MODEL FOR CONDENSATION OF LAMELLAR PHASE FROM MICROEMULSION ☆

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Received 3 January 1989; accepted for publication 18 January 1989
Communicated by A.A. Maradudin

We present a simple model describing a fluctuating ensemble of fluid membranes with curvature stiffness and displaying the formation of a lamellar phase from a microemulsion. At the transition point, the surface tension disappears and a condensate of zero momentum gives rise to a stack of planar membranes.

Recent work on soap membranes in microemulsions has shown that the curvature stiffness of the oil water interfaces can persist only over a certain length scale ζ [1]. Beyond this scale, the interfaces appear wrinkled and are governed by a fluctuation generated tension. On the other hand, it is known that membranes which are stacked periodically on top of each other possess no tension at all, i.e. $\zeta=\infty$. This is beautifully demonstrated by the power-like line shapes of X-ray structure factors of such systems [2].

The purpose of this note is to present a simple model which is capable of describing the transition between the two phases. We consider a set of surfaces $x_n^a(\xi$ $(a=1, 2, 3)$ numbered by n and parametrized by ξ^i $(i=1, 2)$ and approximate their curvature energy linearly by

$$E_1=\frac{\varkappa}{2}\sum_n\int \mathrm{d}\xi\,(\partial^2 x_n^a)^2\,. \tag{1}$$

To this we add the constraint of in-plane incompressibility

$$E_2=\frac{\varkappa}{2}\sum_n\int \mathrm{d}^2\xi\,\lambda(\xi)[(\partial_i x_n^a)^2-2]\,, \tag{2}$$

where λ is a fluctuating Lagrange multiplier. In a third step we replace the numbers n by a third discrete parameter $\xi_n^3=nd$, with spacing d. Introducing the lattice derivative $\nabla_3 x_n^a\equiv x_n^a-x_{n-1}^a$, we add a further energy

$$E_3=\frac{\varkappa}{2}\frac{b}{d^2}\int \mathrm{d}^2\xi\sum_n[(\nabla_3 x_n^a)^2/d^2-\sigma^2]\,. \tag{3}$$

Here b is a fluctuating parameter which plays the role of a Lagrange multiplier to ensure that, on the average, the distance between the surfaces possesses a variation $\sigma^2 d^2$. The model parameter σ characterizes the range of penetration of one membrane layer into the regimes of its neighbours. We now take the continuum limit on the ξ^3 axis, describe the stack by $x^a(\xi^i, \xi^3)$ and arrive at the total model energy

$$E_{\mathrm{tot}}=E[x^a]-N\int \mathrm{d}^2\xi\,\varkappa\lambda-AN\varkappa b\sigma^2/2d^2\,, \tag{4a}$$

with

$$E[x^a]=\frac{\varkappa}{2d}\int \mathrm{d}^3\xi\,[(\partial_i^2 x^a)^2+\lambda(\partial_i x^a)^2 + (b/d^2)(\partial_z x^a)^2]\,, \tag{4b}$$

with $A\equiv\int \mathrm{d}^2\xi\equiv$ base area and $N\equiv$ number of layers $\equiv\int \mathrm{d}\xi^3/d$. Integrating out the x^a fluctuations gives the free effective energy density per unit base area and layer

☆ Work supported in part by Deutsche Forschungsgemeinschaft under grant no. K. 256.

0375-9601/89/$ 03.50

$$E_{\text{eff}} = \frac{1}{AN}\tfrac{3}{2}T \operatorname{tr} \ln[(\partial_i^2)^2 - \partial_i\lambda\partial_i - (b/d^2)\partial_3^2]$$

$$- \frac{\varkappa}{ANd}\int \mathrm{d}^3\xi\,\lambda - \varkappa b\sigma^2/2d^2 . \qquad (5)$$

At the one-loop, we find the free energy density f using the saddle point approximation, in which λ is a constant, so that

$$f = \frac{3}{2}\left(\int \frac{\mathrm{d}^3k\,d}{(2\pi)^3} \ln[(k_i^2)^2 + \lambda k_i^2 + (b/d^2)k_3^2] \right.$$

$$\left. - \tilde{\varkappa}\lambda - \tilde{\varkappa} b\sigma^2/2d^2 \right) \qquad (6)$$

to be extremized in λ, b (where $\tilde{\varkappa} \equiv \frac{2}{3}\varkappa/T$). The extremal value of λ defines the persistence length $\zeta = 1/\sqrt{\lambda}$ over which the surface appears smooth. If the surfaces were to move in infinite dimensions rather than three, the saddle point approximation would, of course, be exact. The integral in (6) can be calculated as follows

$$I = \frac{1}{4\pi}\left[2\Lambda^2(\ln\Lambda^2 - 1) + \lambda \ln(\Lambda^2 d^2/\pi\sqrt{b} + 2)\right]$$

$$- \frac{1}{4}\frac{\sqrt{b}}{d^2} l^2 L(l) , \qquad (7)$$

where

$$L(l) = \int_0^{1/l} \mathrm{d}\kappa \sqrt{1-\kappa^2} \ln \frac{1+\sqrt{1-\kappa^2}}{1-\sqrt{1-\kappa^2}} , \qquad (8)$$

with $l = \lambda d^2/2\pi\sqrt{b}$. We have first performed the integral over k_i^2 with cutoff Λ and then the integral over $k_3 \equiv (\lambda d/2\sqrt{b})\kappa$. For $l > 1$, $L(l)$ can be rewritten with $\kappa \equiv 1/\operatorname{ch}\theta$, $\theta_0 = \operatorname{arch} l = \ln(l + \sqrt{l^2-1})$ as

$$L(l) = 2\int_{\theta_0}^{\infty} \mathrm{d}\theta\,\theta \frac{\operatorname{sh}^2\theta}{\operatorname{ch}^3\theta}$$

$$= 2G - G(\theta_0) + \frac{1}{\operatorname{ch}\theta_0} + \theta_0 \frac{\operatorname{sh}\theta_0}{\operatorname{ch}^2\theta_0} , \qquad (9)$$

where

$$G(\theta_0) = \int_0^{\theta_0} \mathrm{d}\theta \frac{\theta}{\operatorname{ch}\theta}$$

is the integral which for $\theta_0 = \infty$ is equal to twice Catalan's constant $G = 0.915965594\ldots$. For large l, $L(l)$ has the expansion

$$L(l) = \frac{2}{l}[\ln(2l) + 1] - \frac{1}{3l^3}[\ln(2l) + \tfrac{5}{6}] + \ldots . \qquad (10)$$

Since we shall be interested in the phase transition where λ goes to zero we have to know $L(l)$ in the neighbourhood of small l. Then $L(l)$ is the sum $L(0) + L_1(l)$ with

$$L_1 = -2\int_0^{\varphi_0} \mathrm{d}\varphi\,\varphi \frac{\sin^2\varphi}{\cos^3\varphi} ,$$

where $\varphi_0 = \arccos l$. After a partial integration we find

$$L(l) = 2G + \tilde{G}(\varphi_0) + \frac{1}{\cos\varphi_0} - \frac{\varphi_0 \sin\varphi_0}{\cos^2\varphi_0} , \qquad (11)$$

where

$$\tilde{G}(\varphi_0) \equiv G(\mathrm{i}\varphi_0) = \int_0^{\varphi_0} \mathrm{d}\varphi \frac{\varphi}{\cos\varphi} .$$

We need $\tilde{G}(\varphi_0)$ near $l \approx 0$, i.e. near $\varphi_0 \approx \pi/2$. Setting

$$\tilde{\varphi}_0 = \pi/2 - \varphi_0 = \arcsin(l/\sqrt{1-l^2})$$

we have

$$\tilde{G}(\tilde{\varphi}_0) = -2G - \tfrac{1}{2}\pi \ln(\operatorname{tg}\tfrac{1}{2}\tilde{\varphi}_0) + g(\tilde{\varphi}_0) , \qquad (12)$$

with

$$g(z) \equiv \int_0^z \mathrm{d}x \frac{x}{\sin x} ,$$

and obtain the expansion

$$L(l) = -\frac{\pi}{2l^2} + \frac{2}{l} - \tfrac{1}{2}\pi[\ln(l/2) - \tfrac{1}{2}]$$

$$+ \tfrac{2}{3}l - \tfrac{1}{16}\pi l^2 + \tfrac{4}{45}l^3 - \tfrac{1}{64}\pi l^4 + \ldots . \qquad (13)$$

To proceed it is useful to introduce the following quantities,

$$\sqrt{b_0} \equiv \frac{\pi}{8}\frac{1}{\tilde{\varkappa}\sigma^2} , \quad f_0(d) = \frac{\pi\sqrt{b_0}}{16d^2} ,$$

$$\zeta_0 = \lambda_0^{-1/2} = \Lambda^{-1} \mathrm{e}^{2\pi\tilde{\varkappa} - 1/2} , \quad d_c \equiv (\pi\sqrt{b_0})^{1/2}\zeta_0 . \qquad (14)$$

Then, if we measure f, b, d in units of $f_0(d)$, b_0, d_0 and drop a trivial additive constant we can rewrite f simply as

$$f=2\sqrt{b}-b-\frac{4}{\pi}\sqrt{b}\,l^2L_2+\frac{8}{\pi}\sqrt{b}\,l\ln(d^2/\sqrt{b})\,, \tag{15}$$

with $L_2\equiv L+\pi/2l^2-2/l$. Applying $\mathrm{d}/\mathrm{d}b=\partial/\partial b-l/2b\partial_l$ and $\mathrm{d}/\mathrm{d}\lambda=\partial/\partial\lambda+l/\lambda\partial_l$ we find the extremality conditions

$$1-\sqrt{b}+\frac{2}{\pi}l^2(L_2+lL_2')-\frac{4}{\pi}l=0\,, \tag{16}$$

$$-\frac{2}{\pi}l(2L_2+lL_2')+\frac{4}{\pi}\ln\frac{d^2}{\sqrt{b}}=0\,. \tag{17}$$

Adding these we see that at the extremum f becomes simply

$$f=b+\frac{8}{\pi}l\sqrt{b}\,. \tag{18}$$

For increasing values of l we calculate $b(l)$ from (16) and $d(l)$ from (17) (also $\lambda(b)=2\pi l\sqrt{b}/d^2$). The resulting functions are plotted in fig. 1. In the limit of large distances we use (10) and obtain

$$\sqrt{b}=(4/9\pi l)[1+3\ln(2l)]+\dots\,,$$

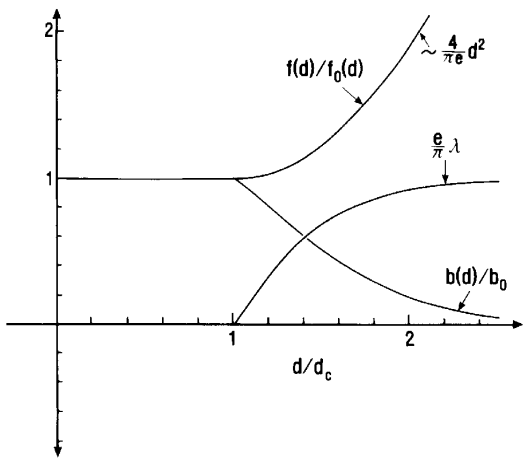

Fig. 1. The behaviour of the free energy $f(d)$, the surface tension $\lambda(d)$, and the Lagrange multiplier $b(d)$ as functions of the distance between the membranes d. The normalizing quantities $f_0(d)$ and b_0 are defined in eqs. (14). Below the critical distance, d_c, the tension vanishes and the microemulsion condenses into a lamellar phase.

$$\ln(d^2/\sqrt{b})=1+\ln(2l)+\dots$$

and hence $2l\to\exp(\alpha)$;

$$\alpha\equiv\frac{3\pi}{8e}d^2-\frac{1}{3},\quad \sqrt{b}\to\frac{8}{3\pi}\alpha\exp(-\alpha)\,,$$

$$f\to\frac{4}{\pi e}d^2,\quad \lambda\to\frac{\pi}{e}\,.$$

For d near 1, i.e. near d_c, $l\approx 0$ we find

$$\sqrt{b}=1-\frac{4l}{\pi}-l^2[\ln(l/2)+\tfrac{1}{2}]+\dots\,,$$

$$\ln(d^2/\sqrt{b})\approx-\tfrac{1}{2}\pi l\ln(l/2)+l^2+\dots\,,$$

$$\ln d^2\sim-\tfrac{1}{2}\pi l[\ln(l/2)+8/\pi^2]+\dots\,,$$

$$f=1-l^2[2\ln(l/2)+16/\pi^2+1]+\dots\,.$$

Notice that our plot of the functions in fig. 1 versus d gives directly the temperature dependence at a fixed distance parameter d. We merely have to replace the d axis by

$$\exp\left(\frac{2\pi\tilde{x}/T_c}{1-T_c/T}\right).$$

In contrast to the case of an individual membrane which has always a fluctuation generated tension, the ensemble of membranes has a non-zero tension only if the spacing is larger than the length d_c which is related to the persistence length of a single membrane ζ_0 by the last eq. (14). If we want to find a solution for more narrow spacing, $d<d_c$, we rewrite eq. (17) as

$$16\pi\tilde{x}[\tfrac{1}{2}\langle(\partial_i x^a)^2\rangle-1]=0\,, \tag{19}$$

with the expectation

$$\langle(\partial_i x^a)^2\rangle=\frac{2}{\tilde{x}}\int\frac{\mathrm{d}^2k}{(2\pi)^2}\int_{-\pi/d}^{\pi/d}\frac{\mathrm{d}^2k}{2\pi}$$

$$\times\frac{k_i^2}{(k_i^2)^2+\lambda k_i^2+(b/d^2)k_3^2}\,. \tag{20}$$

The treatment of a gap equation like (17) is standard in the O(N) non-linear σ-model in three dimensions. There it holds for the expectation of a unit vector field $\langle(u^a)^2\rangle$ that

$$\tilde{x}[\langle(u^a)^2\rangle-1]=0\,, \tag{21}$$

with

$$\langle (u^a)^2 \rangle = \int \frac{d^3k}{(2\pi)^3} (k^2+\lambda)^{-1} .$$

This can be solved for large $\tilde{x}$ (low temperature) by a separate treatment of the zero momentum state. As long as the system has a finite volume, the integral is written as $V^{-1}\sum_k$ and (21) receives from the $k=0$ state a contribution $(V\lambda)^{-1}$. After removing this from the sum, the remainder can again be evaluated using the integral. Now the gap equation (21) can be solved for any large $\tilde{x}$ with a very small λ. In the thermodynamic limit $A\to\infty$ the system is known to develop a non-zero expectation $\langle u^a \rangle \equiv U^a$ that breaks rotational invariance. One can show this also in an infinite system if one uses the effective action formalism in which the free energy density is supplemented by the field energy expressed in terms of the expectation values U^a and the gap equation (21) reads

$$\tilde{x}\{\langle (u^a)^2 \rangle_c - [1-(U^a)^2]\} = 0 . \qquad (22)$$

Thus, all that happens is that the expectation $\langle (u^a)^2 \rangle$ splits into a connected and disconnected part. Eq. (22) shows that in the limit $T\to 0$, U^a becomes a unit vector implying perfect magnetic ordering and that the temperature dependence of $(U^a)^2$ is $(U^a)^2 = 1 - T_c/T$.

The situation in the present model is completely analogous. We supplement the free energy density (6) by $(1/AN)E[X^a]$ where X^a is a non-zero expectation of x^a. This replaces the gap equation (19) by

$$\langle (\partial_i x^a)^2 \rangle_c - [2-(\partial_i X^a)^2] = 0 \qquad (23)$$

(times $8\pi\tilde{x}$). This can now be solved for $T\to 0$, $\tilde{x}\to\infty$ (where $\lambda = 0$). There exists a non-zero expectation $\langle \partial_i x^a \rangle = \partial_i X^a$ which breaks rotational invariance. For instance, $X^1 = U\zeta^1$, $X^2 = U\zeta^2$ and (23) gives $U^2 = 1 - T_c/T$. The "magnetization" describes in this model the formation of lamellar planes of area $U^2 A$.

This is how a microemulsion condenses into a stack of membranes.

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