FLUCTUATION PRESSURE OF MEMBRANE BETWEEN WALLS

W. JANKE [1]

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

and

H. KLEINERT [1,2]

University of California, San Diego, La Jolla, CA 92093, USA

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We prove that a tensionless membrane, fluctuating harmonically with free ends between two parallel plates of spacing $2d$, generates a pressure of the functional form $p = (T/Ad)\tau a(\tau)$, where τ is the dimensionless variable $\tau \equiv (T/\kappa)A/d^2$, κ is the curvature elastic constant, and A the area of the plates. For large A, $a(\tau)$ becomes a constant which we determine by Monte Carlo simulation to be $a_\infty = 0.060 \pm 0.003$.

Membrane layers are attracted to each other by van der Waals forces [1] which decrease at intermediate distances d ($20 < d < 100$ Å) like $1/d^3$ #1. The most important repulsive force to keep them apart is provided by thermal out-of-plane fluctuations [3,4]. In the absence of areal tension, these are so violent that they can be seen in an ordinary microscope [5]. The reason for this is that they are controlled only by the curvature energy [6]

$$e = \tfrac{1}{2}\kappa(c_1 + c_2)^2, \tag{1}$$

where $c_1 = 1/R_1$, $c_2 = 1/R_2$ are the principal curvatures of the membrane and κ is the elastic modulus ($\approx (2.3 \pm 0.3) \times 10^{-12}$ erg for egg lecithin membranes at room temperatures). If the membrane is parametrized by the vertical displacement $u(x, y)$ over an (x, y)-plane, this has the lowest approximation $e = \frac{1}{2}\kappa[(\partial_x^2 + \partial_y^2)u]^2$. The two-dimensional laplacian $\partial^2 = \partial_x^2 + \partial_y^2$ leaves all harmonic field configurations without energy and this causes the violence of the fluctuations. We are thus confronted with the interesting problem of finding the size of the repulsive force between membranes.

For a first estimate we shall study two simplified idealizations of the physical system, as proposed by Helfrich [3,5]. The first is to imagine that the undulating neighboring membranes constrain the fluctuations of each membrane on the average, in a similar way as a harmonic potential would do. Then the partition function of each membrane is

$$Z = \mathrm{e}^{-(A/T)f} = \prod_x \int_{-\infty}^{\infty} \frac{\mathrm{d}u(x)}{\sqrt{2\pi T/\kappa}} \times \exp\left(-\frac{\kappa}{2T}\int \mathrm{d}^2x\left[(\partial^2 u)^2 + m^4 u^2\right]\right), \tag{2}$$

where A denotes the area of the membrane at

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[2] On sabbatical leave from Institut für Theorie der Elementarteilchen, Freie Universität Berlin, Arnimallee 14, 1000 Berlin 33, Germany.

#1 The $1/d^3$ law $P_{\mathrm{vdW}} \approx -1.4 \times 10^{-15}$ erg/d^3 is valid for intermediate distances (see ref. [1]) as long as retardation effects are negligible. These change the falloff to $1/d^5$ for larger distances. For very short distances of order 2–20 Å there are also repulsive hydration forces and electrostatic forces which overwhelm the van der Walls attraction but which drop of exponentially (see ref. [2]).

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$T = 0$. The integral can easily be done giving the free energy density

$$\frac{1}{T}f = \frac{1}{2}\int \frac{d^2k}{(2\pi)^2}\log(k^4 + m^4) = \tfrac{1}{8}m^2 + \text{const.} \tag{3}$$

The displacement variable has a gaussian distribution $P(u) \sim e^{-u^2/2\sigma^2}$ with a squared width

$$\sigma^2 = \langle u^2\rangle = \frac{T}{\kappa}\int \frac{d^2k}{(2\pi)^2}\frac{1}{k^4 + m^4} = \frac{T}{8\kappa m^2}. \tag{4}$$

Combining (3) and (4), we find that the energy changes with average width as follows

$$f = \frac{T^2}{64\kappa\langle u^2\rangle}. \tag{5}$$

For not too small distances d from the neighboring membranes, we may follow Helfrich [3] and expect $\langle u^2\rangle$ to satisfy

$$\langle u^2\rangle = \rho d^2, \tag{6}$$

with ρ varying only slowly with temperature, in which case we obtain the free energy density

$$f = a_{\text{osc}}\frac{T^2}{\kappa d^2}, \tag{7}$$

with

$$a_{\text{osc}} = \frac{1}{64\rho}, \tag{8}$$

resulting in a pressure

$$p = -\frac{\partial f}{\partial(2d)} = a_{\text{osc}}\frac{T^2}{\kappa d^3}. \tag{9}$$

The size of ρ is unknown. If we assume somewhat arbitrarily that the membranes at $u = \pm d$ coincide with the 2σ interval of the u distribution, implying that they enclose 95.45% of all possible configurations, we estimate

$$\rho = \langle u^2\rangle/d^2 \approx \tfrac{1}{4} \tag{10}$$

and

$$a_{\text{osc}} \approx \tfrac{1}{16} \approx 0.0625. \tag{11}$$

Let us now turn to the second idealization which consists of a harmonically fluctuating membrane between two rigid plates. This model has a partition function

$$Z = \prod_x \int_{-d}^{d} \frac{du(x)}{d}\exp\left(-\frac{\kappa}{2T}\int d^2x(\partial^2 u)^2\right) \tag{12}$$

also discussed first by Helfrich [3,5]. He resorts to what may be called an "independent membrane piece approximation" [5]. Observing that the mean displacement

$$\langle u^2\rangle = \frac{T}{\kappa}\int \frac{d^2k}{(2\pi)^2}\frac{1}{k^4} = \frac{T}{4\pi\kappa}\frac{\Delta A}{\pi^2} \tag{13}$$

diverges with the size of the area, he mentally decomposes the membrane into pieces of size ΔA and argues that between plates at $u = \pm d$, the average size of u^2 should be (in contrast to our estimate (10))

$$\langle u^2\rangle \approx \tfrac{1}{6}d^2. \tag{14}$$

This is compatible with (13) if we imagine the membrane to consist of a set of independent pieces of area $\Delta A = \frac{2}{3}\pi^3\kappa d^2/T$. If these behave like an ideal gas, they exert a pressure

$$p = \frac{T}{2d\,\Delta A} = \frac{3}{4\pi^3}\frac{T^2}{\kappa d^3} \tag{15}$$

upon the walls thus resulting in the same law as (9) but with

$$a \approx 0.0242, \tag{16}$$

which is much smaller than (11).

We are able to make decisive progress over these estimates. First we observe that by going to the reduced quantities $u_{\text{red}} = u/d$, $x_{\text{red}} = x/\sqrt{A}$, the partition function is seen to have necessarily the functional form $(\sqrt{2\pi TA/\kappa d^2})^N\tilde{Z}(\tau)$, where τ is the dimensionless variable $\tau \equiv (T/\kappa)A/d^2$, and N the number of fluctuating degrees of freedom in the membrane ($\sim$ number of molecules). As a consequence the free energy density has the form

$$f = -\frac{NT}{2A}\log\left(\frac{2\pi TA}{\kappa d^2}\right) + \frac{T}{A}g\left(\frac{T}{\kappa}\frac{A}{d^2}\right), \tag{17}$$

giving rise to a general pressure law, due to the walls,

$$p = -\frac{\partial\Delta f}{\partial(2d)} = \frac{T^2}{\kappa d^3}a(\tau), \tag{18}$$

where Δf is the second term in (17) and $a(\tau) = \mathrm{d}g(\tau)/\mathrm{d}\tau$.

Our second point is that the existence of a non-trivial thermodynamic limit $A \to \infty$ implies that the function $g(\tau)$ has the limiting behavior $g(\tau) \to a_\infty \tau$ for $\tau \to \infty$. Moreover, since the membrane becomes free for $d \to \infty$, the function $g(\tau)$ cannot contain any powers $1/\tau$ in this limit. Thus, we expect the only corrections to be of the exponential type (for instance $\mathrm{e}^{-\mathrm{const}\times\tau}$).

Our third and main result is a Monte Carlo determination of the limiting value a_∞. We were fortunate to have recently finished a study of the partition function (12) on a lattice for the purpose of understanding a completely different physical process, namely that of defect melting in two-dimensional crystals. The fundamental defects are disclinations [7] and these interact with each other elastically by a potential

$$\int \frac{\mathrm{d}^2k}{(2\pi)^2}\,\frac{1}{k^4}\,\mathrm{e}^{\mathrm{i}k\cdot x},$$

i.e. with the same $1/k^4$ correlations as in the partition function (12). The elastic fluctuations are therefore described by the model (12). The disclinations are brought in by restricting the values of u to *integer* numbers [8]. We had studied such a model on a square lattice of unit spacing, letting u run over integer values from $-h$ to h with $h = 5$. Thus our data contained the effect of walls at distance $2d = 10$. For increasing temperature, the model shows a first-order roughening transition ($T_R/\kappa \approx 1.63$) at which the variables u overcome their discrete energy barriers. This relates via duality to the transition of defect melting (in the freezing direction). Above this transition, the discreteness of u no longer matters. This is why we can use the model with discrete u's as an approximation to the membrane partition function (12).

We update the configurations by sweeping through the entire lattice according to a permutation chosen randomly after each sweep, and apply the standard heat-bath algorithm to each variable $u(x)$ [9]. Using at each temperature 250 sweeps for equilibration and 500 sweeps for measurements, we found for a 32^2 square lattice with periodic boundary conditions the internal energy $\bar{e} = -(\partial \log Z/\partial T^{-1})/A$ shown in fig. 1a ($\kappa = 1$). Right above the roughening ($\hat{=}$ freezing) transition, it displays the Dulong–Petit law $\bar{e} \approx \frac{1}{2}T$ characteristic for the harmonic elastic fluctuations (in the crystalline state) thus demonstrating the irrelevance of the discreteness of u. Further, above the

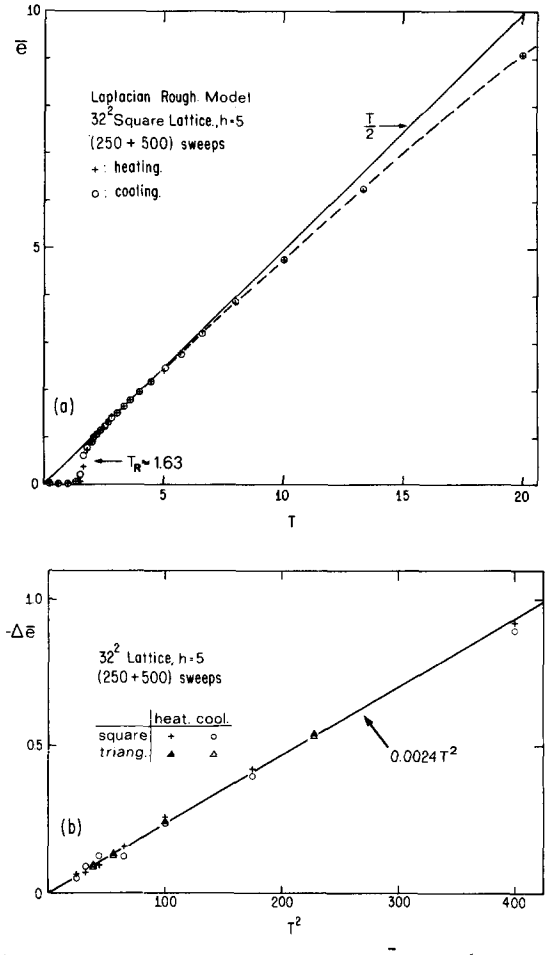

Fig. 1. (a) The internal energy $\bar{e} = -(\partial \log Z/\partial T^{-1})/\text{area}$ of the roughening model (12) on a 32×32 square lattice with periodic boundary conditions ($\kappa = 1$). For $T \approx 1.63$ it shows the first-order [8] roughening transition dual to the 2D model of disclination melting. For larger T it goes over into the Dulong–Petit law, $\bar{e} \approx T/2$, and for $T \gtrsim 5$ we begin seeing the effect of the "walls" at $u = \pm 5$ confining the membrane. The deviations from the Dulong–Petit law $\Delta\bar{e} = T/2 - \bar{e}$ are shown in (b). From these we extract $\Delta\bar{e} = -(0.0024 \pm 0.0001)T^2$ such that $a_\infty = 0.060 \pm 0.003$. The independence of this number on the lattice structure is demonstrated by the data points of a similar run on a triangular lattice which are fitted very well by the same straight line.

transition, the fluctuations begin "feeling" the restrictions of the "walls" at $u = \pm 5$ and the internal energy begins deviating from the Dulong–Petit law. The deviations $\Delta\bar{e} = \bar{e} - T/2$ are plotted against T^2 in fig. 1b for $\kappa = 1$. They are well-fitted by the straight line

$$\Delta\bar{e} = -(0.0024 \pm 0.0001)T^2. \tag{19}$$

This is to be compared with the general form

$$\Delta\bar{e} = \frac{\partial}{\partial(1/T)}\left(\frac{1}{T}f\right) - \tfrac{1}{2}T$$
$$= -(T/A)\tau a(\tau) = -(T^2/\kappa d^2)a(\tau), \tag{20}$$

following from eq. (17). Inserting $d = h = 5$, this implies $a(\tau) = a_\infty$ with

$$a_\infty = 0.060 \pm 0.003 \tag{21}$$

and confirms that the free energy and the pressure have indeed the forms (17), (18) with $g(\tau) \approx a_\infty \tau$. We have checked that our lattice was large enough for this calculation by doing the same run on a 16^2 lattice which gave the same result. The Monte Carlo number for a_∞ is much larger than Helfrich's theoretical estimate (16) and in good agreement with our harmonic oscillator value (11).

It is interesting to see that the distribution of u's between the walls is very close to being gaussian just as assumed in the harmonic oscillator approximation. For $T = 20$ ($\kappa = 1$) this is demonstrated in fig. 2a. The squared width σ^2, however, is smaller than what is estimated in eq. (10). It is more like $d^2/5$ than the assumed $d^2/4$. If we plot how $\langle u^2 \rangle$ varies with temperature in fig. 2b, we find that even though the curve saturates reasonably fast, it is not at all constant in the range $T \in (2, 20)$ where the pressure has the limiting functional form (9).

An important point is to make sure that our number for a_∞ is a universal result and does not depend on the lattice structure. This was done by repeating the study for a triangular lattice which gave, indeed, the same number as before (see fig. 1b). In this comparison, we have to use the energy

$$\frac{\kappa}{2T}\frac{3}{4}\sum_x \left(\frac{2}{3}\sum_{i=1}^{6}[u(x) - u(x+i)]\right)^2,$$

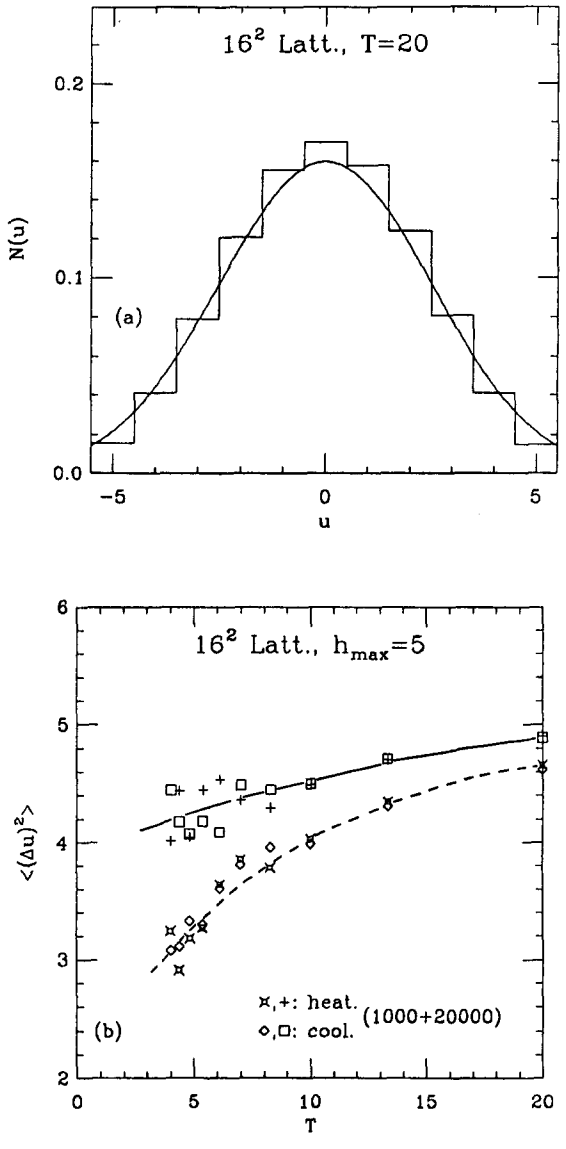

Fig. 2. (a) The discrete distribution of u's of the model (12) on a 16^2 square lattice for $T = 20$ ($\kappa = 1$) in comparison with the continuous gaussian distribution of the harmonic oscillator model (with $\sigma^2 = d^2/4 = 25/4$ such as to include 95.45% of the data within $[-5, 5]$). (b) The squared width $\sigma^2 \equiv \langle u^2 \rangle$ of the model (12) on a 16^2 square lattice against temperature (upper data). The center-of-mass movement of the membrane is included since it contributes to the pressure. Without this movement, we find the lower data points. The squared width of the center-of-mass distribution is given by the difference. The data points are taken in a thermal cycle with 1000 sweeps for equilibration and 20000 sweeps for measurement. The curves are eye-ball fits.

with $x + i$ denoting the next-neighbors such as to have the same continuum limit

$$\frac{\kappa}{2T}\int \mathrm{d}^2k(\partial^2 u)^2.$$

Finally, let us remark that our study was restricted to the harmonic approximation (12) of the curvature energy (1). For physical membranes, the non-linear pieces will have to be considered as well. This will be done in a separate work.

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