Structural force in a presmectic liquid

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The structural interaction in a presmectic film is analyzed theoretically using the Cartesian rather than the polar representation of the smectic order parameter. This representation diagonalizes the phenomenological Hamiltonian of the ordering and leads to a unified description of the mean-field interaction—first studied by de Gennes [Langmuir **6**, 1448 (1990)]—and the fluctuation-induced interaction. The fluctuation-induced interaction turns out to be short-range, attractive, and unaffected by the apparent bidomain structure of the film, which controls the oscillatory mean-field interaction.

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It has been known for a long time that the boundary layer of a liquid in contact with a solid wall is positionally ordered. In a hard-sphere–hard-surface system [1], which represents the zeroth-order description of any liquid-solid interface, the ordering is induced by the impenetrability of the wall that breaks the translational symmetry of the liquid. In addition to the steric force, there may be other liquid-specific and solid-specific mechanisms that promote the layering of the molecules.

In the isotropic phase of a smectogenic liquid crystal, the positional order of molecules at the wall is enhanced by liquid-liquid intermolecular interactions that, in a certain temperature range below the isotropic phase, result in bulk one-dimensional positional order. Although the range of positional correlations in the isotropic smectogen is finite, it can be far larger than in simple liquids [2], say up to about 30 nm in lyotropic systems [3–5]. This implies that a presmectic matrix could be used as the continuous component of a colloid, provided that the interaction it induces between the dispersed particles is repulsive.

Apart from an interesting experimental study of the presmectic structural force in a thermotropic liquid crystal [6], its potential technological importance may well have been one of the main motives of the pioneering theoretical analysis of the interaction [7]. The analysis showed that the structure of the film whose thickness is not an integer multiple of the intrinsic smectic period is determined predominantly by the elastic strain, which enforces either compression or dilation of the film such as to make it fit between the confining walls. However, the modulation of the layer spacing is not distributed evenly across the film but concentrated in its center, where the degree of smectic order is lowest, and it results in additional reduction of the degree of order (Fig. 1). The mean-field interaction induced by the presmectic order is oscillatory [7]—and predominantly repulsive, which is quite the opposite of the interaction in symmetric wetting systems characterized by a scalar order parameter [8]. To some extent, these predictions have been verified experimentally by a comprehensive study of the force in a lyotropic system based on CsPFO [4,5].

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In this Brief Report, we reexamine the model adopted in the original theoretical study. We show that while the analysis is sound and instructive, it could be simplified by choosing a less standard yet mathematically more convenient representation of the smectic order parameter. We provide a unified description of the structural interaction induced by the presmectic film, which includes both the mean-field force rederived and the pseudo-Casimir force caused by fluctuations of the order parameter. In particular, we demonstrate that the fluctuation-induced force is attractive, monotonic, and completely unaffected by the apparent bidomain structure of the film, which makes the mean-field force oscillate.

Following the original study [7], we describe the presmectic ordering by the complex order parameter

$$\Psi = \psi \exp(i\phi), \tag{1}$$

where ψ is the degree of smectic order and $\phi = 2\pi u/a$ is the phase related to the layer displacement u, a being the smectic layer thickness. Far enough above the smectic phase, the associated phenomenological Hamiltonian

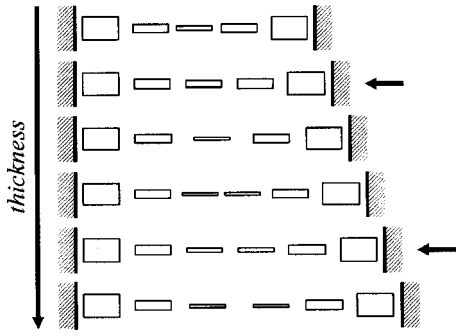

FIG. 1. A schematic of the structure of the presmectic film. The rectangles represent the smectic layers, their height being proportional to the local degree of smectic order. Unless its thickness is an integer multiple of the smectic period, the film must be either compressed or dilated to fit between the walls. However, the modulation of the layer spacing is not uniform but concentrated in the center of the film, where the degree of order is lowest. As shown in the figure, the localized compression/dilation gives rise to additional reduction of the degree of order. The arrows point to the films whose thickness is an integer multiple of the smectic period.

$$H=\frac{1}{2}\int [\alpha\Psi^2+L(\nabla\Psi)^2]\,\mathrm{d}V \tag{2}$$

consists of a second-order Landau term with $\alpha>0$ and of an isotropic elastic term [9]. Within this model, the details of the true smectic elasticity and the smectic-nematic coupling are neglected. To make the analysis as transparent as possible, we assume that the surface interaction is infinitely strong so that it fixes both the degree of order at the two walls located at $z=\pm d/2$ and the position of the layer next to each wall. In other words, $\psi(z=\pm d/2)=\psi_0$ and $\phi(z=\pm d/2)=\pm\phi_0/2$, where ψ_0 is the degree of smectic order prescribed by the walls and $\phi_0=2\pi(d/a \bmod 1)$ is the phase difference related to the compression or dilation of the film whose thickness d is not an integer multiple of the smectic period a.

In terms of the two scalar components of the order parameter, H consists of two coupled partial Hamiltonians,

$$H=H_\psi+H_\phi, \tag{3}$$

where

$$H_\psi=\frac{1}{2}\int [\alpha\psi^2+L(\nabla\psi)^2]\,\mathrm{d}V \tag{4}$$

is characterized by a mass term and an elastic term, and

$$H_\phi=\frac{1}{2}\int L\psi^2(\nabla\phi)^2\,\mathrm{d}V \tag{5}$$

is purely elastic but the effective elastic constant depends on the degree of smectic order.

Although physically meaningful, the polar representation of the order parameter is not very suitable from the mathematical point of view because it does not diagonalize the Hamiltonian. But since H is quadratic, it should be diagonalized easily. Indeed, if $\Psi=\psi\exp(i\phi)$ is replaced by the Cartesian representation

$$\Psi=\mu+i\nu, \tag{6}$$

so that $\mu(z=\pm d/2)=\psi_0\cos(\phi_0/2)$ and $\nu(z=\pm d/2)=\pm\psi_0\sin(\phi_0/2)$, H can be written as a sum of two independent partial Hamiltonians

$$H=H_\mu+H_\nu, \tag{7}$$

where

$$H_\omega=\frac{1}{2}\int [\alpha\omega^2+L(\nabla\omega)^2]\,\mathrm{d}V \tag{8}$$

and ω is either μ or ν.

Now the partition function of the presmectic order can be calculated rather straightforwardly using the analogy with the propagator of a quantum-mechanical harmonic oscillator. We first Fourier decompose the two components of the order parameter in the xy plane: $\omega(\mathbf{r})=\Sigma_{\mathbf{q}}\exp(-i\mathbf{q}\cdot\boldsymbol{\rho})\omega_{\mathbf{q}}(z)$, where ω is either μ or ν, $\mathbf{q}=q_x\mathbf{e}_x+q_y\mathbf{e}_y$, and $\boldsymbol{\rho}=x\mathbf{e}_x+y\mathbf{e}_y$. The transformed boundary conditions read $\mu_{\mathbf{q}}(z=\pm d/2)=\psi_0\cos(\phi_0/2)\,\delta(\mathbf{q})$ and $\nu_{\mathbf{q}}(z=\pm d/2)=\pm\psi_0\sin(\phi_0/2)\,\delta(\mathbf{q})$. After integration over x and y, the partial Hamiltonians reduce to

$$H_\omega=\frac{LS}{2}\sum_{\mathbf{q}}\int_{-d/2}^{d/2}[(\xi^{-2}+q^2)\omega_{\mathbf{q}}^2+\omega_{\mathbf{q}}'^2]\,\mathrm{d}z, \tag{9}$$

where S is the area of the walls, $\xi=\sqrt{L/\alpha}$ is the smectic correlation length, and the prime stands for $\mathrm{d}/\mathrm{d}z$.

The partition function of each of the two degrees of freedom is given by the integral of the Boltzmann statistical weight over all configurations of the field ω that satisfy the boundary conditions

$$\exp(-F_\omega/kT)=\int \mathcal{D}\omega\exp(-H_\omega/k_BT) \tag{10}$$

and we have literally at once [10]

$$\exp(-F_\mu/k_BT)\propto\exp\left(-\frac{LS\psi_0^2}{k_BT\xi}\cos^2(\phi_0/2)[\coth(d/\xi)-\sinh^{-1}(d/\xi)]\right)\prod_{\mathbf{q}}\sinh^{-1/2}(\sqrt{\xi^{-2}+q^2}d) \tag{11}$$

and

$$\exp(-F_\nu/k_BT)\propto\exp\left(-\frac{LS\psi_0^2}{k_BT\xi}\sin^2(\phi_0/2)[\coth(d/\xi)+\sinh^{-1}(d/\xi)]\right)\prod_{\mathbf{q}}\sinh^{-1/2}(\sqrt{\xi^{-2}+q^2}d). \tag{12}$$

In both expressions, the exponential factor corresponds to the mean-field free energy and the rest to the free energy of fluctuations.

In order to calculate the interaction free energy, the free energy of the reference bulk configuration has to be subtracted from $F_\mu+F_\nu$ [11], which leads to

$$F_{\mathrm{int}}=\frac{LS\psi_0^2}{\xi}\left[\coth(d/\xi)-\frac{\cos(2\pi d/a)}{\sinh(d/\xi)}-1\right]+\frac{k_BTS}{2\pi}\int_{\xi^{-1}}^{\infty}\ln[1-\exp(-2pd)]p\,\mathrm{d}p, \tag{13}$$

where we have substituted ϕ_0 by $2\pi d/a$ and the sum over $\mathbf{q}$'s by $(S/2\pi)\int_{\xi^{-1}}^{\infty}p\,dp$, where $p^2=\xi^{-2}+q^2$. The first term is the mean-field interaction free energy, and consists of a purely repulsive part and of an oscillatory part [7]. The second one is nothing but the usual pseudo-Casimir attraction induced by massive fluctuations around a *uniform configuration* in the strong-anchoring regime [12], which decays algebraically at distances smaller than the correlation length and exponentially at large d's,

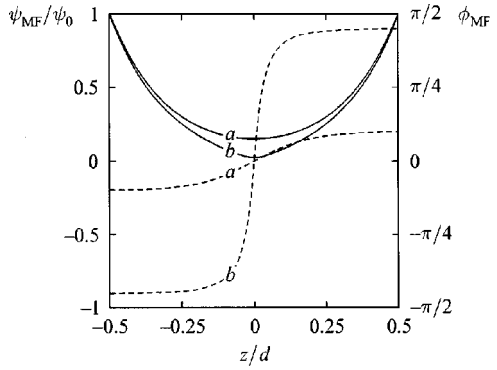

FIG. 2. The polar representation of the structure of a moderately $[d=10.1a,\ \xi=2a$; curves (a)] and a highly strained presmectic film $[d=10.45a,\ \xi=2a$; curves (b)]. In this representation, the film is characterized by a bidomain configuration with a localized variation of the phase (dashed line) and a reduced degree of smectic order (solid line) in the center.

$$F_{\text{fluct}}=-\frac{k_BTS}{4\pi}\times\begin{cases}\dfrac{\zeta(3)}{2d^2}, & d\ll\xi\\[2ex] \dfrac{\exp(-2d/\xi)}{\xi d}, & d\gg\xi\end{cases} \tag{14}$$

where $\zeta(3)=1.202\,056\,9\ldots$ is the Riemann zeta function.

The absence of signature of the smectic periodicity in the fluctuation-induced interaction is a bit surprising. The original analysis of the structure of the film has shown that unless its thickness modulo smectic period is zero, the mean-field configuration appears to consist of two domains of more or less uniform layer spacing (Fig. 1); a typical profile of the presmectic film—asymptotically given by

$$\psi_{\text{MF}}=\psi_0\sqrt{2}\exp(-d/2\xi)\sqrt{\cosh(2z/\xi)+\cos(2\pi d/a)} \tag{15}$$

and

$$\phi_{\text{MF}}=\arctan[\tan(\pi d/a)\tanh(z/\xi)] \tag{16}$$

—is shown in Fig. 2. One would expect that the spectrum of excitations in such a system will be characterized by slow modes associated with fluctuations of the position and shape of the domain wall, and that these slow modes will modify the free energy of fluctuations. But this does not seem to be the case, because the partition function of fluctuations is clearly the same as in uniform systems. How can one resolve the apparent contradiction?

The key to the answer lies in the nature of the bidomain configuration, which is quite different from the true domain structures found, e.g., in ferromagnets, in transient patterns in nematic liquid crystals beyond the Fréedericksz threshold, etc. A true domain structure occurs whenever the bulk Hamiltonian of the system is characterized by at least two degenerate minima [13], and a domain structure is preferred to uniform configuration because of larger entropy. On the other hand, the bidomain structure of the presmectic film is induced solely by the surface interaction which fixes the position of the smectic layers at the walls. That is why one can find a representation of the smectic order parameter associated with boundary conditions that completely absorb the incompatibility of the film thickness and the smectic period. In the Cartesian representation, the profiles of ψ_{MF} and ϕ_{MF} are substituted by

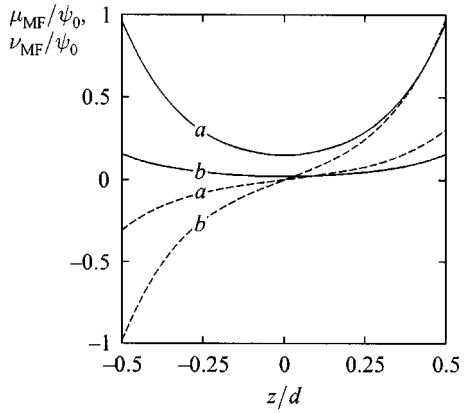

FIG. 3. The Cartesian representation of the moderately (a) and the highly strained film (b) shown in Fig. 2; solid line, μ; dashed line, ν. In this picture, the apparent bidomain structure typical for the (ψ,ϕ) representation is absent.

$$\mu_{\text{MF}}=2\psi_0\exp(-d/2\xi)\cos(\pi d/a)\cosh(z/\xi) \tag{17}$$

and

$$\nu_{\text{MF}}=2\psi_0\exp(-d/2\xi)\sin(\pi d/a)\sinh(z/\xi), \tag{18}$$

which are free of localized deformation in the center of the film (Fig. 3). This supports the conclusion that the bidomain presmectic film is not a true domain structure—and that one should not expect it to behave as such.

Having identified the reason for the unanticipated simple form of the fluctuation-induced interaction in the presmectic liquid, we can estimate its contribution to the total structural interaction. Firstly we note that asymptotically the fluctuation-induced force decays twice as fast as the mean-field force, which is proportional to $\exp(-d/\xi)$. This implies that F_{fluct} could be important at thicknesses up to $\sim\xi$, which, as shown experimentally [3,4], can reach about 30 nm. The relative strength of the fluctuation-induced and mean-field force depends on their energy scales, k_BT/ξ^2 and $L\psi_0^2/\xi$. The effective elastic constant can be calculated from the layer compressibility $B=(2\pi\psi/a)^2L$, and in lyotropics typical values of L range from 1 to 10 pN [3–5]. If we assume that $\psi_0\approx0.3$, we find that for $L\approx5$ pN and $\xi\approx20$ nm the relative strength of the two forces is given by

$$\frac{k_BT}{L\psi_0^2\xi}\approx0.5. \tag{19}$$

This is a clear indication that the fluctuation-induced interaction represents an important part of the total interaction at distances smaller than the correlation length.

It is possible that the fluctuation-induced structural interaction in a presmectic film has been detected already. A few force profiles recorded by surface force apparatus in CsPFO-based lyotropic systems [3,4] can be described well by the mean-field force, whereas others seem to be characterized by a considerable attractive offset which is particularly promi-

nent at small distances. The extra attraction can be caused by the prenematic mean-field force [8], the van der Waals force, or either the nematic or isotropic pseudo-Casimir force [12,14]—but it can also be attributed to the interaction induced by fluctuations of the presmectic (actually prelamellar) order. In order to decide which of the potential sources of the extra attraction is the dominant one, further characterization studies of (i) the degrees of smectic and nematic order at the wall and (ii) the smectic and the nematic correlation lengths are required.

In a quantitative analysis of experimental data that would include the fluctuation-induced force, a more realistic model of the surface interaction should be used instead of the strong anchoring approximation. The generalization is quite straightforward: as far as the fluctuation-induced force is concerned, the presmectic film is equivalent to uniform systems, and one can readily resort to the analysis of the phenomenon in an ordinary isotropic phase [12]. In addition, the elastic anisotropy may also become important, implying that the one-constant gradient term $\frac{1}{2}L(\nabla\Psi)^2$ should be replaced by $\frac{1}{2}L_{\parallel}(d\Psi/dz)^2+\frac{1}{2}L_{\perp}[(d\Psi/dx)^2+(d\Psi/dy)^2]$, where $L_{\parallel}$ and $L_{\perp}$ are proportional to the smectic compressibility and the bend modulus, respectively. Such an extension of the original Hamiltonian has been already discussed in the context of nematic liquid crystals [14], and it merely renormalizes the magnitude of the fluctuation-induced interaction by a factor of $L_{\parallel}/L_{\perp}$.

In conclusion, we analyzed the force mediated by a presmectic film, and we showed that although the film seems to be structured, the fluctuation-induced force is the same as in any uniform system characterized by short-range correlations. The paradox can be resolved by recognizing that the mean-field configuration of the film is in fact a surface-stabilized bidomain structure and not a bulk, entropic domain structure which should make the behavior of the pseudo-Casimir force more complex. The fluctuation-induced force is important at distances not exceeding the smectic correlation length, and it may be responsible for the observed deviation of the structural force from the mean-field prediction [3–5].

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[1] See, e.g., D. Henderson, F. F. Abraham, and J. A. Barker, Mol. Phys. **31**, 1291 (1976).
[2] R. G. Horn and J. N. Israelachvili, Chem. Phys. Lett. **71**, 192 (1980).
[3] P. Richetti, P. Kékicheff, J. L. Parker, and B. W. Ninham, Nature (London) **346**, 252 (1990).
[4] L. Moreau, P. Richetti, and P. Barois, Phys. Rev. Lett. **73**, 3556 (1994).
[5] P. Richetti, L. Moreau, P. Barois, and P. Kékicheff, Phys. Rev. E **54**, 1749 (1996).
[6] R. G. Horn, J. N. Israelachvili, and E. Perez, J. Phys. (France) **42**, 39 (1981).
[7] P. G. de Gennes, Langmuir **6**, 1448 (1990).
[8] A. Poniewierski and T. J. Sluckin, Liq. Cryst. **2**, 281 (1987).
[9] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals* (Clarendon Press, Oxford, 1993).
[10] C. Grosche and F. Steiner, *Handbook of Feynman Path Integrals* (Springer Verlag, Berlin, 1998), p. 180.
[11] See, e.g., J. N. Israelachvili, *Intermolecular and Surface Forces* (Academic Press, London, 1992).
[12] P. Ziherl, R. Podgornik, and S. Žumer, Chem. Phys. Lett. **295**, 99 (1998).
[13] The model Hamiltonian, Eq. (2), is in fact a truncated Landau-type Hamiltonian which includes (at least) a fourth-order term that stabilizes the smectic phase [9]. However, even the Ψ^4 Hamiltonian is characterized by two minima only in the immediate vicinity of the smectic-isotropic (or smectic-nematic) transition; more precisely, between the phase transition temperature and the superheating limit. In this range, the Ψ^4 term can give rise to a steplike profile of the order parameter on top of the bidomain structure described above, and in such a state the fluctuation-induced force should depart from the predictions of the current model. But the temperature range in question is usually rather narrow (≈ 0.1 K), implying that at temperatures $\gtrsim 0.1$ K above the smectic phase the Ψ^4 term—and its consequences—can be safely neglected.
[14] A. Ajdari, L. Peliti, and J. Prost, Phys. Rev. Lett. **66**, 1481 (1991).