RELATION BETWEEN FLUCTUATION PRESSURE AND X-RAY STRUCTURE OF STACK OF MEMBRANES ☆

H. KLEINERT

Institut für Theorie der Elementarteilchen, Freie Universität Berlin, Arnimallee 14, 1000 Berlin 33, Germany

Received 24 February 1989; accepted for publication 21 April 1989
Communicated by A.A. Maradudin

While Helfrich's theory explains roughly the size of the algebraic decay exponent η_1 in the X-ray structure of stacks of membranes, it gives a fluctuation pressure $p=2aT^2/\varkappa d^2$ with $a\approx 0.23$ which is too large by about a factor 2. We present an alternative theory which resolves this conflict. Our new central prediction is the relation $\eta_1=\gamma\pi^2/64a$ where for infinitely thin membranes $\gamma=8/\pi^2$, i.e. $\eta_1=1/8a$. Using the most accurate Monte Carlo determination of $a=0.101\pm0.003$ the latter case yields $\eta_1=1.24\pm0.07$, to be compared with Helfrich's value 4/3.

Some time ago, Helfrich [1] pointed out that the entropy of a stack of fluctuating self- and mutually avoiding membranes (which are surfaces without tension and an extrinsic curvature stiffness $\varkappa$) would push the layers apart with a pressure law

$$p=2a\frac{T^2}{\varkappa d^2}, \qquad (1)$$

where T is the temperature in units of the Boltzmann constant and d the distance between the membranes. He also presented an estimate for the constant a based on the assumption that the mutual avoidance condition can be taken into account by an effective harmonic interaction. If the stack of membranes is positioned in the planes $z_n=nd$ with vertical displacements $u_n(\boldsymbol{x})=u(z_n,\boldsymbol{x})$, the energy reads

$$E=\sum_n\int d^2x\,[\tfrac{1}{2}\varkappa(\partial^2u_n)^2+Bd^{-1}(u_n-u_{n-1})^2], \qquad (2a)$$

with a bare (i.e. $T=0$) layer compressional modulus B depending on the distance in an a priori unknown way, say $B=B(d)$. In the continuum limit this reduces to the smectic liquid crystal energy

$$E_H=\int d^2x\,dz\left(\frac{\varkappa}{2d}(\partial^2u)^2+\tfrac{1}{2}B(\partial_zu)^2\right). \qquad (2b)$$

By integrating out the u fluctuations one obtains their free energy density (A is the area, N the number of membranes)

$$\begin{aligned}\Delta f(B,d)&=\frac{1}{AN}[F-F(B=0)]\\&=\tfrac{1}{2}\left[\operatorname{tr}\log\left((\partial^2)^2-\frac{Bd}{\varkappa}\partial_z^2\right)-(B=0)\right]\\&=\frac{T}{8\pi}\left(\frac{Bd^3}{\varkappa}\right)^{1/2}\int_0^{\pi/d}dk_z\,k_z\,. \end{aligned}\qquad (3)$$

This implies a renormalization of the bare (i.e. $T=0$) modulus B to the fluctuation corrected value,

$$B_R=B+d\frac{\partial^2\Delta f(B(d),d)}{\partial d^2}. \qquad (4)$$

Now Helfrich takes a bold step and determines $B(d)\equiv B_H(d)$ by the following self-consistency postulate (which cannot be deduced from (4)!),

$$B_H(d)\equiv d\frac{\partial^2\Delta f(B)_H(d),d)}{\partial d^2}. \qquad (5)$$

We shall indicate all his quantities by a subscript H. Eq. (5) yields

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

$$B_H(d)=\left(\frac{3\pi}{8}\right)^2\frac{T^2}{\varkappa d^3}, \tag{6a}$$

$$\Delta f_H\equiv\Delta f(B_H)=\tfrac{1}{6}dB_H\,. \tag{6b}$$

This gives the fluctuation pressure

$$p_H=-\frac{\partial\Delta f_H}{\partial d}=\frac{2}{d}\Delta f_H=\tfrac{1}{3}B_H(d)\,. \tag{7}$$

Hence the constant a in (1) is predicted to have the value

$$a_H=\frac{1}{6}\frac{d^3\varkappa}{T^2}B_H=\frac{3\pi^2}{128}\approx 0.23\,. \tag{8}$$

Unfortunately, this number is not in agreement with Monte Carlo measurements of the fluctuation pressure which give [2,3] [#1]

$$a\approx 0.101\pm 0.003\,. \tag{9}$$

In view of this disagreement it is surprising that the value of B_H in (8) has recently been found to be consistent with experimental X-ray structure factors in lamellar phases which are stable over a wide range of distances $d\in(100\text{ Å}, 500\text{ Å})$ much larger than the membrane thickness ≈ 20 Å. The Bragg peaks show an algebraic decay described by the Fourier transform of

$$\langle\exp\{iq[u_n(\boldsymbol{x},z)-u_n(0)]\}\rangle$$
$$\propto(\boldsymbol{x}^2)^{-\eta}\exp\left\{-\eta\left[2\gamma+E_1\left(\frac{\boldsymbol{x}^2}{4z}\sqrt{\frac{Bd}{\varkappa}}\right)\right]\right\}$$

(E_1 is the exponential integral, $\gamma=0.557...$ Euler's number) with an exponent $\eta=\eta_m$ of the mth harmonic reflex, with momentum transfer $q=q_m=2\pi m/d$ given by

$$\eta_m=\frac{Tqm^2}{8\pi(B\varkappa/d)^{1/2}}\,. \tag{10}$$

Inserting Helfrich's $B=B_H$ gives $\eta_1=\eta_H\equiv\frac{4}{3}$ in good agreement with experiment [4,5].

It is the purpose of this note to present a simple model which makes the two findings consistent with each other. We shall describe the stack of membranes by the following energy,

$$E=\int d^2x\sum_n\tfrac{1}{2}\varkappa(\partial_i^2u)^2$$
$$+\frac{B}{2d}\int d^2x\sum_n[(\nabla_zu)^2-\sigma^2]d^2\,, \tag{11}$$

where $\nabla_zu\equiv(u_n-u_{n-1})/d$. In contrast to Helfrich's liquid crystal ansatz (2b) with fixed d-dependent $B=B(d)$, our B is a fluctuating parameter which plays the role of a Lagrange multiplier to ensure that the average width of distance fluctuations between the membranes is a fixed fraction of d, i.e. $u_n-u_{n-1}=\sigma^2d^2$ or

$$\langle(\nabla_zu)^2\rangle=\sigma^2\,. \tag{12}$$

We shall refer to the dimensionless parameter σ as the *penetrability parameter*. It is a material parameter characterizing how far a membrane can invade into the fuzzy regimes of the neighbours ($\sigma=\infty$ implies perfect interpenetrability of the surfaces). For dimensional reasons, σ taken to be independent of d. This is consistent with Monte Carlo data [2,3]. The value of σ for complete mutual avoidance is unknown a priori.

Since the model is soluble for discrete layers we do not take the continuum approximation to the n sum. Integrating out the u fluctuations gives their free energy density

$$\Delta f_{new}=\gamma\Delta f(B,d)-\tfrac{1}{2}dB\sigma^2. \tag{13}$$

We now determine B by extremizing Δf_{tot} in B. Since $\partial\Delta f/\partial B=\Delta f/2B$, this yields

$$2\frac{\partial\Delta f_{new}}{\partial B}=\gamma B\Delta f(B,d)-d\sigma^2=0\,, \tag{14}$$

thus fixing

$$B=B(d)\equiv\frac{\gamma^2}{\sigma^4}\frac{T^2\pi^2}{2\times128}=\frac{\gamma^2}{36\sigma^4}B_H(d)\,. \tag{15}$$

Here γ is a factor which brings the integral $\int_0^{\pi/d}dk_z\,k_z$ in the continuum energy Δf in (3) to the sharply layered form $\int_0^{\pi/d}dk_z\,2d^{-1}\sin(k_zd/2)$,

$$\gamma=\frac{8}{\pi^2}\,. \tag{16}$$

Helfrich uses the continuum approximation $\gamma\approx1$.

[#1] The result in ref. [2] was extracted from previously existing Monte Carlo data of a completely different physical process (two-dimensional defect melting) and were inaccurate due to the effects of the melting transition. The new data remove these shortcomings.

In contrast to Helfrich's ansatz, various choices of the penetrability allow for different sizes of $B(d)$. An important property of our model is that the energy (13) is a combination of one term linear and another quadratic in $\sqrt{B}$. On inserting (14) into (13) this generates the experimentally needed factor $\frac{1}{2}$ between total and fluctuation energy:

$$\Delta f_{\rm tot} = \tfrac{1}{2}\Delta f(B,d) = \frac{1}{2}\frac{\gamma^2}{6\sigma^2}\Delta f_{\rm H} . \qquad (17)$$

Since the mutual avoidance condition does not enter into Helfrich's postulate, the good agreement of η_1 with $\eta_{\rm H}$ can only be fortuitous. From (17) we find the pressure law

$$p = -\frac{\partial \Delta f_{\rm tot}}{\partial d} = \frac{1}{2}\frac{\gamma^2}{6\sigma^2} p_{\rm H} . \qquad (18)$$

Hence our constant a in the pressure law (1) is related to Helfrich's by

$$a = \frac{1}{2}\frac{\gamma^2}{6\sigma^2} a_{\rm H} = \frac{\gamma^2}{6\sigma^2}\frac{3\pi^2}{256} \approx \frac{\gamma^2}{6\sigma^2} 0.115 . \qquad (19)$$

Consider now the critical index η_1. It is given by (10) and is thus equal to

$$\eta_1 = \frac{4}{3}\sqrt{\frac{B_{\rm H}}{B}} = \frac{6\sigma^2}{\gamma}\frac{4}{3} \equiv \frac{6\sigma^2}{\gamma}\eta_{\rm H} . \qquad (20)$$

Our theory predicts therefore the relation

$$\eta_1 = \gamma\pi^2/64 , \qquad (21)$$

i.e., for sharply layered membranes

$$\eta_1 a = \tfrac{1}{8} . \qquad (22)$$

This is to be contrasted with Helfrich's prediction $\eta_{\rm H} a_{\rm H} = \pi^2/32$ which is about twice as large. On the basis of the Monte Carlo value [3] $a \approx 0.101 \pm 0.003$ we predict

$$\eta_1 = 1.24 \pm 0.04 . \qquad (23)$$

When looking at the data in fig. 4 of ref. [4] we see that our value of η_1 provides for a better fit than Helfrich's if we use a slightly smaller thickness parameter $\delta = 27$ Å. Our value is also compatible with the data in ref. [5].

In conclusion, the model (9) provides a satisfactory description of all presently known data on stacks of membranes. This has been achieved at the cost of one free parameter, the penetrability σ, which is given by

$$\sigma^2 = \gamma\eta_1/8 = \eta_1/\pi^2 = \gamma/64a \approx 0.124 . \qquad (24)$$

The author thanks Dr. W. Janke for useful discussions.

References

[1] W. Helfrich, Z. Naturforsch. A 33 (1978) 305.
[2] W. Janke and H. Kleinert, Phys. Rev. Lett. 58 (1987) 144; Phys. Lett. A 117 (1986) 353.
[3] W. Janke, H. Kleiner and M. Meinhart, Phys. Lett. B 217 (1989) 525.
[4] C.R. Safinya, D. Roux, G.S. Smith, S.K. Sinha, P. Dimon, N.A. Clark and A.M. Bellocq, Phys. Rev. Lett. 57 (1986) 2718.
[5] D. Roux and C.R. Safinya, J. Phys. (Paris) 49 (1988) 307.