Fluctuation Pressure of a Stack of Membranes

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We show by Monte Carlo simulation that the fluctuations in a stack of membranes with spacing d produce a pressure $p=(0.148\pm0.006)T^2/\kappa d^3$, where T is the temperature (in units of k_B) and κ is the curvature elastic modulus.

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Lamellar systems such as lecithin in water are kept from sticking to each other by violent out-of-plane fluctuations.[1,2] For biophysical applications it is important to know the precise pressure law, as a function of the distance d and temperature, which keeps the layers apart. This problem was addressed first theoretically by Helfrich[1] who obtained

$$p\approx 0.46T^2/\kappa d^3 \tag{1}$$

where κ is the curvature elastic modulus. He derived this result from what might be called a "self-consistent liquid-crystal approximation." The starting point is the curvature energy of a single layer,

$$E=\tfrac{1}{2}\kappa\int d^2x(1+u_l^2)^{1/2}\{\partial_l[u_l/(1+u_l^2)^{1/2}]\}^2, \tag{2}$$

linearized to

$$E\approx\tfrac{1}{2}\kappa\int d^2x(\boldsymbol{\partial}^2 u)^2. \tag{3}$$

Here $u(x,y)$ is the vertical displacement of the membrane and $u_l\equiv\partial_l u$. Helfrich then assumed that a stack of such layers can be treated like a smectic liquid crystal with an energy $(\partial_\perp^2\equiv\partial_x^2+\partial_y^2)$

$$E_{\text{l.c.}}=\int dz\int d^2x\left[\frac{B}{2}(\partial_z u)^2+\frac{\kappa}{2d}(\partial_\perp^2 u)^2\right], \tag{4}$$

in which the effect of steric hindrance of neighboring layers is accounted for by a bare vertical compressibility. It is normalized by insertion of the displacement field $u(\mathbf{x})=[(d'-d)/d]z$, and the formation of the derivative

$$B=(1/AdN)d^2\partial^2 E_{\text{l.c.}}/\partial d'^2. \tag{5}$$

Here, A is the area at $T=0$ and N the number of layers on top of each other. Integrating out the fluctuations yields the free energy

$$\Delta F=F-F(B=0)=\frac{T}{2}ANd\int_{-\pi/d}^{\pi/d}\frac{dk_z}{2\pi}\int\frac{dk_\perp^2}{4\pi}\left[\ln\left(Bk_z^2+\frac{\kappa}{d}k_\perp^4\right)-\ln\left(\frac{\kappa}{d}k_\perp^4\right)\right]$$

$$=\frac{TANd}{16\pi}\left(\frac{Bd}{\kappa}\right)^{1/2}\int_{-\pi/d}^{\pi/d}dk_z|k_z|=AN\frac{T}{16\pi}\left(\frac{\pi}{d}\right)^2\left(\frac{Bd^3}{\kappa}\right)^{1/2}. \tag{6}$$

By a change of the vertical size of the system, the free energy of fluctuations exhibits a compressibility,

$$B_{\text{fl}}=(1/AdN)d^2\partial^2\Delta F(B,d)/\partial d^2. \tag{7}$$

By postulating the equality of the compressibility B and the compressibility of the fluctuations B_{fl}, Helfrich considers Eq. (7) as a differential equation for $B(d)=B_{\text{fl}}(d)$ which is solved by

$$B(d)=(3\pi^2/128)T^2/\kappa d^3. \tag{8}$$

Reinserted into (6) this gives the free-energy density

$$\Delta f\equiv\Delta F/NA=(3\pi^2/128)T^2/\kappa d^2\approx 0.23T^2/\kappa d^2, \tag{9}$$

and a pressure law

$$p=-\partial\Delta f/\partial d\approx 0.46T^2/\kappa d^3. \tag{10}$$

Apart from the dependence of the result on a quadratically divergent integral with a cutoff at π/d—one could, for instance, have worked with an array of layers in the z direction rather than a continuum in which case k_z^2 would become $[2-2\cos(k_z d)]/d^2$ and the final answer, Eqs. (9) and (10), would change by a factor

$$\left[\frac{\int dk_z [2-2\cos(k_z d)]^{1/2}/d}{\int dk_z |k_z|}\right]^2 = \left(\frac{8}{\pi^2}\right)^2 \approx 0.66,$$

—the harmonic nature of the model may be of limited value in describing the hard-core repulsion between the membranes. It is therefore worth while to find out what the pressure law really is. To do this we have studied the linearized theory (3) on a square lattice with L^2 lattice sites and evaluated the partition function

$$Z = \exp\left(-\frac{1}{T}NL^2 f\right) = \prod_{n=1}^{N}\prod_{\mathbf{x}}\int \frac{du_n(\mathbf{x})}{d}\exp\left[-\frac{\kappa}{2T}\sum_{n,\mathbf{x}}(\bar{\nabla}\nabla u_n)^2\right] \equiv \left(\frac{TA}{\kappa d^2}\right)^{NL^2/2} Z_0, \tag{11}$$

$$0 < u_1 < \cdots < u_n < \cdots < u_N < (N+1)d,$$

via Monte Carlo simulations where $\mathbf{x}$ runs over the discretized xy plane and $\bar{\nabla}\nabla$ is the lattice version of the two-dimensional Laplacian. The constraints on the vertical displacements u_n account for the steric interactions between neighboring membranes and between the outer membranes and walls at $z=0$ and $z=(N+1)d$ which are introduced to stabilize the system for finite N (=number of layers). In order to save computer time, we have restricted the variables $u_n(\mathbf{x})$ to integer numbers. In the temperature range in which we are interested, this is a very good approximation as is well known from previous studies of a similar model in the context of defect melting.[3]

By a trivial scaling argument we see that Z_0 can depend only on $(T/\kappa)^{1/2}/d$ such that we can fix d and κ and study only the temperature dependence. In our simulations on 16^2 and 32^2 square lattices (with periodic boundary conditions), we have chosen $d=5$, $\kappa=1$, and varied the number of layers over $N=2,\ldots,5$. As a typical example, we show in Fig. 1(a) our data of the internal energy

$$\bar{e} = \frac{\bar{E}}{NL^2} = \frac{\partial}{\partial(1/T)}\left(\frac{1}{T}f\right)$$

taken on a 32^2 lattice with $N=3$ layers. For low $T\approx 2$, we see the roughening transition above which the discrete nature of the variables $u_n(\mathbf{x})$ becomes irrelevant. This is demonstrated by the fact that the energy first approaches the linear Dulong-Petit law, $\bar{e}=T/2$, valid for continuous Gaussian fluctuations. The deviations from the Dulong-Petit law which appear for higher T contain

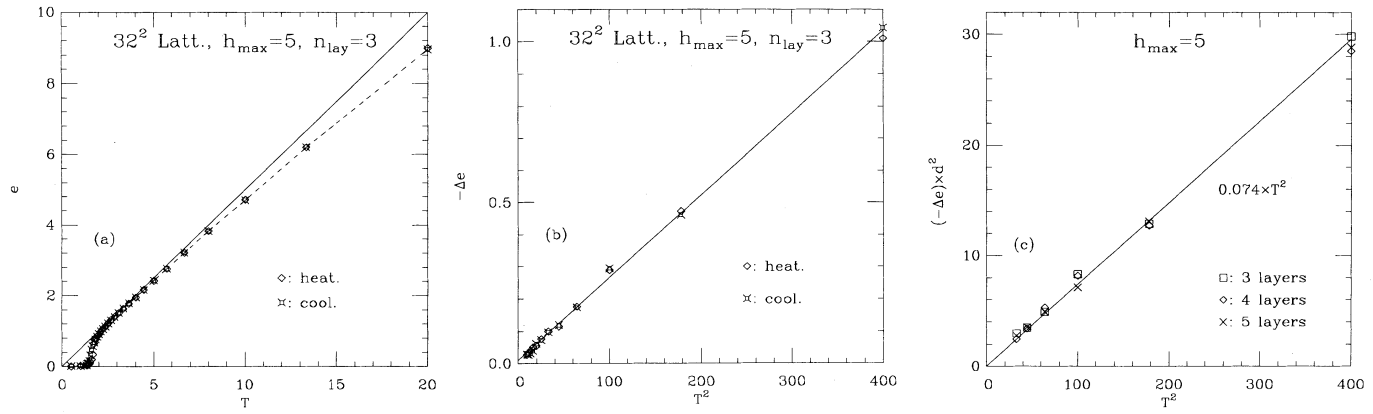

FIG. 1. (a) The internal energy $e=[\partial/\partial(1/T)][(1/T)f]$ of a stack of three layers on a 32^2 square lattice between plates spaced $4h_{\max}=20$ units apart ($\kappa=1$). The data points are taken in a thermal cycle with 250 sweeps for equilibration and 500 sweeps for measurements. At small $T\approx 2$, we see the roughening transition above which the discreteness of our displacement variables becomes unimportant. Above this transition, e follows first a Dulong-Petit law $e=T/2$ (continuous line). For larger T there are deviations $\sim T^2$ due to the steric hindrance by the neighboring membranes. The dashed line is a guide to the eye. (b) The quadratic deviations in (a) plotted against T^2. The slope of the linear fit is 0.0025 ± 0.0001. (c) A plot of $(-\Delta e)d^2$ for systems of $N=3$, 4, and 5 layers between walls spaced 20, 25, and 30 units apart where d is the distance between the inner layers. To reduce statistical errors, d has been averaged with respect to both neighbors. The case $N=3$ was done on a 32^2 square lattice, the cases $N=4$, 5 on a 16^2 square lattice. The universal straight line gives the pressure law (17).

the desired information on the pressure. First of all, we observe in Fig. 1(b) that they grow linearly in T^2 such that the free-energy density behaves like

$$\Delta f = aT\left[\frac{1}{d}\left(\frac{T}{\kappa}\right)^{1/2}\right]^2 = a\frac{T^2}{\kappa d^2}, \tag{12}$$

confirming the above theoretical expectations. Recalling $d=5$, $\kappa=1$, from the slope we read off

$$a = 0.063 \pm 0.003. \tag{13}$$

This amounts to a pressure of the entire stack of layers upon the walls,

$$p \approx 0.126 T^2/\kappa d^3. \tag{14}$$

We still have to make some corrections due to the finite number of layers. For this we observe that after the fluctuations set in, the distance between the inner layers is slightly larger than between the outer layers and the walls. For example, for three layers at $T=20$ [see Fig. 2(a)],

$$\frac{d_{\text{layer-layer}}}{d_{\text{layer-wall}}} \approx \frac{5.58}{4.42} \approx 1.26. \tag{15}$$

This implies that a neighboring fluctuating membrane is slightly more repulsive than a neighboring wall. When we correct for d with this factor, the results for systems of $N=3$, 4, and 5 layers fall on top of each other, as shown in Fig. 1(c), and we find

$$a = 0.074 \pm 0.003, \tag{16}$$

and thus for the central membrane the pressure

$$p = (0.148 \pm 0.006) T^2/\kappa d^3 \tag{17}$$

which differs in size from Helfrich's estimate (10).

In view of the small equilibrium difference between $d_{\text{layer-layer}}$ and $d_{\text{layer-wall}}$ it is not surprising that the energy carried by each membrane is almost the same as for a single membrane between two rigid plates at distance d (to each side) which was found before.[4]

The distribution of the central membrane is, to a very good approximation, a Gaussian with width $\sigma^2 \approx 6.14$ at $T=20$ [see Fig. 2(a)]. The width is somewhat larger than what we can calculate from (5), which would give the expression

$$\sigma^2 = \langle u^2 \rangle = T\int \frac{dk_z}{2\pi}\int \frac{dk_\perp^2}{4\pi}\left(Bk_z^2 + \frac{\kappa}{d}k_\perp^4\right)^{-1}$$

$$= \frac{T}{16\pi}\left(\frac{\kappa}{Bd}\right)^{1/2}\frac{d}{\kappa}\times 2\int_0^{\pi/d} dk_z \frac{1}{k_z}. \tag{18}$$

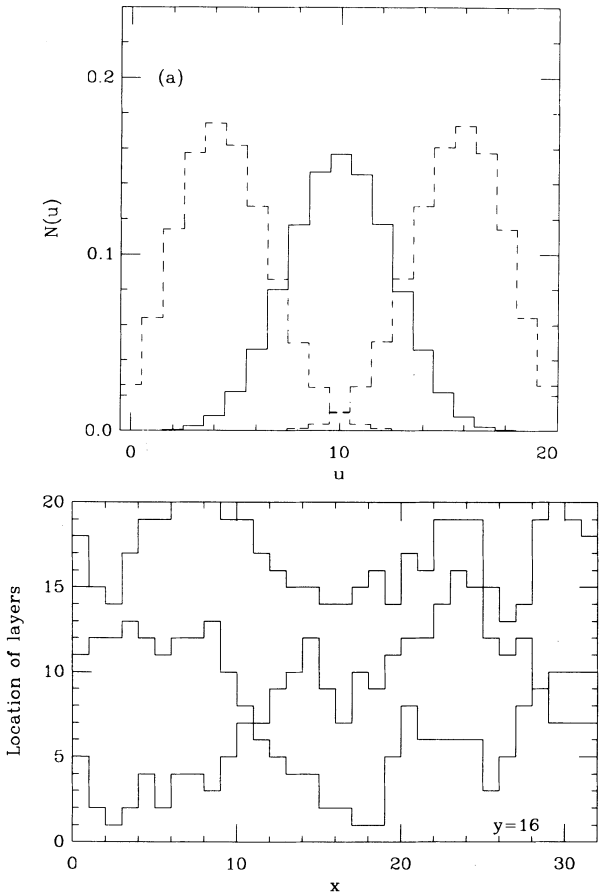

FIG. 2. (a) The distribution of the three layers on a 32^2 lattice at $T=20$. They are practically Gaussian. Notice that the distance to the walls (≈ 4.4) is almost the same as between the layers (≈ 5.6). A neighboring membrane is slightly more repulsive than a wall placed at its mean position. (b) A particular membrane configuration cut in the middle of the 32^2 lattice at $T=20$. Notice that because of our choice of lattice parameters, the area of each membrane is about 2.5 times larger than the base area.

With $u(\mathbf{x})$ vanishing at the plates, the integral becomes

$$\left(1+\frac{1}{2}\cdots\frac{1}{N}\right)$$

$$\approx \frac{\ln(N)+\ln(N+1)}{2} + 0.577 + O\left(\frac{1}{N^2}\right).$$

On insertion of $N=3$, this gives the temperature-independent result

$$\sigma^2 = \left(\frac{2}{3}\right)^{1/2}\left(\frac{d}{\pi}\right)^2\left(1+\frac{1}{2}+\frac{1}{3}\right) \approx 4.72.$$

If we take, more realistically, three discrete layers, $1/k_z$

has to be replaced by

$$\frac{\pi}{N+1}\left[2-2\cos\left(\frac{\pi}{N+1}n\right)\right]^{-1/2}$$

and σ^2 is raised to 5.17.

Notice that the area of each membrane is so rough that it is much larger (about 2.5 times at $T=20$) than the base area [see Fig. 2(b)]. This does not mean, however, that the physical membrane has such a rough area. The above roughness is a consequence of our choice of lattice parameters which is made possible by the scaling properties of the energy. If we go back to physical scales for κ,T,d, we find that the area of a lecithin membrane at room temperature is enlarged by only a factor 1.02.

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