx\, dy, \tag{5}$$

$$H = \mathrm{div}[\phi(1 + \phi^2)^{-1/2}]. \tag{6}$$

Substituting these expressions into (3) and expanding in powers of ϕ, one sets up a loop expansion for quantities such as the effective potential $\Gamma[U]$:

$$\Gamma[U] = \int dx\, dy\, \lambda(x,y) U(x,y) - \ln \int \mathscr{D} u \exp\left[-F[u]/T + \int dx\, dy\, \lambda(x,y) u(x,y)\right], \tag{7}$$

which generates the vertex functions as derivatives with respect to $U(x,y) = \langle u(x,y) \rangle$. Invariance of the free energy (3) with respect to translations parallel to the z axis as well as to rotations around an axis lying in the $z = 0$ plane imply that for an almost planar membrane $\Gamma[U]$ should have the same functional dependence on U as F has on u, possibly with different coefficients.[13] It is, in fact, sufficient to calculate the two-point vertex function $\Gamma^{(2)}$.

In the perturbative calculations the quantity T/κ plays the role of the expansion parameter. Its experimentally measured value appears to be rather small.[3,14] One faces, however, divergences which should be regularized by introducing an infrared cutoff in wave number proportional to the inverse base size and an ultraviolet one proportional to some inverse microscopic length. It is in fact more convenient to exploit r as an infrared cutoff and to dispose of the ultraviolet one by dimensional regularization.[15] One generalizes the model to $3 - \epsilon$ space dimensions and performs all integrals over the $2 - \epsilon$ transverse dimensions. Poles in ϵ appear, reminiscent of the divergences at $d = 2$, which are removed by minimal subtraction.[15] One thus obtains a renormalized surface tension r and a renormalized rigidity, which one expresses as $\kappa \mu^{-\epsilon}$, thereby introducing a renormalization wave number μ. The renormalization-group equations are obtained by expressing the variation of the renormalized parameters r, κ, for a varying μ at fixed values of the bare parameters r_0, κ_0. They are given by

$$\mu[dr/d\mu]_0 = -r \times 3\tau/2\kappa, \tag{8}$$

$$\mu[d\kappa/d\mu]_0 = \kappa(\epsilon + 3\tau/2\kappa), \tag{9}$$

where $\tau = 2T(4\pi)^{-d/2}/\Gamma(d/2)$. If we take μ^{-2} to be proportional to the membrane base area S_0, we obtain from Eqs. (8) and (9) the increase of the effective surface tension and the variation of the effective rigidity

with increasing membrane size. For the physical case $\epsilon = 0$ the effective rigidity decreases with increasing membrane size, in a way which agrees qualitatively with that suggested by Helfrich,[8] although with slightly different coefficients. It is indeed easier to bend a membrane which already contains some ripples. If one defines a wave-number–dependent rigidity $\kappa(q)$, one likewise obtains, in the limit of large rigidity $(\tau/\kappa \ll 1)$,

$$\kappa(q) = \kappa_0 + (3T/4\pi)\ln(qa), \tag{10}$$

where a is some microscopic length. This reduction of κ with increasing observation scale qualitatively agrees with the discrepancy among values of κ obtained by different experimental techniques.[14,16]

If the effective surface tension r vanishes, Eq. (9) implies, for $\epsilon < 0$ (ambient space with more than three dimensions), a transition between a low-temperature phase with infinite effective rigidity for infinitely large membranes ("rigid") and a high-temperature phase where rigidity decreases with increasing membrane size ("crumpled"), separated by a critical point where $\tau/\kappa = -2\epsilon/3$, corresponding to an unstable fixed point of the flow equations. We call this transition the "crumpling" transition.[17] In the low-temperature phase, Euclidean symmetry is spontaneously broken. For two-dimensional membranes one is always in the high-temperature phase, and orientational correlations decay *exponentially* over a length scale ξ which may be identified with the persistence length of de Gennes and Taupin.[6] Its scaling behavior at low temperature T (high rigidity κ_0) may be obtained by integrating Eq. (9) and is given by

$$\xi = a \exp(4\pi\kappa_0/3T). \tag{11}$$

One may also calculate the increase in effective membrane area S with increasing base area S_0. Introducing

the fractal dimension D of the membrane via the relation $S \propto S_0^{D/2}$, one obtains

$$\frac{D}{2} = \frac{d \ln S}{d \ln S_0} = 1 - \frac{1}{2} \frac{d \ln S}{d \ln \mu}$$

$$= 1 + \frac{\tau}{4\kappa} - \left(\frac{\tau}{4\kappa}\right)^2 . \tag{12}$$

Equation (9) implies that the membrane becomes more and more flexible as its size increases, whereas Eq. (12) shows that it becomes at the same time more and more corrugated. One can also show that for asymmetric membranes the spontaneous curvature H^s increases with increasing size. This may have observable effects on the dependence of liposome shapes on their size.

We have thus defined a theoretical model of an interface with negligible surface tension (a membrane), representing systems such as certain liposomes and interfaces in microemulsions. A renormalized perturbation-theoretical treatment of this model leads to the conclusion that thermal fluctuations change not only the surface tension, but also the effective rigidity and the spontaneous curvature, which were so far considered as constants. For a two-dimensional membrane, this implies that for a sufficiently large base area, the surface becomes so corrugated that it tends to fill up the whole space. It would be tempting to relate this behavior with the physical phenomenon of the creation of microemulsions. One should nevertheless keep in mind that our calculations cannot be extrapolated to situations in which different parts of the surface come in contact with one another. We expect that microscopic, molecular details become important in this situation. One should also consider fluctuations which change the topology of the surface and therefore take into account the Gaussian curvature term.

Within its range of validity, our theory predicts that orientational correlations decay exponentially at any temperature $T > 0$, with a well-defined correlation length ξ. Membranes appear as rigid at scales smaller than ξ, and flexible and crumpled at scales larger than ξ. For hypothetical systems of dimensionality larger than two (or in presence of long-range forces), we predict a crumpling transition between a low-temperature phase, where the membrane is rigid, and a high-temperature one, where it is crumpled. It would be extremely interesting if this transition could be related to the recently observed change between a stiff and a flexible state in some lyotropic systems.[18] The analysis of the dependence of the effective rigidity on wave number and the search for this transition appear as the most exciting directions for further study.

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[8]W. Helfrich, unpublished.

[9]This is due to the well-known effect of the reduction of the lower critical dimension in presence of long-range forces.

[10]Cf. Helfrich, Ref. 2.

[11]Several physical effects contribute in fact to the renormalization of the surface tension and the rigidity: in particular density fluctuations (see Ref. 1) and tilt modes. Their contribution to the renormalization of κ is not singular for an infinite membrane. One can therefore take them into account by a suitable redefinition of the bare parameters r_0 and κ_0 and explicitly consider only shape fluctuations (undulations).

[12]See, e.g., M. Spivak, A Comprehensive Introduction to Differential Geometry (Publish or Perish, Berkeley, 1979), Vol. III, Chaps. 2 and 6.

[13]The problem is similar to the renormalization of interface fluctuations in Ising-type systems, considered by D. J. Wallace and R. K. P. Zia, Phys. Rev. Lett. 43, 808 (1979). For a recent review, see D. J. Wallace, in "Gauge Theories and Experiments in High Energy," edited by K. C. Bowler and D. G. Sutherland (SUSSP Publications, Edinburgh, to be published).

[14]J. F. Lennon, thesis, 1977 (unpublished); J. M. Di Meglio, thesis, 1984 (unpublished).

[15]See, e.g., D. J. Amit, Field Theory, the Renormalization Group, and Critical Phenomena (McGraw-Hill, New York,

1978), Secs. 9-9 and 9-10.

[16]The logarithmic behavior displayed by Eq. (10) is only to be expected in the limit of large rigidity. When the effective κ becomes too small, higher orders in τ/κ must be taken into account in Eq. (9) and one should expect deviations from Eq. (10).

[17]"Crumpling" manifests itself in the divergence of $\langle (\nabla u)^2 \rangle$ for an infinite surface. This is reminiscent of the divergence of $\langle u^2 \rangle$ for a wandering interface, relevant when the surface tension is not small.

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