On a Possible Microscopic Mechanism Underlying the Vapor Pressure Paradox

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ABSTRACT   We investigate the free energy and the profile of the displacement field in a stack of sterically interacting smectic multilayers bounded by surfaces under tension. We show that this tension can lead to a significant change in the multilayer free energy. It creates an additional long-range attraction (a pseudo-Casimir attraction) of the van der Waals type and leads to a perturbation in the spatial profile of the displacement field fluctuations. This perturbation can extend to macroscopic distances into the multilayer, away from the perturbing surfaces. The lowering of the free energy of the layers varies explicitly as an inverse power of the thickness of the stack, but also depends implicitly on the bare interactions between the smectic layers. One may regard this lowered energy as being due to a kind of mechanical van der Waals force. We investigate in detail the characteristics and magnitude of the free energy as well as the fluctuations in the displacement field for some typical situations of underlying interlamellar interactions.

INTRODUCTION

Among the greater embarrassments avoided by theorists and discussed *sotto voce* by experimentalists is the vapor pressure paradox. Why do phospholipid multilayers take up less water from a 100% relative humidity vapor than they do from liquid water (Rand and Parsegian, 1989)? Why do these same multilayers imbibe less water when they are adsorbed to a solid substrate than when they are suspended in liquid water (Jendrasiak and Hasty, 1974; Jendrasiak and Mendible, 1976; Torbet and Wilkins, 1976)? Nor is this curious phenomenon seen only with membranes. Solid boundaries are also known to induce nematic order on rodlike polysaccharides (W. Orts, personal communication) and on colloidal spheres (J. Cohen, personal communication). We propose that the tension of a vapor/multilayer surface or adsorption to a solid surface creates effective attractive stabilizing forces within multilamellar arrays. One effect of a bounding surface is to suppress mechanical undulations of layers, either because of surface tension or because of forces that cause the first bilayer to adhere to a solid surface. We inquire into the remarkable persistence of this suppression into neighboring layers.

This is not a trivial surface phenomenon. The effect of exposed surfaces is of sufficiently long range that the inhibited swelling is seen in well-defined x-ray diffraction that requires many uniformly spaced layers. In this respect an anomalously long-range coupling of the surface to the bulk is required, a coupling that can hardly be seen as an ordinary surface phenomenon.

It has already been shown that surface suppression of fluctuations in a smectic array can, in principle, create long-range attractive forces across the array (Mikheev, 1989; Ajdari et al., 1992). Here we have undertaken a quantitative investigation of these attractive forces to see their possible role in experimental systems where boundary-surface perturbations have been seen or inferred to account for odd behavior or equilibrium spacings.

We have written the multilayer energy as a competition between direct, spatially varying interlayer interactions (Leikin et al., 1993) (to maintain bilayer separation) versus a work of bending (to maintain bilayer flatness). Because both competing contributions to the net energy involve the same parameter, the membrane bending modulus, their equilibrium in suspension is highly vulnerable to added perturbation. Enforced stiffening in one layer can be successively communicated over long ($\cong$ nm to mm) distances. In this way a vapor or solid surface can suppress undulations and limit water absorption almost on a macroscopic scale.

ANALYSIS

Model effective Hamiltonian

We assume that our system is composed of N smectic layers stacked to a thickness D, so that on average there is a separation $d = D/N$ between two successive layers, assuming negligible thickness of the layers. Apart from the elastic energy of smectic deformation, we assume that there exists an additional surface contribution to the total energy of the system in the form of a surface energy of the first and last layers (see Fig. 1).
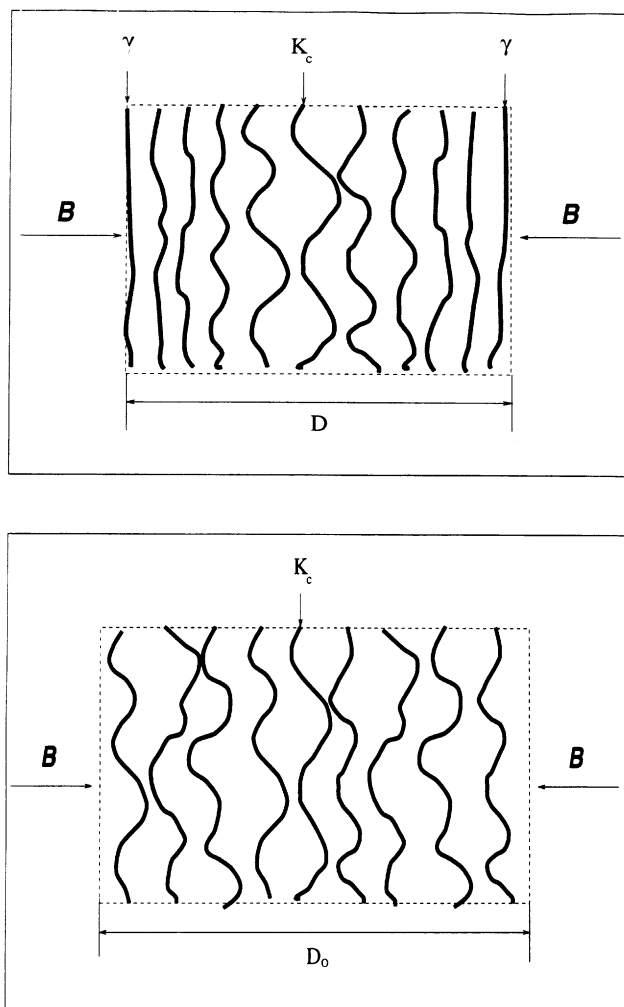
FIGURE 1   Schematic representation of the different energy contributions in the model Hamiltonian Eq. 1. K_C and γ are connected with the bulk and surface energy of the layers, and $\mathcal{B}$ is the transverse compressibility.

The Hamiltonian of the system is composed of a bulk $\mathcal{H}_B$ and a surface $\mathcal{H}_S$ part. Following common notation, fluctuations from the mean position of a layer are measured in terms of a displacement field $u(z, \boldsymbol{\rho})$ where z is taken normal to the average plane of the membranes and $\boldsymbol{\rho}$ is a vector in the (x, y) plane. The energy density of the bulk part consists of two terms: the first uses a compressibility modulus B for changes in energy with changes in the density of packing; the second is the work of bending the layers against the restraint of a bending modulus K_c and varies as the square of the local curvature of the layers, i.e., as a second derivative of $u(z, \boldsymbol{\rho})$ taken in the $\boldsymbol{\rho} = (x, y)$ plane:

$$\mathcal{H}_B(u(z, \boldsymbol{\rho}))$$

$$= \int d^2\boldsymbol{\rho}dz \left[\frac{1}{2} \mathcal{B}\left(\frac{\partial u(z, \boldsymbol{\rho})}{\partial z}\right)^2 + \frac{1}{2} K_c (\nabla_\perp^2 u(z, \boldsymbol{\rho}))^2 \right], \quad (1)$$

while

$$\mathcal{H}_S\left(u\left(z = \pm\frac{D}{2}, \boldsymbol{\rho}\right)\right) = \int d^2\boldsymbol{\rho} \left[\frac{1}{2} \gamma\left(\nabla_\perp u\left(z = -\frac{D}{2}, \boldsymbol{\rho}\right)\right)^2 \right.$$

$$\left. + \frac{1}{2} \gamma\left(\nabla_\perp u\left(z = +\frac{D}{2}, \boldsymbol{\rho}\right)\right)^2 \right], \quad (2)$$

$\nabla_\perp$ is the gradient operator in the $\boldsymbol{\rho} = (x, y)$ plane. We have assumed above that the first and the last layer are situated at $z = +D/2$ and $z = -D/2$ with stack thickness D. The consequence of the tension γ is to stretch the two layers on the surface and quench their displacement $u(z = \pm D/2; \boldsymbol{\rho})$.

We now proceed with the formal development to obtain a closed expression for the free energy of the system characterized by the mesoscopic Hamiltonian (Eqs. 1 and 2). Ajdari et al. (1992) used somewhat different approaches, based either on the closed form expression of a harmonic propagator or on the Langevin dynamics of displacement fields, to derive the free energy. All approaches are, of course, equivalent and lead to the same results.

Our thinking was influenced to a large extent by the formal similarity between the macroscopic theory of van der Waals forces and the problem enunciated above. Our derivation of the thermodynamic properties will thus basically follow a pattern that is usual for van der Waals forces (Mahanty and Ninham, 1976).

The free energy

The free energy $\mathcal{F}$ as a function of D can be obtained in the standard fashion from the partition function $\Xi(D)$, where the integration over phase space is limited to integrating out fluctuations in the displacement field $u(z, \boldsymbol{\rho})$. The details are relegated to the Appendix; here we merely quote the final result:

$$\mathcal{F}(D) = -kT \ln \Xi(D)$$

$$= -kT \ln\langle e^{-\beta\mathcal{H}_B(u(z,\rho))-\beta\mathcal{H}_S(u(z=\pm D/2,\rho))}\rangle_{u(z,\rho)}, \quad (3)$$

where we have symbolically indicated the average over the displacement field $u(z, \boldsymbol{\rho})$ with an index. The partition function is evaluated in the Appendix by two different routes, a Green function method and an eigenfunction-expansion method. Both lead to the following simple form of the free energy, where the summations are done with respect to the two-dimensional wave vector $\mathbf{Q}$, describing different fluctuation modes of the displacement field:

$$\mathcal{F}(D) = \mathcal{F}_B(D) + kT \sum_{\mathbf{Q}} \ln\left(1 + \frac{\gamma}{\sqrt{K_c\mathcal{B}}}\right)$$

$$+ \frac{kT}{2} \sum_{\mathbf{Q}} \ln(1 - \Delta^2 e^{-\sqrt{(K_c/\mathcal{B})}Q^2D}). \quad (4)$$

The three terms stand for the bulk or volume free energy $\mathcal{F}_B$, the surface and the finite-size contributions to the free energy. In the case of an electrolyte the different parts of the free energy would correspond to Debye-Hückel, Onsager-Samaras, and van der Waals-Lifshitz contributions to the free energy (Podgornik, 1989). The bulk part corresponds to the free energy of a slab D thick but without taking into account any boundary effects.

After performing the Q summations (integrations) one can rewrite Eq. 4 in the final form, again in the order bulk, surface, finite-size contributions,

$$\frac{\mathcal{F}(D)}{S} = \frac{\mathcal{F}_B}{S} + \frac{kT}{4\pi} Q_{max}^2 \ln\left(1 + \frac{\gamma}{\sqrt{K_c \mathcal{B}}}\right) + \frac{kT}{8\pi}\sqrt{\frac{\mathcal{B}}{K_c}}\frac{\zeta(\Delta)}{D},$$

(5)

where we have defined

$$\zeta(\Delta) = \int_0^\infty du \, \ln(1 - \Delta^2 e^{-u}),$$

(6)

and

$$\Delta = \frac{\gamma - \sqrt{K_c \mathcal{B}}}{\gamma + \sqrt{K_c \mathcal{B}}},$$

(7)

Here and in what follows $S = L^2$ is the projected area of the sample. Obviously, $\zeta(\Delta) < 0$, so that the $1/D$ finite-size term is attractive. We also have $0 < \zeta(\Delta) < \pi^2/2$. The dependence of the free energy on $\mathcal{B}$ and D is basically the same as derived by Ajdari et al. (1992) and clearly shows that the suppressed boundary fluctuations lead to two additional attractive contributions to the free energy. Any stiffening of the layers by increasing K_c lessens this additional attraction, because intrinsically stiff layers feel little extra perturbation from surface stiffening. The cutoff Q_{max} corresponds to the shortest wavelength of fluctuations in the (x, y) directions and must be on the order of the inverse molecular size.

As can be quickly ascertained, the largest contribution to the above free energy comes from the surface term, which depends implicitly, through $\mathcal{B} = \mathcal{B}(d)$, on the layer density. There is no corresponding term in the electrodynamic van der Waals force, because at the same level of approximations as assumed here, the dielectric susceptibility, analogous to $\mathcal{B}$, does not depend on the interlayer separation.

The spatial profile of fluctuations

In addition to seeing the dependence of the free energy on the tension restraint of the bounding surfaces at $z = \pm D/2$, we are interested in the transverse profile of the layer displacement field. This profile is especially important if one wants to assess the range and the relaxation of the surface perturbation propagating into the bulk region.

Formally, the long-range nature of surface perturbation is connected with the fact that the effective energy Eq. 1

describing the fluctuating displacement field $u(z, \boldsymbol{\rho})$ is critical, i.e., it does not contain any "mass" terms, and thus leads to long-range correlations. In the case of a small number of discrete smectic layers, an analogous problem has been solved by Holyst et al. (1990).

The spatial profile of the fluctuations in the displacement field for $|z| \leq D/2$ can be obtained straightforwardly (see Appendix) as

$$\sigma^2(z; D) = S^{-1}\int d^2\boldsymbol{\rho}\langle u^2(z, \boldsymbol{\rho})\rangle$$

$$= \frac{1}{2}\sum_Q \frac{1}{\sqrt{\mathcal{B}K_c}Q^2}\left[1 + \frac{2\Delta e^{-2\sqrt{(K_c/\mathcal{B})}Q^2 D}}{1 - \Delta^2 e^{-2\sqrt{(K_c/\mathcal{B})}Q^2 D}}\right.$$

$$\left.\left(\Delta + e^{\sqrt{(K_c/\mathcal{B})}Q^2 D}\cosh\sqrt{\frac{K_c}{\mathcal{B}}}Q^2(2z)\right)\right].$$

(8)

The fluctuations of the displacement field in the transverse direction depend only on the ratio z/D and are thus of long range. There is no finite intrinsic length, analogous to the Debye decay length, that would describe the extent of fluctuations. This dependence on z is a direct consequence of the smectic effective Hamiltonian that produces long-range (critical) fluctuations.

In the bulk case one has the well-known result (de Gennes and Prost, 1993) for the displacement field fluctuations in the transverse direction to the smectic planes:

$$\sigma_0^2 = \frac{kT}{8\pi\sqrt{K_C\mathcal{B}}}\int_{u_{min}}^{u_{max}}\frac{du}{u} = \frac{kT}{4\pi\sqrt{K_C\mathcal{B}}}\ln Q_{max}L,$$

(9)

where we introduced the integration variable $u = \sqrt{K_c/\mathcal{B}}\,Q^2 D$ with $u_{max} = \sqrt{K_c/\mathcal{B}}\,Q_{max}^2 D$ and $u_{min} = \sqrt{K_c/\mathcal{B}}(2\pi/L)^2 D$. Q_{max} is the maximum wave vector associated with the breakdown of the macroscopic form of the elastic energy, and L is the linear dimension of the sample (we necessarily work in the limit $L \gg D$).

A simple rationalization of the long range of the surface perturbation can be obtained as follows: a single-layer elastic deformation that requires very little energy due to small K_c can only be relaxed through layer compression that, because of the large $\mathcal{B}$, requires a lot of energy and can thus only relax over a substantial number of layers.

The general profile of displacement field fluctuations across the sample of thickness D is given by the following dependence on z, with $|z| \leq D/2$:

$$\sigma^2(z, D) - \sigma^2\left(z = \pm\frac{D}{2}, D\right) = 2\Delta f(z, \Delta)\sigma_0^2,$$

(10)

where

$$f(z, \Delta) = \int_{u_{min}}^{u_{max}}\frac{du}{u}\frac{e^{-u}(\cosh 2u(z/D) - \cosh u)}{1 - \Delta^2 e^{-2u}}\bigg/\int_{u_{min}}^{u_{max}}\frac{du}{u}.$$

(11)

Similarly, one gets for the mean square fluctuation at the constraining surfaces of the sample,

$$\sigma^2\left(z = \pm\frac{D}{2}, D\right) = (1 - \Delta)(1 - g(\Delta))\sigma_0^2, \quad (12)$$

with

$$g(\Delta) = \int_{u_{min}}^{u_{max}} \frac{du}{u} \frac{\Delta(1 + \Delta)e^{-2u}}{1 - \Delta^2 e^{-2u}} \bigg/ \int_{u_{min}}^{u_{max}} \frac{du}{u}. \quad (13)$$

The mean square displacement field fluctuation in the middle of the sample $z = 0$ is similarly obtained as

$$\sigma^2(z = 0, D) = e(\Delta)\sigma_0^2, \quad (14)$$

with

$$e(\Delta) = \int_{u_{min}}^{u_{max}} \frac{du}{u} \frac{1 - \Delta e^{-u}}{1 + \Delta e^{-u}} \bigg/ \int_{u_{min}}^{u_{max}} \frac{du}{u}. \quad (15)$$

The three quantities (Eqs. 12–14) completely specify the changes in the diplacement field fluctuations compared to the bulk case. Obviously they are all proportional but are smaller then the unconstrained fluctuations σ_0^2. The dimensionless profile $(\sigma^2(z, D) - \sigma^2(z = \pm D/2, D))/\sigma_0^2$ derived from Eq. 10 is computed for four different values of Δ in Fig. 2, making it clear that the perturbation of fluctuation always extends across the entire stack of thickness D.

Because $\sigma^2(z, D)$ is a function of z, the position of the layer to which it refers, the local separation between the layers, $d(z)$, is also a function of their position. One can set, following Helfrich (1978), $d^2(z) \cong \mu\sigma^2(z, D)$. This assump-
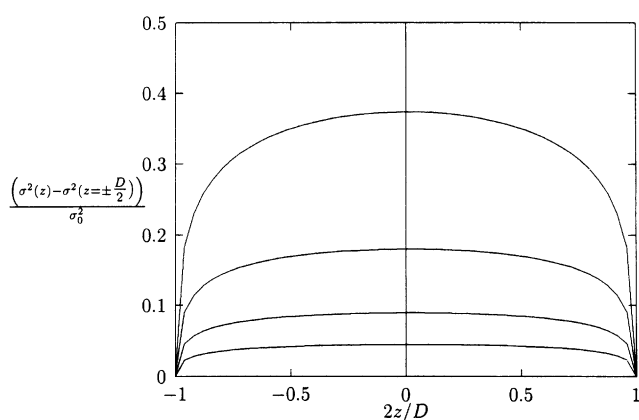

FIGURE 2   Normalized mean square fluctuations $\sigma^2(z)$ as a function of relative position z/D for four different values of Δ. Fluctuations are plotted as a difference between $\sigma^2(z)$ at each position and $\sigma^2(z = \pm D/2)$ at the surfaces taken relative to the mean square fluctuation σ_0^2 of layers in an infinite stack with the presumed compressibility $\mathcal{B}$ and bending modulus K_c. The values for Δ used here were: $\Delta = 1.0, 0.5, 0.25, 0.125$ from top to bottom. The u integral in Eq. 11 was taken from $u_{min} = 0.0001$ to $u_{max} = 200$ and is only weakly sensitive to the choice of these bounds. The long-range nature of the fluctuations is clearly discernible.

tion, and the fact that the sum of $d(z)$ across the sample should add up to D for all N layers, completely specifies the profile of local separation between the layers. This notation assumes negligible layer thickness; $d(z)$ here may be considered to be interlayer separation only.

It is clear from the above derivations that our approach to the problem is effectively limited to the case of small perturbations in the fluctuations of the smectic layers as compared to the bulk. In this case the constraining effect of the boundaries can be treated perturbatively with respect to the bulk. If this were not the case, the compressibility $\mathcal{B}$ would have to be evaluated self-consistently in conjunction with the assumption that it can, in general, vary along the transverse coordinate of the multilamellar stack.

LIMITING RESULTS

Although we have derived the general dependence of the fluctuations on the macroscopic parameters $\mathcal{B}$ and K_c, we need a connection to the microscopic interlayer potential to get the total dependence of the free energy on the effective interlayer separation. This can be obtained rather straightforwardly in several limiting cases.

Mechanical van der Waals force for a stable smectic array

We first consider large interlayer distances where, in the absence of surface perturbations or applied osmotic stress, the system has settled into an equilibrium thickness D_0. A small disturbance of the lamellar lattice to a thickness D costs a bulk compression energy that is quadratic in the difference $(D - D_0)$. That is, to within an additive quantity, the bulk free energy goes as

$$\mathcal{F}_B \cong \frac{1}{2} \mathcal{B}S \frac{(D - D_0)^2}{D_0}, \quad (16)$$

where the inverse longitudinal compressibility is measured by osmotic stress, using polymers as a stressing agent (Parsegian et al., 1986), and varies from 10^6 to 10^2 N/m^2 (Rand and Parsegian, 1989; Safinya, 1989).

We now ask what happens to the lattice thickness when one adds a mechanical van der Waals energy. For small perturbations one can treat $\mathcal{B}$ as a constant, and we can write for the total free energy of the layered system (cf. Eqs. 15 and 16)

$$\mathcal{F} = \frac{1}{2} \mathcal{B}S \frac{(D - D_0)^2}{D_0} + \frac{kT}{2} \frac{S}{4\pi} \sqrt{\frac{\mathcal{B}}{K_c}} \frac{\zeta(\Delta)}{D}, \quad (17)$$

where the D-independent surface terms have been omitted, as they do not affect the equilibrium value of D. The new equilibrium thickness D can be obtained from the minimization condition as

$$\frac{\partial \mathcal{F}}{\partial D} = 0; D \cong D_0 - \frac{kT}{8\pi} \frac{1}{\sqrt{\mathcal{B}K_c}} \frac{|\zeta(\Delta)|}{D_0}, \quad (18)$$

where we have emphasized the fact that $\zeta(\Delta)$ is negative.

Converting now to an average interlayer spacing $d = D/N$ and $d_0 = D_0/N$, we obtain

$$d \cong d_0\left(1 - \frac{kT}{8\pi} \frac{|\zeta(\Delta)|}{\lambda \mathcal{B} N^2 d_0^2}\right), \tag{19}$$

for the first leading term in the surface tension effect on undulation. We have introduced an anisotropy length scale $\lambda = \sqrt{\mathcal{B}/K_c}$. Inserting numerical values for $\mathcal{B}$, K_c, and kT into Eq. 19, we obtain the following estimate:

$$d \simeq d_0\left(1 - \frac{(10^4 - 10^1)|\zeta(\Delta)|}{N^2}\right).$$

The range in the numerical factor is due to the range in the value of $\mathcal{B}$, and $\zeta(\Delta)$ goes from 0 to $\pi^2/2$. Clearly, a finite value of N can allow surface tension to rescale the value of the average surface spacing substantially.

Mechanical van der Waals force in the case of pure steric fluctuation forces

Another tractable limit can be developed by assuming a certain model form for the compressibility modulus $\mathcal{B} = \mathcal{B}(d)$, and then evaluating the change in equilibrium spacing in the array due to the presence of the mechanical van der Waals force. In what follows we adopt a philosophy similar to the one invoked in the calculation of the actual van der Waals force and argue that the appropriate value of $\mathcal{B}$ is simply its value for a corresponding infinite bulk system at spacing d, just as the dielectric susceptibility of a layer in the calculation of the van der Waals force is taken to be the bulk dielectric function. Furthermore, if we assume that the interlayer interactions are governed by Helfrich steric repulsion forces, this assumption leads to the following form of $\mathcal{B}$:

$$\mathcal{B}(D) = \frac{9\pi^2}{64} \frac{(kT)^2}{K_c}\left(\frac{N}{D}\right)^4, \tag{20}$$

an expression taken directly from the Helfrich calculation (Helfrich, 1978). Assuming this form of the bulk compressibility, we are led to the following expression for the total free energy, including the mechanical van der Waals term:

$$\mathcal{F}(D) = \frac{kV}{8\pi}\sqrt{\frac{\mathcal{B}(D)}{K_c}} \frac{\pi^2}{2}\left(\frac{N}{D}\right)^2 + \frac{kTS}{4\pi}Q_{max}^2 \ln\left(1 + \frac{\gamma}{\sqrt{K_c\mathcal{B}(D)}}\right)$$

$$+ \frac{kTS}{8\pi}\sqrt{\frac{\mathcal{B}(D)}{K_c}} \frac{\zeta(\Delta)}{D} = \mathcal{F}_{bulk} + \mathcal{F}_{surface} + \mathcal{B}_{'vdW'}, \tag{21}$$

where V is the total volume of the sample, i.e., $V = SD$. Clearly, in this case we had to retain the surface energy term (second term, Eq. 21), because $\mathcal{B}$ is an explicit function of D.

Evaluating the corresponding free energy per single layer

per surface area in the stack, we get

$$\frac{\mathcal{F}(d)}{SN} \cong \frac{3\pi^2}{128}\frac{(kT)^2}{k_c\, d^2}\left(1 - \frac{|\zeta(\Delta)|}{\pi^2 N}\right) \tag{22}$$

$$+ \frac{kT Q_{max}^2}{4\pi N}\ln\left(1 + \frac{\gamma d^2}{(3\pi/8)}kT\right),$$

where we have introduced the curvature modulus of a single layer $K_c = (N/D)k_c$, because K_c is for an energy per unit volume.

Equation 22 displays several instructive features of undulation interaction inhibited by a surface tension γ. As the number of layers $N \to \infty$, Eq. 22 smoothly and predictably approaches the original Helfrich result. For finite N, the first term in Eq. 22 retains the $1/d^2$ Helfrich form, but with a rescaled, stiffer curvature modulus:

$$k_c \to \frac{k_c}{(1 - |\zeta(\Delta)|/\pi^2 N}$$

The second term in Eq. 22, with the form of an "Onsager-Samaras" surface energy, varies as d^2 for γ small enough that $\gamma d^2/kT \ll 1$. Even for moderate values of d and γ, this second term varies as $\ln d$.

As a result, the form of the free energy (Eq. 22) drastically changes the characteristics of the purely sterically interacting smectic array. First of all, even in the absence of external stress compressing the array, minimization of Eq. 22 gives an equilibrium spacing of the form

$$d^2 \cong \frac{12\pi^3}{128}\frac{(kT)\,N}{k_c\, Q_{max}^2}\left(1 - \frac{|\zeta(\Delta)|}{\pi^2 N}\right). \tag{23}$$

For sufficiently large external osmotic pressure—or what amounts to the same thing, sufficiently small interlamellar separation—the change in equilibrium spacing when the mechanical van der Waals force is turned on can be obtained from the linear response relation, which in this case assumes the form

$$\frac{\delta d_0}{d_0} = \frac{d - d_0}{d_0} \cong \mathcal{B}(d_0)^{-1}\delta\Pi(d_0), \tag{24}$$

where $\delta\Pi(d_0)$ is the part of the osmotic pressure due to the mechanical van der Waals attraction (in this case obtainable from Eq. 22), thus:

$$d \cong d_0\left(1 - \frac{256 k_c\,(Q_{max}d_0)^2\,(\gamma d_0^2)}{27\pi^4(kT)^2 N}\right), \tag{25}$$

where d_0 is the equilibrium spacing at a certain value of the osmotic pressure when only steric interactions are present, and d is its value when the steric interaction is modified by the mechanical van der Waals interaction.

Clearly, in the case of small or vanishing osmotic pressure (Eq. 23), the change in behavior is qualitative, because there is no stable minimum without the mechanical van der Waals force, whereas in the case of large osmotic pressures it is quantitative, changing d_0 to d (given by Eq. 25).

Interestingly, the changes in the equilibrium spacing (Eqs. 23 and 25) both attest to the extreme importance of the surface energy term, which is proportional to Q_{max}^2. This is a term missing from the electrodynamic van der Waals force because (a) dielectric susceptibility, corresponding loosely to $\mathcal{B}$, is not a function of d and (b) the van der Waals force contains no upper cutoff in the Q integral. (The divergence that arises here must be treated in a completely different way; see the discussion in Ajdari et al., 1992.)

Conjectures for a general type of interlamellar interaction

The general problem of calculating the free energy of surface-suppressed fluctuations in the presence of general interlamellar potentials is, of course, extremely difficult. Instead of proceeding ab initio, we approach the problem phenomenologically. Consider two separate experiments: first measure the free energy versus layer separation of a multilamellar array filling the space, so that no surface suppression of fluctuations is operating; second, do the same on a finite array, where the surface free energy of the type of Eq. 2 tends to suppress the fluctuations.

The general formulas for the interaction free energy now establish the connection between both measured free energies. If the free energy (per unit area per single layer) of an array unconfined by high energy surfaces is F_0/S, and its osmotic pressure is equal to Π, then the corresponding inverse compressibility is

$$\mathcal{B}(d) = -V \frac{\partial \Pi(d)}{\partial V}\bigg|_{T,N} = -d \frac{\partial \Pi(d)}{\partial d}\bigg|_{T,N}, \quad (26)$$

where V is the volume of the array that is supposed to contain N layers and is D thick, and again the mean interlayer separation is $d = D/N$. Obtaining $\mathcal{B}(d)$ from the first experiment, one can immediately write down the free energy per surface area per lamella in the presence of surface constraints:

$$\frac{F}{SN} = \frac{F_0}{SN} + \frac{kT}{4\pi}\frac{Q_{max}^2}{N}\ln\left(1 + \frac{\gamma d}{\sqrt{k_c(d\mathcal{B}(d))}}\right)$$
$$- \frac{kT}{8\pi}\sqrt{(d\mathcal{B}(d))k_c}\frac{|\zeta(\Delta)|}{d N^2}. \quad (27)$$

For succinctness, we give osmotic pressure Π the form of an exponential repulsion and a power law attraction (or repulsion):

$$\Pi(d) = P_0\, e^{-\kappa d} \pm \frac{H}{6\pi d^3}. \quad (28)$$

After a minus sign H is the Hamaker constant of the van der Waals attraction; after a plus sign the last term represents a more complicated potential with positive H simulating the effects of the undulation renormalized interactions (Evans and Parsegian, 1986; Podgornik and Parsegian, 1992). This

form provides a convenient vehicle for taking the derivative (Eq. 26), for $\mathcal{B}(d)$ to be introduced into Eq. 27 for the surface-tension-modulated free energy F/NS.

In the case of the underlying interaction potential (Eq. 28), one can obtain an explicit d dependence of F presented for several sets of numerical parameters on Fig. 3. The systematics of this behavior are difficult to discern, but the application of the linear response relation, in the case that underlying interactions (Eq. 28) show a secondary minimum, permits us to evaluate the displacement of the secondary minimum. To the lowest order in N^{-1} for the underlying interaction pressure of the form Eq. 28, we obtain the following relation:

$$\frac{\delta d_0}{d_0} = \mathcal{B}(d_0)^{-1}\delta\Pi(d_0) \cong \frac{kT}{4\pi}\frac{Q_{max}^2\lambda}{\mathcal{B}(d_0)}\frac{\gamma}{\gamma + \sqrt{\mathcal{B}(d_0)K_c}}. \quad (29)$$

The N^{-1} dependence also seems to be supported by numerical calculations (see Fig. 4). The above relation, derived from the linear response *ansatz*, can also be generalized to arbitrary forms of the interaction pressure.

If one evaluates the average value of the surface part of the model Hamiltonian (Eq. 1), one obtains

$$\langle \mathcal{H}_S \rangle = \frac{1}{2}\gamma\sum_Q\left(Q^2\left\langle u^2\left(Q; z = +\frac{D}{2}\right)\right\rangle + Q^2\left\langle u^2\left(Q; z = -\frac{D}{2}\right)\right\rangle\right)$$
$$(30)$$

$$= \frac{kT}{4\pi}\frac{\gamma}{\gamma + \sqrt{\mathcal{B}K_c}}Q_{max}^2\left(1 + \frac{(1+\Delta)}{2\sqrt{(K_c/\mathcal{B})}Q_{max}^2 D}\sum_{n=0}^{\infty}\frac{\Delta^{n+1}}{(n+1)}\right)$$

$$\cong \frac{kT}{4\pi}\frac{\gamma}{\gamma + \sqrt{\mathcal{B}K_c}}Q_{max}^2,$$

where the last term in the brackets on the second line is much smaller than 1 and can be safely omitted for any reasonable Q_{max} and D. The averages $\langle u^2(Q; z = \pm D/2)\rangle$ have been obtained from Eq. A.24.
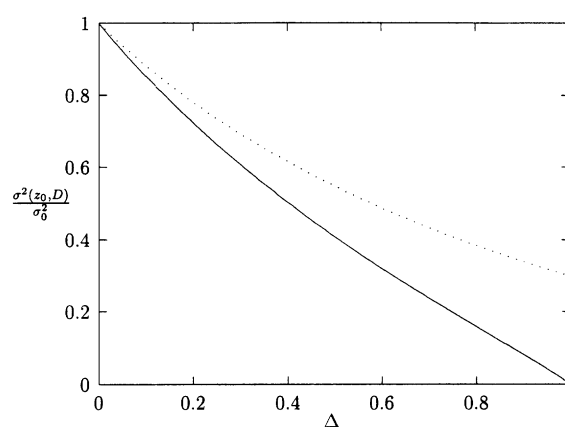
FIGURE 3 The dependence of fluctuations in the middle of the stack $\sigma^2(z_0 = 0, D)/\sigma_0^2$ (⋯) and at the boundaries $\sigma^2(z_0 = \pm D/2, D)/\sigma_0^2$ (——) on Δ. At a constant value of d this is effectively the dependence on the surface tension γ. The calculational details are the same as in Fig. 2.
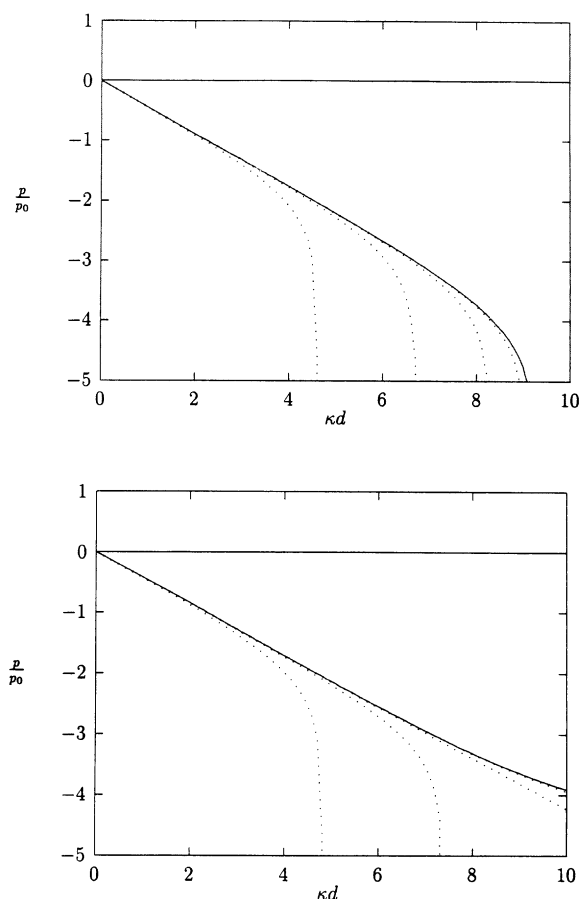
FIGURE 4   Dimensionless interlamellar pressure versus dimensionless separation in finite versus infinite arrays. Solid lines indicate the pressure versus separation with an inverse-square attractive energy (*top*) and repulsive energy (*bottom*) together with exponential repulsion of the form $P_0 e^{-\kappa d}$ (cf. Eq. 11 with parameter H positive or negative), where $d = D/N$. Dotted lines show pressure versus separation for stacks of finite thickness, $N = 10^2, 10^3, 10^4, 10^5$ layers; the greatest effect is for slabs of the least thickness. Pressure is given in reduced units and separation is in dimensionless κd units. For these computations, the surface tension γ was taken to be 64 erg/cm^2, and H was chosen so that the secondary minimum was at $\kappa d = 9.5$. In all cases there is a prediction of finite swelling, even where there are no direct interlamellar attractive forces.

Taking into account the form of $\langle \mathcal{H}_S \rangle$, one can connect the change of the free energy (Eq. 5) due to the presence of surface constraints with the average of the surface free energy (Eq. 30). Writing the change of the free energy as an integral of the corresponding interaction pressure, one is left with the following simple energy balance, valid in the limit of small surface perturbation, effectively for $\gamma / \sqrt{\mathcal{B} K_c} \ll 1$:

$$N \int_{d_0}^{d} \Pi(d) \mathrm{d}d \cong \langle \mathcal{H}_S \rangle. \tag{31}$$

$\Pi(d)$ is the interaction pressure of the bulk phase (Fig. 4, *solid line*), and the work $\int_{d_0}^{d} \Pi(d) \, \mathrm{d}d$ is needed to bring the spacing from d_0 to d, the spacing shown in the presence of surface perturbation. If the underlying interaction pressure is of the form in Eq. 28, the meaning of this relation is not difficult to discern. The total work involved in changing the apparent secondary minimum in the potential from d_0 to d is equal to the change in surface energy due to the boundary suppression of fluctuations.

Again, both numerical investigations (see Fig. 4), as well as the formula (Eq. 31), confirm the paramount importance of the surface energy term, which is proportional to Q_{max}^2 (Eq. 5), which is absent from the electrodynamic van der Waals forces. As previously discussed (Ajdari et al., 1992), this difference is due to a natural cutoff in the Q integrals of the theory of mechanical van der Waals forces stemming from the atomic dimensions of the smectic layer molecules, below which the continuum elastic energy *ansatz* loses meaning, as well as to the fact that $\mathcal{B}$, which plays a role similar to the dielectric response function in the theory of electrodynamic van der Waals forces, depends on the density of the system, d.

DISCUSSION

The fundamental reasoning in our analysis almost has the rhythm of a syllogism:

1. Undulations create repulsive forces (Eq. 1).
2. Surface tension suppresses undulation (Eq. 2).
3. Surface tension suppresses repulsive forces (Eq. 5 and Eq. 31).

It is the range and the energy distribution of this suppression, even effecting an attractive force between tense walls, that startle. The mode-summation formalism used here to estimate surface perturbation of undulations is, in principle, the same as the summation-over-modes used to formulate electromagnetic fluctuation forces between macroscopic bodies (Mahanty and Ninham, 1976). There, one is selecting from the infinity of all possible electromagnetic fluctuations those particular modes that are perturbed by the presence of boundaries whose dielectric properties differ from that of the medium between. Here, in a manner similar to that used by Adjari et al. (1992), we sum those mechanical undulations that are changed by the presence of tense surfaces bounding a bilayer stack of thickness D.

The bulk phase Hamiltonian (Eq. 1) has a straight spring term for compressibility $\mathcal{B}$ perpendicular to the layers but, in the absence of applied lateral tension, the lateral compressibility depends on the square of curvature, creating a soft balance between lateral and perpendicular compressibilities.

Surface tension γ adds a Q^2 dependence (Eq. 2) to the energy of the two surface layers. There are two kinds of consequences from this term. First, the surface energy itself is dominated by the highest-Q, shortest wavelength undulations, which in the limit of small γ vary as $\sim kT\gamma Q_{\mathrm{max}}^2 / \sqrt{B K_c}$ (second term, Eq. 5, and Eq. 30). Moreover, this contribution disturbs the behavior of the lowest-Q, longest wavelength modes. These modes extend to the full lateral dimension allowed by the size of the sample, probably the domain size of the particular multilayer preparation. Be-

cause the transverse and lateral perturbations are connected by the same Q's, the tension-suppressed, long-wavelength modes reach into the layered structure as well as along it. The effect of suppression, at least, in principle, reaches into the multilayer to depths as great as the lateral extent of the lamellar domains.

As amply demonstrated by Adjari et al. (1992), mechanical van der Waals (or Casimir) forces have a nominally $1/D$ power-law variation (third term, Eq. 15) when moduli $\mathscr{B}$ and K_c have fixed values (as do electromagnetic susceptibilities in Lifshitz/Casimir theory). Here, however, because the transverse compressibility $\mathscr{B}$ itself is a function of thickness D, this $1/D$ contribution appears to have less energy than the straight surface energy (Eq. 5).

Equation 31 shows the equivalence between the surface energy $\langle H_S \rangle$ and the work done on the stack of N layers to displace it from the mean spacing d_0 in a $\gamma = 0$ multilayer of effectively infinite thickness, to d_γ, the average spacing of a finite-thickness multilayer subject to surface tension. Because $\langle H_S \rangle$ is independent of N, this equivalence shows that surface-induced compression is spread throughout the entire multilayer stack. By comparing the work done to compress layers under surface tension with those free of tension, one finds that the work per layer is inversely proportional to the number of layers N (Fig. 4).

At the same time, the profile of surface-suppressed undulation almost rescales with the height of the smectic stack (see Eq. 31 and Fig. 2). This rescaling seems to emerge naturally from the fact that the longest wavelength modes dominate the range of interaction. As in any two-dimensional system under tension, any undulation is spread over the entire available surface. In the case of lipid multilayers, one expects this available surface to be on the order of the domain size. Hence very long-range surface perturbations can be expected on carefully prepared samples; the range of perturbation might well be controlled in an observable way by breaking up domains.

To a first approximation, the attractive forces of which we speak act in addition to the compressibilities of the same layers when in contact with solutions that impose negligible surface energies. Anticipating later application of these ideas to the "vapor pressure paradox," we note that lipid multilayers in liquid water or in osmotically stressing polymer solutions are a good example of layers bounded by low-energy surfaces (Rand and Parsegian, 1989); multilayers adsorbed on a solid surface or bounded by a vapor surface are necessarily bounded by high-energy surfaces (Smith et al., 1987; Tristram-Nagle et al., 1993).

At this point we can only speculate about the generality of the proposed mechanism. It is not immediately obvious to what extent it should also apply to the stacks of solid membranes with a finite in-plane shear modulus that have also been reported to exhibit a "vapor pressure paradox" (Smith et al., 1990; Yi Shen et al., 1993) or to the hydrogels of polymer networks that seem to display the same anomaly.

(We thank the anonymous referee for pointing out this example to us).

We work, then, from a reference state for mechanical susceptibility built on bulk free energy terms only. In practice, this state can be, for example, the osmotic stress on a layered structure in a liquid and subject to an osmotic stress at each particular lamellar repeat spacing, the spacing that a surface-inhibited sample would achieve infinitely far from the surface. For formal convenience in our derivation, we have used most-simple approximations for the osmotic compressibility, the steric repulsion formula of Helfrich, or the form of the osmotic compressibility measured in actual multilamellar arrays.

Our illustrative computations show that the strength of suppressed undulation is enough to compress smectic layers, even against net repulsion between bilayers (Fig. 4).

The stubborn persistence of the vapor paradox itself and the long reach of boundary surfaces that emerge from the present analysis suggest that there is still a lot to learn about the confinement of layered systems in finite spaces. Can mechanical van der Waals forces explain the paradox? The energies involved are large enough to suggest that they might. The present formulation suggests a systematic strategy for measurements on charged and uncharged lamellae using osmotic stress of vapor pressure and of polymer solutions to focus on what might be a dominant but neglected consequence of molecular confinement. The first step should probably be to reexamine the variation of multilayer spacings near vapor interfaces. After that, parallel osmotic stress studies on samples of different thickness—in vapor and in liquids—can be used to test the competition between surface and bulk energies suggested by Eq. 31.

In the first experiments of this type, spacings in hydrated lipid multilayers have been observed after the creation of a vapor space within. Near the vapor, bilayer separations decrease by several angstroms compared to the original spacings. A gradient of spacings develops to a depth of several millimeters from the vapor surface (Podgornik et al., 1996).

There is good reason to expect surface effects similar to those formulated here to act in polymer systems such as in assemblies of DNA or other semiflexible molecules. Considering that the length of these molecules is often much larger than the compartments into which they are confined, one might have to think about molecular packing in these small spaces in terms much different from what is expected from measurements in large solutions.

APPENDIX

Free energy through Green function

The analysis of the model defined by Eqs. 1 and 2 now proceeds by the standard decomposition of the displacement field $u(z, \boldsymbol{\rho})$ into Fourier components:

$$u(z, \boldsymbol{\rho}) = \sum_{\boldsymbol{Q}} u(z, \mathbf{Q}) e^{-i\mathbf{Q}\boldsymbol{\rho}}. \tag{A.1}$$

The partition function can be written in this way in the form

$$\Xi(D) = \prod_Q \int \ldots \int \mathcal{D}u(z, \mathbf{Q}) e^{-(\beta/2)\int\int dz dz'\, u(z, \mathbf{Q})\mathcal{H}(z, z'; \mathbf{Q})u(z', \mathbf{Q})}$$

$$= \prod_Q (\det \mathcal{H}(z, z'; \mathbf{Q}))^{-1/2}, \quad (A.2)$$

where the mode Hamiltonian is

$$\mathcal{H}(z, z'; Q) = \left[-\mathcal{B}\frac{\partial^2}{\partial z^2} + K_c Q^4 + \gamma Q^2 \delta\left(z + \frac{D}{2}\right) \right.$$

$$\left. + \gamma Q^2 \delta\left(z - \frac{D}{2}\right) \right] \delta(z - z')$$

$$= \left[-\mathcal{B}\frac{\partial^2}{\partial z^2} + \Gamma_Q(z) \right] \delta(z - z'). \quad (A.3)$$

In deriving Eq. A.3, we used the well-known properties of Gaussian integrals.

The corresponding free energy thus follows as

$$\mathcal{F} = -kT \ln \Xi(D) = \frac{kT}{2} \sum_Q \ln \det \mathcal{H}(z, z'; \mathbf{Q})$$

$$(A.4)$$

$$= \frac{kT}{2} \sum_Q \text{Tr} \ln \mathcal{H}(z, z'; \mathbf{Q}).$$

or in a simplified form (Podgornik, 1989),

$$\mathcal{F}(D) = \sum_Q \text{Tr } \Gamma_Q(z) \int_0^{\mathcal{B}^{-1}} d\mu \, \mathcal{G}_\mu(z, z'; \mathbf{Q}), \quad (A.5)$$

where $\mathcal{G}_\mu(z, z'; \mathbf{Q})$ is the Green function, being a solution of

$$\frac{\partial \mathcal{G}_\mu(z, z'; \mathbf{Q})}{\partial z^2} - \mu K_c Q^4 \mathcal{G}_\mu(z, z'; \mathbf{Q}) = -\delta(z - z'), \quad (A.6)$$

with the boundary condition at $z = \pm D/2$,

$$\frac{\partial \mathcal{G}_\mu(z = \pm D/2, z'; \mathbf{Q})}{\partial z} - \mu \, \gamma Q^2 \mathcal{G}_\mu\left(z = \pm\frac{D}{2}, z'; \mathbf{Q}\right) = 0. \quad (A.7)$$

This particular form of the boundary condition follows from the model form of the surface free energy $\mathcal{H}_S(u(z, \boldsymbol{\rho}))$ and is due to the two surface δ functions in the definition of $\Gamma_Q(z)$.

In terms of the Green function, the integration in μ is in effect the coupling constant integration in the compressibility $\mathcal{B}^{-1}$. The two limits of integration represent a totally incompressible system and, at the other end, a system with a chosen value of $\mathcal{B}$. In this respect the above formalism is quite close to the evaluation of van der Waals forces between surfaces immersed in an electrolyte, where the coupling constant integration is performed with respect to the dielectric permeability and the boundary condition stems from the general electrostatic boundary condition (Podgornik, 1989).

The solution of the above set of equations turns out to be

$$\mathcal{G}_\mu(z, z'; \mathbf{Q}) = \frac{1}{2}\sqrt{\frac{\mathcal{B}}{K_c}} Q^{-2}\left[e^{-\sqrt{K_c/\mathcal{B}}Q^2|z-z'|} + \frac{2\Delta e^{-2\sqrt{K_c/\mathcal{B}}Q^2 D}}{1 - \Delta^2 e^{-2\sqrt{K_c/\mathcal{B}}Q^2 D}} \right.$$

$$\left. \left(e^{\sqrt{K_c/\mathcal{B}}Q^2 D}\cosh\sqrt{\frac{K_c}{\mathcal{B}}} Q^2(z + z') + \Delta \cosh\sqrt{\frac{K_c}{\mathcal{B}}} Q^2(z - z') \right)\right],$$

$$(A.8)$$

with

$$\Delta \equiv \frac{\gamma - \sqrt{K_c\mathcal{B}}}{\gamma + \sqrt{K_c\mathcal{B}}} \quad (A.9)$$

being independent of Q. The detailed form of the boundary condition (Eq. A.7) affects only the form of Δ. The function Δ is analogous to the difference over sum of dielectric permitivities in the Lifshitz formulation of the van der Waals forces (Mahanty and Ninham, 1976). The quantity $\sqrt{K_c\mathcal{B}}$ has the form of a surface energy from terminating what would otherwise be an infinitely thick multilayer (de Gennes and Prost, 1993).

Furthermore, one can straightforwardly prove that

$$\text{Tr } \Gamma_Q(z)\mathcal{G}_\mu(z, z'; \mathbf{Q}) = \frac{\partial}{\partial\mu} \mathcal{T}(\mu; \mathbf{Q}), \quad (A.10)$$

where

$$\mathcal{T}(\mu; \mathbf{Q}) = \sqrt{\frac{K_c}{\mathcal{B}}} Q^2 D - \ln(1 - \Delta^2)$$

$$+ \ln\left(\frac{\gamma}{\sqrt{K_c\mathcal{B}}}\right) + \ln(1 - \Delta^2 e^{-2\sqrt{K_c/\mathcal{B}}Q^2 D}). \quad (A.11)$$

The free energy can thus be obtained from the coupling constant integral (Eq. A.5) up to an additive constant in a simple form:

$$\mathcal{F}(D) = \mathcal{F}_B(D) + kT \sum_Q \ln\left(1 + \frac{\gamma}{\sqrt{K_c\mathcal{B}}}\right)$$

$$+ \frac{kT}{2} \sum_Q \ln(1 - \Delta^2 e^{-2\sqrt{(K_c/\mathcal{B})}Q^2 D}), \quad (A.12)$$

where the three terms stand for the bulk or volume free energy $\mathcal{F}_B$, the surface, and the finite-size contributions to the free energy. In the case of an electrolyte, the different parts of the free energy would correspond to Debye-Hückel, Onsager-Samaras, and van der Waals-Lifshitz contributions to the free energy (Podgornik, 1989). The bulk part corresponds to the free energy of a slab D thick, but without taking into account any boundary effects.

Free energy through eigenfunction expansion

An alternative yet equivalent path to the free energy can be followed if the Gaussian integral in the partition function (Eq. A.2) is evaluated by means of the eigenfunctions of the bulk Hamiltonian (Eq. 1). Using again the Fourier decomposition of the displacement field,

$$u(z, \boldsymbol{\rho}) = \sum_Q u(z, \mathbf{Q})e^{-iQ\rho}. \quad (A.13)$$

the equation for the eigenfunctions of the bulk Hamiltonian can be derived in the form

$$\frac{\partial^2 u(Q; z)}{\partial z^2} - \frac{K_c Q^4}{\mathscr{B}} u(Q; z) = 0. \qquad (A.14)$$

These eigenfunctions have the Fourier amplitudes of the general form

$$u(Q; z) = A(Q)e^{\sqrt{(K_c/\mathscr{B})}Q^2 z} + B(Q)e^{-\sqrt{(K_c/\mathscr{B})}Q^2 z}. \qquad (A.15)$$

Expressed through the eigenfunctions of its bulk part, the Hamiltonian of the system can be cast into the form

$$\mathscr{H}(u(Q; z)) = \mathscr{H}_B(u(Q; z)) + \mathscr{H}_S(u(Q; z))$$

$$= \sum_Q \left(\left[K_c Q^4 \frac{\sinh \sqrt{(K_c/\mathscr{B})}Q^2 D}{\sqrt{(K_c/\mathscr{B})}Q^2} \right. \right. \qquad (A.16)$$

$$\left. + \gamma Q^2 \cosh \sqrt{\frac{K_c}{\mathscr{B}}}Q^2 D \right] (A^2(Q) + B^2(Q))$$

$$+ 2\gamma Q^2 A(Q)B(Q)).$$

The nondiagonal parts in $A(Q)$ and $B(Q)$ stem exclusively from the surface part of the Hamiltonian $\mathscr{H}_S(u(Q; z))$, as the eigenfunctions diagonalize only the bulk part $\mathscr{H}_B(u(Q; z))$. Because now $\mathscr{H}(u(Q; z))$ is a Gaussian function of only the Fourier amplitudes of the displacement field, the trace in the partition function can be evaluated as

$$\Xi(D) = \prod_Q \int \int dA(Q)dB(Q)\exp(-\beta\mathscr{H}(A(Q), B(Q))) \qquad (A.17)$$

$$= \prod_Q \frac{\sqrt{\pi}}{\sqrt{\det(\beta \mathbf{G}_{ik}(Q))}},$$

where we introduced the 2×2 matrix,

$$\mathbf{G}(Q) =$$

$$\begin{vmatrix} K_c Q^4 \dfrac{\sinh \sqrt{(K_c/\mathscr{B})}Q^2 D}{\sqrt{(K_c/\mathscr{B})}Q^2} & \\ \quad + \gamma Q^2 \cosh \sqrt{(K_c/\mathscr{B})}Q^2 D & \gamma Q^2 \\ & \\ & K_c Q^4 \dfrac{\sinh \sqrt{(K_c/\mathscr{B})}Q^2 D}{\sqrt{(K_c/\mathscr{B})}Q^2} \\ \gamma Q^2 & \quad + \gamma Q^2 \cosh \sqrt{(K_c/\mathscr{B})}Q^2 D \end{vmatrix}$$

$$\qquad (A.18)$$

$$= \begin{pmatrix} \mathscr{D}(Q) & \mathscr{D}'(Q) \\ \mathscr{D}'(Q) & \mathscr{D}(Q) \end{pmatrix},$$

where we also defined the quantities $\mathscr{D}(Q)$ and $\mathscr{D}'(Q)$. With these definitions the Hamiltonian can be succinctly written as

$$\mathscr{H}(A(Q), B(Q)) = [A(Q), B(Q)]\mathbf{G}(Q)\begin{bmatrix} A(Q) \\ B(Q) \end{bmatrix}. \qquad (A.19)$$

We are now in a position to evaluate first the mean squared values of the Fourier amplitudes of the eigenfunctions in Eq. A.15. By applying the equipartition theorem to the Hamiltonian (Eq. A.19), we deduce that only

the combinations $u_+(Q) = A(Q) + B(Q)$ and $u_-(Q) = A(Q) - B(Q)$ are zero mean Gaussian variables, i.e.,

$$\langle u_\pm^2(Q) \rangle = \frac{kT}{\mathscr{D}(Q) \pm \mathscr{D}'(Q)}. \qquad (A.20)$$

From this we obtain

$$\det(\beta \mathbf{G}(Q)) = \frac{1}{\langle u_+^2(Q) \rangle \times \langle u_-^2(Q) \rangle}$$

$$= \beta^2 K_c \mathscr{B} Q^4 \sinh \sqrt{\frac{K_c}{\mathscr{B}}}Q^2 D \qquad (A.21)$$

$$\times \left(1 + \frac{\gamma}{\sqrt{K_c \mathscr{B}}} \tanh \sqrt{\frac{K_c}{\mathscr{B}}}Q^2 \frac{D}{2}\right)\left(1 + \frac{\gamma}{\sqrt{K_c \mathscr{B}}} \cotanh \sqrt{\frac{K_c}{\mathscr{B}}}Q^2 \frac{D}{2}\right).$$

The corresponding free energy can now be evaluated as

$$\mathscr{F}(D) = \frac{kT}{2} \sum_Q \ln \det(\beta \mathbf{G}(Q))$$

$$\qquad (A.22)$$

$$= -\frac{kT}{2} \sum_Q \ln\langle u_+^2(Q) \rangle - \frac{kT}{2} \sum_Q \ln\langle u_-^2(Q) \rangle,$$

which is in the form of the fluctuation free energy first derived by Helfrich (1978). Rearranging the determinant in Eq. A.21, one is now led to the final form of the free energy as

$$\mathscr{F}(D) = \mathscr{F}_B(D) + kT \sum_Q \ln\left(1 + \frac{\gamma}{\sqrt{K_c \mathscr{B}}}\right)$$

$$\qquad (A.23)$$

$$+ \frac{kT}{2} \sum_Q \ln(1 - \Delta^2 e^{-2\sqrt{(K_c/\mathscr{B})}Q^2 D}),$$

in complete agreement with what was evaluated before Eq. A.12.

Fluctuation profile

The spatial profile of the fluctuations in the layer displacement field for $|z| \leq D/2$ can be characterized by first defining the total single-layer fluctuation $\sigma^2(z)$:

$$\sigma^2(z; D) = \frac{1}{S} \int d^2\boldsymbol{\rho} \langle u^2(z, \boldsymbol{\rho}) \rangle = \sum_Q \langle |u(z, \mathbf{Q})|^2 \rangle \qquad (A.24)$$

$$= \sum_Q \mathscr{A}(z, z; \mathbf{Q}).$$

where

$$\mathscr{A}(z, z'; \mathbf{Q}) = \langle u(z, \mathbf{Q})u(z', -\mathbf{Q}) \rangle. \qquad (A.25)$$

Because the average in the above equation is over a Gaussian ensemble

with the measure $\mathcal{H}(z, z'; \mathbf{Q})$ (Eq. 1),

$$\mathcal{A}(z, z; \mathbf{Q}) = \prod_{\mathbf{Q}} \int \cdots \int$$

$$\mathcal{D}\mathbf{u}(\mathbf{z}, \mathbf{Q}) u(z, \mathbf{Q}) u(z', -\mathbf{Q}) e^{-(\beta/2)\iint dz dz' u(z,\mathbf{Q}) \mathcal{H}(z,z';\mathbf{Q}) u(z'\mathbf{Q})},$$

$$\text{(A.26)}$$

we obtain after elementary Gaussian integrations

$$\mathcal{A}(z, z'; \mathbf{Q})^{-1} = \mathcal{H}(z, z'; \mathbf{Q}) = \left[-\mathcal{B}\frac{\partial^2}{\partial z^2} + \Gamma_Q(z) \right] \delta(z - z').$$

$$\text{(A.27)}$$

The above result is due to the fact that $\mathcal{A}(z, z'; \mathbf{Q})$ is just an inverse of the Hamiltonian operator. Thus it follows that

$$\mathcal{A}(z, z'; \mathbf{Q}) = \mathcal{B}^{-1} G_{\mu=\mathcal{B}^{-1}}(z, z'; \mathbf{Q}). \qquad \text{(A.28)}$$

where $G_\mu(z, z'; \mathbf{Q})$ is given by Eq. A.8. Finally, we arrive at

$$\sigma^2(z; D) = \mathcal{B}^{-1} G_{\mu=\mathcal{B}^{-1}}(z, z; \mathbf{Q})$$

$$= \frac{1}{2}\sum_Q \frac{1}{\sqrt{\mathcal{B}K_c}Q^2}\left[1 + \frac{2\Delta e^{-2\sqrt{(K_c/\mathcal{B})}Q^2 D}}{1 - \Delta^2 e^{-2\sqrt{(K_c/\mathcal{B})}Q^2 D}} \right.$$

$$\left. \left(\Delta + e^{\sqrt{(K_c/\mathcal{B})}Q^2 D} \cosh\sqrt{\frac{K_c}{\mathcal{B}}}Q^2(2z) \right) \right].$$

$$\text{(A.29)}$$

The fluctuations of the displacement field in the transverse direction depend only on the ratio z/D and are thus of long range. The same derivation could be again repeated by means of the eigenfunction expansion, but we refrain from explicitly doing this exercise. The results are exactly the same.

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