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## Effect of thermal undulations on the rigidity of fluid membranes and interfaces

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**Résumé.** — On montre que les ondulations thermiques des couches fluides, dont la résistance dépend de la rigidité de la couche, réduisent la rigidité effective. Cette diminution est calculée dans une approximation du premier ordre pour de faibles ondulations. Les modes d'ondulation sont définis comme des ondes de directeur de telle sorte que les courbures satisfassent le principe de superposition.

**Abstract.** — Thermal undulations of fluid layers, whose strength depends on layer rigidity, are shown to reduce the effective rigidity. The decrease is calculated in a first-order approximation for weak rippling. The undulation modes are defined as director waves so that the curvatures satisfy the superposition principle.

### 1. Introduction.

Curvature elasticity is a useful concept to understand some of the properties of fluid layers. It permits the theoretical treatment of vesicle shapes [1], in particular the analysis of observed contours [2]. It also provides criteria for the stability of the various structures formed by fluid bilayers and monolayers [3]. A striking property of such layers is their tendency to perform pronounced out-of-plane fluctuations. The strength of these thermal undulations or ripples is mostly controlled by curvature elasticity and lateral tension [4-8]. The shape fluctuations of giant vesicles, which may be regarded as long-wavelength undulations, are visible in optical microscopy. The thermal undulations have been shown, at first theoretically [9-11], to induce a repulsive steric interaction or, to use another name, undulation forces between fluid bilayers. A review of curvature elasticity and out-of-plane fluctuations of fluid membranes has been written by Petrov and Bivas [12].

The bending rigidity  $\kappa$ , which is one of the elastic moduli of fluid membranes, was measured for egg lecithin [13-15] and three synthetic lecithins [16] by means of vesicular shape fluctuations. The rigidities ( $\kappa \approx 2 \times 10^{-12}$  erg) seem just small enough to let steric repulsion overcome van der Waals attraction. The close competition between the two interactions may explain a number of otherwise contradictory findings : Lecithin in plenty of water forms giant

vesicles which do not stick to each other [13, 17, 18]. Similarly, well-ordered egg-lecithin multilayer systems take up water without limit [19]. On the other hand, disordered lecithin-water dispersions display a so-called equilibrium spacing of the membranes [20, 21]. Unilamellar lecithin vesicles do cohere if one [8] or both [18] of the membranes are slightly stretched or if they form very thin tubes, which first adhere to a glass slide [22]. We may infer that cohesion is absent when the undulations are fully developed, but is easily turned on by any factor limiting their amplitude, such as lateral tension or finite size.

The notion of curvature elasticity has also been applied to the surfactant layer forming the oil/water interface in microemulsions [23-28]. Bicontinuous systems with a critical point of phase separation are of special interest because of their relationship to the Ising model of ferromagnetism. In a pioneering paper, de Gennes and Taupin [23] predicted the very low rigidity which the surfactant layer must have to produce a bicontinuous microemulsion. For this purpose they calculated a persistence length of layer orientation, identifying it with the typical droplet size of 100 Å in such systems.

In the following we wish to show that thermal undulations are not only controlled by layer rigidity, but reduce it for long-wavelength ripples. The effective rigidity as well as the effective spontaneous curvature are calculated for a square piece of layer. The correc-

tions of the local (or bare) values are considered only in the lowest possible order. Their validity is, therefore, limited to the weakly rippled membrane. After the presentation of some basic formulae (Sect. 2) and the calculation of the effective quantities (Sect. 3), we will briefly discuss some possible applications of the results (Sect. 4).

## 2. Basic formulae.

The bending elastic energy per unit area of fluid bilayer or monolayer may be written as [29]

$$g = \frac{1}{2} \kappa_0 (c_1 + c_2)^2 - \kappa_0 c_{s0} (c_1 + c_2) + \bar{\kappa} c_1 c_2. \quad (1)$$

Here  $c_1, c_2$  are the principal curvatures and  $c_{s0}$  is the spontaneous curvature.  $\kappa_0$  and  $\bar{\kappa}$  are curvature-elastic moduli; the first one is also called rigidity. The subscript zero indicates the local (or bare) values which would hold in the absence of undulations. The Gaussian curvature  $c_1 c_2$  does not affect undulations as its integral is known to depend only on the genus of the (closed) surface. Accordingly, it will be ignored in the present context. Equation (1) is complete up to quadratic terms in the curvatures.

The undeformed flat layer is thought to coincide with the  $xy$  plane. Ripples may then be described by the displacement  $u(x, y)$  parallel to the  $z$  axis. Alternatively, one may use the director  $\mathbf{n}(x, y)$ , i.e. the layer

normal, which apart from  $|\mathbf{n}| = 1$  must satisfy the surface condition

$$\mathbf{n} \cdot \text{curl } \mathbf{n} = 0. \quad (2)$$

Director and displacement fields are related by

$$\mathbf{n} = \frac{(-\partial u/\partial x, -\partial u/\partial y, 1)}{[1 + (\partial u/\partial x)^2 + (\partial u/\partial y)^2]^{1/2}}. \quad (3)$$

We demand  $n_z > 0$  to ensure that  $u(x, y)$  and  $\mathbf{n}(x, y)$  are unique functions.

In a local coordinate system  $\xi, \eta, \zeta$ , also Cartesian, with the  $\zeta$  axis parallel to  $\mathbf{n}$  and arbitrary orientation of the  $\xi\eta$  cross one has

$$c_1 + c_2 = n_{\xi,\xi} + n_{\eta,\eta} \quad (4)$$

where  $n_{\xi,\xi} = \partial n_\zeta / \partial \zeta$ , etc. Supposing for a moment the director field  $\mathbf{n}(x, y)$  to fill all space defines in addition  $n_{\xi,\xi}$  which, of course, vanishes because of  $|\mathbf{n}| = 1$ . This permits the invariant representation

$$c_1 + c_2 = \text{div } \mathbf{n}, \quad (5)$$

$\text{div } \mathbf{n}$  being in principle the three-dimensional divergence. Since  $n_{z,z} = 0$  the equation reduces to

$$c_1 + c_2 = n_{x,x} + n_{y,y}. \quad (6)$$

Note that the curvature of a sine wave is positive in our notation. Insertion of (3) yields

$$c_1 + c_2 = - \frac{\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial x^2} \left( \frac{\partial u}{\partial y} \right)^2 - 2 \frac{\partial^2 u}{\partial x \partial y} \frac{\partial u}{\partial x} \frac{\partial u}{\partial y} + \frac{\partial^2 u}{\partial y^2} \left( \frac{\partial u}{\partial x} \right)^2}{[1 + (\partial u/\partial x)^2 + (\partial u/\partial y)^2]^{3/2}}. \quad (7)$$

The relationship between the true area of a piece of layer and its projection on the  $xy$  base may be expressed by

$$dA_{\text{real}} = \frac{1}{n_z} dA_{\text{base}}. \quad (8)$$

We will in general assume a square base and periodic boundary conditions. Undulation modes of amplitude  $u_{\mathbf{q}}$  are commonly defined by the Fourier expansion

$$u(\mathbf{r}) = \sum_{\mathbf{q}} u_{\mathbf{q}} e^{i\mathbf{q} \cdot \mathbf{r}} \quad (9)$$

with  $u_{-\mathbf{q}} = u_{\mathbf{q}}^*$ . The positions  $\mathbf{r} = (x, y)$  and the wave vectors  $\mathbf{q}$  refer to the base. The use of displacement modes implies, because of (7), that the curvatures which determine the elastic energies do not strictly obey the superposition principle. We will therefore employ the displacement only where this undesirable property has no consequences.

A representation of the undulation modes in terms of the director avoids the defect. Its Fourier expansion is

$$\mathbf{n}(\mathbf{r}) = \sum_{\mathbf{q}} \mathbf{n}_{\mathbf{q}} e^{i\mathbf{q} \cdot \mathbf{r}} \quad (10)$$

with  $\mathbf{n}_{-\mathbf{q}} = \mathbf{n}_{\mathbf{q}}^*$ . We are primarily interested in the longitudinal components of the mode amplitudes  $\mathbf{n}_{\mathbf{q}}$

$$l_{\mathbf{q}} = (\mathbf{n}_{\mathbf{q}} \cdot \mathbf{q}) \mathbf{q} / q^2. \quad (11)$$

At least for small  $l$  we can freely choose

$$l(\mathbf{r}) = \sum_{\mathbf{q}} l_{\mathbf{q}} e^{i\mathbf{q} \cdot \mathbf{r}}. \quad (12)$$

The transverse components are then fixed. To evaluate them we use

$$\text{curl } \mathbf{n} = (n_{z,y} - n_{z,x}, n_{y,x} - n_{x,y}) \quad (13)$$

and, upon eliminating  $n_z$  by means of  $|\mathbf{n}| = 1$ , write the surface condition (2) in the form

$$n_{y,x} - n_{x,y} = n_x^2 n_{y,x} - n_y^2 n_{x,y} - n_x n_y (n_{x,x} - n_{y,y}). \quad (14)$$

By definition  $\mathbf{l}$  obeys  $(\text{curl } \mathbf{l})_z = 0$ . However, the two other components of the curl do not generally vanish. To maintain the surface condition we adopt  $(\text{curl } \mathbf{n})_z$  as given by the r.h.s. of (14) which is of the order of  $(n_x^2 + n_y^2) \times (n_{x,x} + n_{y,y})$ . Incorporating the components of the resulting vortex field into the r.h.s. will cause new violations of (2) which are equally corrected. The infinite series of corrections making  $\mathbf{n} \cdot \text{curl } \mathbf{n}$  zero for a fixed set of  $\mathbf{l}_q$  should converge rapidly, provided

$$n_x^2 + n_y^2 \approx \left(\frac{\partial u}{\partial x}\right)^2 + \left(\frac{\partial u}{\partial y}\right)^2 \ll 1. \quad (15)$$

This is the limit of the weakly rippled membrane which shall be studied here. As the ratio of  $\text{curl } \mathbf{n}$  to  $\text{div } \mathbf{n}$  is of the order of  $n_x^2 + n_y^2$  we will disregard  $\text{curl } \mathbf{n}$  and the corrections required by the surface condition.

The total elastic energy of a rippled layer is

$$U = \frac{1}{2} \kappa_0 \int \frac{1}{n_z} [(\text{div } \mathbf{n})^2 - 2 c_{s0} \text{div } \mathbf{n}] dA_{\text{base}} \quad (16)$$

where, according to (10),

$$\text{div } \mathbf{n} = \sum_{\mathbf{q}} i\mathbf{q} \cdot \mathbf{n}_{\mathbf{q}} e^{i\mathbf{q} \cdot \mathbf{r}}. \quad (17)$$

The two equations are exact. Only the longitudinal component of  $\mathbf{n}_{\mathbf{q}}$  enters the sum of curvatures  $\text{div } \mathbf{n}$ . The fact that we are dealing with a surface is taken account of by  $n_z$  alone.

### 3. Effective quantities.

The effective rigidity is calculated for vanishing spontaneous curvature. From now on, the ripples are thought to be thermal undulations. We take the statistical averages over the base separately, writing for the elastic (or internal) energy

$$U = \frac{1}{2} \kappa_0 \left\langle \frac{1}{n_z} \right\rangle \langle (\text{div } \mathbf{n})^2 \rangle A_{\text{base}}. \quad (18)$$

The separation is valid in the limit of weak rippling where the correlation of mode amplitudes is negligible, provided the contribution of each single mode to  $\langle (n_x^2 + n_y^2) \rangle$  is insignificant. We have

$$\left\langle \frac{1}{n_z} \right\rangle = \frac{A_{\text{real}}}{A_{\text{base}}} \quad (19)$$

because of (8) and

$$\langle (\text{div } \mathbf{n})^2 \rangle = \sum_{\mathbf{q}} q^2 \langle |\mathbf{n}_{\mathbf{q}}|^2 \rangle \quad (20)$$

because of (17). In the last equation we have dropped the distinction between  $\mathbf{n}_{\mathbf{q}}$  and its longitudinal component, exploiting that the transverse part is negligible. For the weakly rippled membrane we may also write

$$\left\langle \frac{1}{n_z} \right\rangle = 1 + \frac{1}{2} \langle (n_x^2 + n_y^2) \rangle = 1 + \frac{1}{2} \sum_{\mathbf{q}} \langle |\mathbf{n}_{\mathbf{q}}|^2 \rangle. \quad (21)$$

Inserting (20) and (21) into (18) yields

$$U = \frac{1}{2} \kappa_0 \left( 1 + \frac{1}{2} \sum_{\mathbf{q}'} \langle |\mathbf{n}_{\mathbf{q}'}|^2 \rangle \right) \sum_{\mathbf{q}} q^2 \langle |\mathbf{n}_{\mathbf{q}}|^2 \rangle. \quad (22)$$

Although not correlated, the modes are coupled in this formula by the factor in parentheses.

We briefly recall some earlier calculations in which coupling was ignored, i.e. the factor was unity. The equipartition theorem gives the mean-square amplitudes

$$\langle |\mathbf{n}_{\mathbf{q}}|^2 \rangle = \frac{kT}{\kappa_0 q^2 A_{\text{base}}} \quad (23)$$

where  $k$  is Boltzmann's constant and  $T$  temperature. If the sum over the modes is replaced by an integral,

$$\sum_{\mathbf{q}} \rightarrow \frac{A_{\text{base}}}{(2\pi)^2} \int_{q_{\text{max}}}^{q_{\text{min}}} 2\pi q dq, \quad (24)$$

between lower and upper cutoff wave numbers, one obtains with (19) and (21)

$$\frac{A_{\text{real}} - A_{\text{base}}}{A_{\text{base}}} = \frac{kT}{4\pi\kappa_0} \ln \frac{q_{\text{max}}}{q_{\text{min}}}. \quad (25)$$

The well-known formula describes a first effect of undulations in the limit of the weakly rippled membrane.

Let us now take coupling into account. The natural way of writing the equipartition theorem is then

$$\langle |\mathbf{n}_{\mathbf{q}}|^2 \rangle = \frac{kT}{\kappa_0 q^2 A_{\text{base}} \left[ 1 + \frac{1}{2} \sum_{\mathbf{q}'} \langle |\mathbf{n}_{\mathbf{q}'}|^2 \rangle \right]}. \quad (26)$$

Only this form satisfies  $\langle |\mathbf{n}_{\mathbf{q}}|^2 \rangle \sim 1/q^2$  which may be expected to hold at least for long-wavelength modes ( $q$  near  $q_{\text{min}}$ ). The validity is confirmed by examining the free energy of the undulating layer. We start by introducing the renormalized mode amplitude

$$\mathbf{t}_{\mathbf{q}} = \mathbf{n}_{\mathbf{q}} \langle 1/n_z \rangle. \quad (27)$$

It describes a particular long-wavelength mode if all other undulations are smeared out. The interpretation is more difficult for short-wavelength modes ( $q$  near  $q_{\text{max}}$ ). However, inspection shows that in both cases  $-iq \cdot \mathbf{t}_{\mathbf{q}}/q^2$  represents the  $z$  component of the material displacement amplitude in the limit of the weakly

rippled layer. Accordingly, the total entropy of the modes is

$$S = \frac{k}{2} \sum_{\mathbf{q}} \ln \langle |\mathbf{t}_{\mathbf{q}}|^2 \rangle q_s^2, \quad (28)$$

apart from additive constants. Upon inserting (27) into (28), one obtains (26) from the set of equilibrium conditions  $\partial F / \partial \langle |\mathbf{n}_{\mathbf{q}}|^2 \rangle = 0$  for the free energy  $F = U - TS$ . (The whole set is needed because of the coupling term.)

The concept of an effective rigidity makes sense only for the long-wavelength modes with  $q$  near  $q_{\min}$ . In other words, the effective rigidity felt by a given mode is reduced only by the undulations of shorter wavelength. The effective rigidity is the curvature-elastic modulus acting on the renormalized deformation  $\mathbf{t}_{\mathbf{q}}$ . To find it we rewrite the equipartition theorem (26). Substituting for  $\langle |\mathbf{n}_{\mathbf{q}}|^2 \rangle$  on the left-hand side by means of (27) leads to

$$\langle |\mathbf{t}_{\mathbf{q}}|^2 \rangle = \frac{kT \langle 1/n_z \rangle}{\kappa_0 q^2 A_{\text{base}}}. \quad (29)$$

Comparison with (23) gives the effective rigidity

$$\kappa = \kappa_0 \frac{1}{\langle 1/n_z \rangle} = \kappa_0 \left( 1 - \frac{1}{2} \sum_{\mathbf{q}} \langle |\mathbf{n}_{\mathbf{q}}|^2 \rangle \right). \quad (30)$$

In analogy to the derivation of (25) the result can be cast into the form

$$\kappa - \kappa_0 = -\frac{kT}{4\pi} \ln \frac{q_{\max}}{q_{\min}}. \quad (31)$$

It is interesting to note that the decrement of  $\kappa$  is independent of  $\kappa_0$ .

For calculating the effective spontaneous curvature of a rippled membrane it is advantageous to give up the notion of a flat base. We adopt a cylindrical curvature with radius  $R$  of a suitably chosen midplane of the rippled layer. For  $R \rightarrow \infty$  the undulations should be like those of the flat base, apart from minor modifications. The base curvature is taken along the  $x$  direction and  $xyz$  are kept as local or cylindrical coordinates. If, e.g., the function  $u(\mathbf{r})$  is thought to be unchanged in the new coordinates, the functions  $\mathbf{n}(\mathbf{r})$  and  $\text{div} \times \mathbf{n}(\mathbf{r})$  must be slightly different. The relationships

$$c_1 + c_2 = \frac{n_z}{R+u} + \frac{R}{R+u} n_{x,x} + n_{y,y} \quad (32)$$

and

$$dA_{\text{real}} = \frac{1}{n_z} \frac{R+u}{R} dA_{\text{base}} \quad (33)$$

are readily seen to hold in the new coordinates. Together they lead to

$$\int (c_1 + c_2) dA_{\text{real}} = \int \left[ \frac{1}{R} + \frac{1}{n_z} (n_{x,x} + n_{y,y}) + \frac{u}{n_z R} n_{y,y} \right] dA_{\text{base}}. \quad (34)$$

The central term in the brackets of (34) does not contribute as the average of  $n_{x,x} + n_{y,y}$  over  $A_{\text{base}}$  must vanish again if the undulations on the bent base obey periodic boundary conditions in the cylindrical coordinates. The last term in the brackets may be replaced, to a first approximation, with  $-(u/R) \times \partial^2 u / \partial y^2$  and transformed by partial integration,

$$-\int u \frac{\partial^2 u}{\partial y^2} dA_{\text{base}} = \int \left( \frac{\partial u}{\partial y} \right)^2 dA_{\text{base}}. \quad (35)$$

The second integral is exchanged for the symmetric expression

$$\begin{aligned} \frac{1}{2} \int \left[ \left( \frac{\partial u}{\partial x} \right)^2 + \left( \frac{\partial u}{\partial y} \right)^2 \right] dA_{\text{base}} &= \\ &= \frac{1}{2} \langle (n_x^2 + n_y^2) \rangle A_{\text{base}} \end{aligned} \quad (36)$$

where it is safe, for  $R \rightarrow \infty$ , to employ the average of the flat base.

As a consequence, equation (34) takes the form

$$\begin{aligned} \int (c_1 + c_2) dA_{\text{real}} &= \\ &= \frac{1}{R} \left( 1 + \frac{1}{2} \sum_{\mathbf{q}} \langle |\mathbf{n}_{\mathbf{q}}|^2 \rangle \right) A_{\text{base}}. \end{aligned} \quad (37)$$

The effective spontaneous curvature  $c_s$  may be defined by the equation

$$\kappa_0 c_{s0} \int (c_1 + c_2) dA_{\text{real}} = \kappa c_s \frac{1}{R} A_{\text{base}}. \quad (38)$$

Inserting (37) and using (21), one obtains

$$c_s = \frac{\kappa_0}{\kappa} \left\langle \frac{1}{n_z} \right\rangle c_{s0} = \left( \left\langle \frac{1}{n_z} \right\rangle \right)^2 c_{s0}. \quad (39)$$

Recalling (30) and (31), one arrives at

$$\frac{c_s - c_{s0}}{c_{s0}} = \frac{kT}{2\pi\kappa_0} \ln \frac{q_{\max}}{q_{\min}}. \quad (40)$$

Clearly, there are two equal contributions to the relative increment of  $c_s$ , one originating from  $\kappa/\kappa_0$  and the other from the sum in (37).

#### 4. Discussion.

Two special cases of an undulation superimposed on a uniform bend can be studied rigorously and in detail. The wave vector of a single sinusoidal ripple is parallel to the bend in one case and perpendicular to it in the other. In the first example the bend is taken to be uniform on the rippled layer, not with respect to a curved base. Checking the two cases (in straightforward but cumbersome calculations), we found parallel and perpendicular ripples to have, in first order, the same effect on the rigidity  $\kappa$ . However, the

perpendicular ripple alone is responsible for the second increment of the spontaneous curvature  $c_s$  mentioned below equation (40). If the model is generalized (at the expense of rigor) by permitting all wave vectors and taking  $c_s$  to be the average over the two « principal » directions, one obtains the formulae for  $\kappa$  and  $c_s$  which were derived above.

We emphasize again that displacement modes  $u_q$  are ill suited to calculate the effective rigidity. The associated curvatures ( $c_1 + c_2$ ), i.e. the elastic strains, are not additive in such a representation. There are similar problems with director modes on a bent base if (10) is used with local coordinates. Whenever the superposition principle for the curvatures was violated the calculations showed that the modes including a uniform curvature « feed » on each other, thus simulating an additional coupling which should not be there. (It would increase  $\kappa_0 - \kappa$  by a numerical factor.)

The cutoff wave numbers  $q_{\max}$  and  $q_{\min}$  remain to be specified. The former is defined by a molecular cross section  $A_0$ ,

$$q_{\max}^2 = \pi^2/A_0. \quad (41)$$

The latter may be determined by the size of the square piece of layer,

$$q_{\min}^2 = \pi^2/A_{\text{base}}. \quad (42)$$

Lateral tension or steric hindrance of undulations provide lower cutoffs for infinite layers as well. These external factors were omitted in the present treatment.

It does not matter whether  $A_{\text{base}}$  or  $A_{\text{real}}$  is kept constant in the above calculations which are exact only for small relative corrections. There is a slight variation of the number of molecules and, thus, modes if  $A_{\text{base}}$  is fixed. The situation is reversed in the other case. Higher-order terms of the relative corrections of area, rigidity, and spontaneous curvature as functions of  $\kappa_0$ ,  $q_{\min}$ , and  $q_{\max}$  seem very difficult to obtain. In addition, a theory considering undulations only may be too simple at very small rigidities, as is discussed below.

The effective rigidity is of particular interest if it differs markedly from the local one. Let us ask for the base area  $A_{\text{base}}^{\max}$  at which  $\kappa$  reaches zero. This limit may be expected to characterize, if only approximately, the transition of a layer (or layers) to a microemulsion in suitable systems. From equation (31) one obtains

$$A_{\text{base}}^{\max} = A_0 \exp\left(\frac{8 \pi \kappa_0}{kT}\right). \quad (43)$$

The equation suggests that the typical microemulsion droplet size of 100 Å ( $A_{\text{base}}^{\max} \approx 10^4 \text{ Å}^2$ ,  $A_0 \approx 25 \text{ Å}^2$ ) requires the local rigidity to be less than  $kT = 4 \times 10^{-14}$  erg. Equation (43) differs only by a factor in the exponent ( $8 \pi$  instead of  $4 \pi$ ) from the corresponding relationship of de Gennes and Taupin [23], if  $A_{\text{base}}^{\max}$

is equated with the square of their persistence length of membrane orientation. The good agreement of the two formulae may surprise as the persistence length was calculated with constant rigidity.

However, all models confined to an undulating layer must fail near the microemulsion limit for several reasons. A very flexible interface will tend to break up, forming coated droplets of each phase in the other. Also, the layer should become multiply self-connected, thus changing its topology. An intact layer would be hindered in its undulations by self-collisions. Generally speaking, there is a vast gap between the single undulating monolayer and the bicontinuous microemulsion which remains to be filled.

The concept of an effective rigidity may also be convenient in studies of vesicles and multilayer systems. There are probably many fluid bilayers with a rigidity smaller than that of lecithin. If stable enough vesicles are formed, their shape fluctuations could be governed by a size dependent effective rigidity. In multilayer systems, where either bilayers alternate with water or monolayers with oil and water, the layer undulations are hindered by the steric interaction of the layers. The lower cutoff is not abrupt, but the equivalent of  $q_{\min}$  decreases with increasing spacing of the layers [9-11]. The effective rigidity controlling the undulation forces between layers should diminish correspondingly. The result would be an enhancement of the undulation forces at large layer spacings.

### Conclusion.

The present calculations show that the thermal undulations of fluid layers affect not only the real area as compared to that of a flat base, but also the rigidity and spontaneous curvature. The relative changes  $(A_{\text{real}} - A_{\text{base}})/A_{\text{base}}$ ,  $(\kappa - \kappa_0)/\kappa_0$  and  $(c_s - c_{s0})/c_{s0}$  are all proportional to  $(kT/4 \pi \kappa_0) \ln(q_{\max}/q_{\min})$ . The theory is a first approximation and valid only if this function, and in particular  $kT/4 \pi \kappa_0$ , is much smaller than unity. The logarithmic dependence of physical quantities on upper and lower cutoff wave numbers or, instead, on size is frequent in the statistical mechanics of two-dimensional systems. A special feature of planar fluid layers is their freedom to escape into the third dimension, e.g. by thermal undulations. It is this escape that underlies all three effects.

In our theory the undulation modes are coupled to each other by the tilt or gradient of the layer which they produce, as is shown most clearly by equation (22). The tilt associated with long-wavelength modes does, of course, not change the physics of short-wavelength ripples, but their description. For instance, their angular amplitudes become smaller and their wavevectors larger when referring to the base. The tilt due to short-wavelength ripples was shown to lower the effective rigidity of the layer for long-wavelength undulations. The interpretation of coupling thus depends on whether the ratio of the wave numbers

is larger or smaller than unity. The situation appears ambiguous if the two wave numbers are similar, but

the region of ambiguity does not matter in a broad enough spectrum.

*Note added in proof.*

The entropy seems most appropriately defined in terms of strain (= curvature) amplitudes. Accordingly, one may write the equipartition theorem in the form  $\kappa_0 q^2 \langle |n_q|^2 \rangle A_{\text{real}} = kT$ , thus avoiding the delicate use of displacements. Insertion of (19) leads to (26).

In a letter published in the meantime, L. Peliti and S. Leibler (*Phys. Rev. Lett.* **54** (1985) 1960) found  $\kappa_0 - \kappa$  to be three times larger than our value, referring to a powerful renormalization method. On the basis of correspondence with L. Peliti, who kindly sent a reprint, we suspect that they dealt with  $u_q$  modes indiscriminately.

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