

Range of interlayer interactions in smectic-*C* liquid crystals

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The fact that the elastic constant for bending a layer of smectic-*C* liquid crystal along its *c* director differs from the value for bending in the perpendicular direction has recently been shown to give rise to interactions between distant layers. The effect of this entropy-induced interaction is to favor a parallel or antiparallel alignment of the *c* directors in these nonadjacent layers. We calculate in detail the range and strength of this interaction in both infinite and finite samples, and find the results to depend mainly on the ratio of the average layer bending elastic constant to the layer compression modulus. At low values of this ratio, the interlayer interaction is of long range in a bulk sample, while at high values of the ratio it decays as the inverse cube of the interlayer distance. For a sample confined between rigid substrates parallel to the layers, the interaction is greatly reduced. For a free-standing film the interaction may be enhanced if the surface tension is weak, but may be diminished if the surface tension is strong.

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I. INTRODUCTION

Ferroelectric liquid crystals exhibit a rich variety of phase sequences on heating from the low-temperature crystalline phase to the high temperatures at which they become isotropic liquids [1,2]. The smectic phases that have been observed in chiral materials include not only the antiferroelectric smectic-*C* (Sm-C_A^*), the ferroelectric smectic-*C* (Sm-C^*), and smectic-*A* (Sm-A), but also the incommensurate Sm-C_α^* phase and the intermediate Sm-C_{F1}^* and Sm-C_{F2}^* helical phases.

It is generally agreed that, in order for these phases to form, there must be not only an interaction between adjacent layers, but also an interaction of longer range that tends to align the in-plane component of the liquid crystal director in next-nearest and more distant layers. Several studies have explored the phase sequences that result from proposed phenomenological models in which interactions occur between first-, second-, and even third-nearest neighboring layers [3–6].

The present authors have recently drawn attention [7,8] to a physical mechanism that can lead to an aligning interaction between distant layers. This arises because the amplitude of thermal fluctuations in layer shape is sensitive to correlations in director orientation in layers that are not nearest neighbors. This makes the entropy of the system dependent on the relative alignment of the director in all the smectic layers.

In our earlier treatments of this problem, a mean-field approximation was made in order to obtain an order-of-magnitude estimate of the strength of the interlayer interaction. While this was sufficient to demonstrate the significance of the mechanism, it led to an overestimate of the overall strength of the interaction because it included a self-energy term related to the anisotropy of a single layer. It was thus not well suited to form the building block for a detailed calculation of the phase sequence for a specific material. It is the purpose of the present paper to remedy this by evaluating

in more detail the interlayer interaction due to layer shape fluctuations.

The accurate prediction of the sequence of phases in any smectic liquid crystal requires a precise knowledge of the form of both the long-range interlayer interaction and the energy of interaction between adjacent layers. The energy of interaction between nearest-neighbor layers is dominated by steric and electrostatic forces, and has so far defied all attempts at calculation. The molecules of materials that form antiferroelectric and related phases are sufficiently large as to preclude the use of atomistic molecular-dynamics simulations as a tool. The use of simplified models, in which groups of atoms are combined to form a single unit, appears unlikely to succeed, given that the addition of a single extra CH_2 group to the achiral alkyl chain of a molecule such as 10-OHFBBB1M7 can radically modify the behavior of the material [9].

It may, however, eventually be possible to perform accurate calculations of the forces between adjacent layers if new techniques and much faster computers become available. At that time it will then be highly desirable to have an accurate expression for the energy of interaction between more distant layers. This is the justification for the work that follows.

The procedure we follow is to first note that the Hamiltonian of the system can be considered as representing a sum of independent harmonic oscillators. The Helmholtz free energy \mathcal{F} of such a system is proportional to the logarithm of the product of the eigenfrequencies of all these oscillators. We can then examine this expression for \mathcal{F} to find contributions that depend on the relative orientations of the liquid crystal director in distant smectic layers. These will be the terms we seek that can be interpreted as interactions leading to correlations in orientation in layers that are not nearest neighbors.

II. HAMILTONIAN

The orientation of each molecule in a Sm-C liquid crystal is determined by two angles. The molecular tilt θ is the angle between the molecular axis and the layer normal, which we

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here take to be along the z axis. The azimuthal angle ϕ describes the orientation of the c director, which is the projection of the molecular axis onto the plane of the smectic layer, here taken to be the x - y plane. The dominant interaction between layers will be the short-range potential that arises mainly from steric forces. This will be effective only between adjacent layers, and so may be written as

$$V_{\text{sr}} = \sum_l v_{\text{sr}}[\phi_{l+1}(x,y) - \phi_l(x,y)], \quad (1)$$

with $\phi_l(x,y)$ the azimuthal angle describing the orientation of the c director at position (x,y) in the l th layer. The form of v_{sr} will reflect the atomic structures of the molecules, and in the case of chiral molecules will be solely responsible for the introduction of chirality into the macroscopic phase structure. As discussed above, there exists no explicit microscopic model for the form of v_{sr} .

In this paper θ is taken to be constant throughout the sample, and the in-plane fluctuations of the c director are ignored. Consequently, in the l th layer, for example, all the c directors are parallel and their angle with the x axis is ϕ_l . The justification for this assumption lies in the fact that the elastic forces resisting such intralayer fluctuations are approximately linear in θ , and vanish at the smectic- C -smectic- A transition. The phase transitions that we are concerned with are those in which one smectic- C phase transforms into another smectic- C phase, and these occur at temperatures appreciably lower than the smectic- C -smectic- A transition temperature. Because optical observations do not show time-dependent textures even quite close to the smectic- C -smectic- A transition temperature, we can be confident that fluctuations can be ignored when considering smectic- C -smectic- C transitions. This absence may be accounted for by noting that the electric dipole moments associated with chiral molecules result in local accumulations of bound charge when ϕ is spatially varying, and these impose an electrostatic energy penalty.

The model we are then left with is one in which ϕ_l is uniform and constant within a layer, but in which each layer may be displaced in the z direction by an amount $u_l(x,y,t)$. To investigate the interaction between the c directors of distant layers in a sample consisting of N smectic layers, the free energy of the system must be written in terms of the N variables ϕ_l and the N functions $u_l(x,y,t)$.

The part of the Hamiltonian related to the long-range interactions between the layers, can be written as the sum of four terms—the kinetic energy \mathcal{H}_{kin} , the elastic energy $\mathcal{H}_{\text{bend}}$ associated with bending the layers, the elastic energy $\mathcal{H}_{\text{comp}}$ due to compression or expansion of the layers, and the surface energy $\mathcal{H}_{\text{surf}}$ [7,8]. The surface term is important only in the case of free-standing films. For a system of N layers of thickness d whose equilibrium position lies in the x - y plane, we can write

$$\mathcal{H}_{\text{kin}} = \int \int \sum_{l=1}^N \frac{1}{2} \rho d \left(\frac{\partial u_l}{\partial t} \right)^2 dx dy, \quad (2)$$

where ρ is the density of the liquid crystal. The contribution due to bending is

$$\mathcal{H}_{\text{bend}} = \int \int \sum_{l=1}^N \left[\frac{1}{2} A_{12} \left(\frac{\partial^2 u_l}{\partial x_l^2} \right)^2 + \frac{1}{2} A_{21} \left(\frac{\partial^2 u_l}{\partial y_l^2} \right)^2 + A_{11} \left(\frac{\partial^2 u_l}{\partial y_l \partial x_l} \right)^2 \right] dx dy, \quad (3)$$

with A_{12} , A_{21} , and A_{11} being the elastic constants for bending the layer in different directions [10,11]. In this equation x_l is an axis in the direction of the c director of the l th layer and y_l is the perpendicular axis in the x - y plane. These axes are rotated relative to the original x - y axes by the angle ϕ_l . The compressive energy is

$$\mathcal{H}_{\text{comp}} = \int \int \sum_{l=1}^{N-1} \left(\frac{1}{2} k (u_{l+1} - u_l)^2 \right) dx dy, \quad (4)$$

where k is an elastic constant related to the layer compression modulus. The surface energy $\mathcal{H}_{\text{surf}}$ is written as

$$\mathcal{H}_{\text{surf}} = \frac{1}{2} \sigma \int \int [(\nabla u_1)^2 + (\nabla u_N)^2] dx dy, \quad (5)$$

where the surface tension σ is assumed to be isotropic, and the two-dimensional gradient operator ∇ acts solely in the x - y plane. The nonlinear elastic terms demanded by symmetry considerations [12], and which are necessary to stabilize the smectic structure, are neglected in this treatment.

With the assumption of periodic boundary conditions in the x and y directions, one can partially diagonalize the Hamiltonian by use of the transformation

$$u_l(x,y,t) = \sum_{\mathbf{q}} \tilde{u}_l(\mathbf{q},t) \exp i(q_x x + q_y y). \quad (6)$$

Here $q_x = 2\pi n_x/L$ and $q_y = 2\pi n_y/L$, with L^2 being the area of each layer, and $\mathbf{q} = q_x \hat{\mathbf{x}} + q_y \hat{\mathbf{y}}$. The discrete molecular structure of each smectic layer imposes an upper limit to the magnitudes of the integers n_x and n_y . It has been suggested, in the context of fluctuations in smectic- A films, that the lower limit for the wavelength of a fluctuation should be the molecular diameter D [13]. This appears to be an underestimate, for a number of reasons. If the molecules lying along some line in the x - y plane had displacements u of alternating sign, then the wavelength would be $2D$. However, the restoring forces would be harmonic, and the oscillations would be phononlike, and not be those characteristic of bending in a rigid layer. In order for there to be a well-defined bending, with a restoring force leading to a wave with a frequency proportional to the square of the wave number, the wavelength would need to be appreciably greater than $4D$. In addition, the flexible alkyl groups at each end of most molecules of antiferroelectric liquid crystals add to the effective width of the molecule. It thus seems reasonable to choose a wavelength at least an order of magnitude larger than D , and so we choose 2 times the layer thickness d as our cutoff wavelength, making $q_{\text{max}} = \pi/d$, and $|n_x| < L/2d$ and $|n_y| < L/2d$. The Hamiltonian can then be written as

$$\mathcal{H} = \sum_{\mathbf{q}} \mathcal{H}_{\mathbf{q}}, \quad (7)$$

making the contribution to the free energy similarly a sum over the independent modes \mathbf{q} , the number of which is about $(L/d)^2$.

Each partial Hamiltonian $\mathcal{H}_{\mathbf{q}}$ represents a set of N coupled harmonic oscillators. For the case with free boundaries we can write

$$\mathcal{H}_{\mathbf{q}} = \frac{1}{2} k L^2 \left[\sum_{l=1}^N \left(\frac{\rho d}{k} \left| \frac{\partial \tilde{u}_l(\mathbf{q})}{\partial t} \right|^2 + W_l(\mathbf{q}) |\tilde{u}_l(\mathbf{q})|^2 \right) + \sum_{l=1}^{N-1} |\tilde{u}_l(\mathbf{q}) - \tilde{u}_{l+1}(\mathbf{q})|^2 \right], \quad (8)$$

with $W_l(\mathbf{q})$ a term that contains the bending energy and, in the cases where $l=1$ or $l=N$, the surface energy. [For fixed boundaries an additional term $|u_1(\mathbf{q})|^2 + |u_N(\mathbf{q})|^2$ is present.] From this expression we see that the squared frequencies of the normal modes of each system of coupled oscillators are proportional to the eigenvalues of the tridiagonal matrix whose elements are

$$M_{ll'}(\mathbf{q}) = [W_l(\mathbf{q}) + 2] \delta_{l,l'} - \delta_{l,l'\pm 1}, \quad (9)$$

except that for free boundaries the diagonal element is $W_l(\mathbf{q}) + 1$ when $l=1$ or $l=N$.

III. HELMHOLTZ FREE ENERGY

The Helmholtz energy of a set of independent harmonic oscillators of angular frequency ω_i in equilibrium at temperature T is

$$\mathcal{F} = k_B T \sum_i \ln \omega_i = \frac{1}{2} k_B T \ln \prod_i \omega_i^2. \quad (10)$$

Within the context of the problem of interacting smectic layers we have

$$\mathcal{F} = \frac{1}{2} k_B T \sum_{\mathbf{q}} \ln[\det M_{ll'}(\mathbf{q})], \quad (11)$$

the determinant of $M_{ll'}(\mathbf{q})$ being the product of its eigenvalues, and the fact that \mathcal{F} depends only on the logarithm of these frequencies rendering unimportant the constant of proportionality.

At this point we note that our interest lies in the effects of the *anisotropy* of the elastic properties of the layers, and that this anisotropy is comparatively weak. This provides us with one or two small parameters, in terms of which we can make an expansion of the matrix elements of $M_{ll'}(\mathbf{q})$. The contribution to $W_l(\mathbf{q})$ from the bending energy described in Eq. (3) is

$$W_l^{\text{bend}}(\mathbf{q}) = \frac{q^4}{k} \left(\frac{1}{8} [3(A_{12} + A_{21}) + 2A_{11}] + \frac{1}{2} (A_{12} - A_{21}) \cos[2(\varphi - \phi_l)] + \frac{1}{8} (A_{12} + A_{21} - 2A_{11}) \cos[4(\varphi - \phi_l)] \right), \quad (12)$$

where φ describes the orientation of \mathbf{q} in the x - y plane, and is defined by $q_x = q \cos \varphi$ and $q_y = q \sin \varphi$. This can be rewritten as

$$W_l^{\text{bend}}(\mathbf{q}) = p \{ 1 + \Gamma_1 \cos[2(\varphi - \phi_l)] + \Gamma_2 \cos[4(\varphi - \phi_l)] \}, \quad (13)$$

with $p = q^4 [3(A_{12} + A_{21}) + 2A_{11}] / 8k$. The quantities $\Gamma_1 \equiv 4(A_{12} - A_{21}) / [3(A_{12} + A_{21}) + 2A_{11}]$ and $\Gamma_2 \equiv (A_{12} + A_{21} - 2A_{11}) / [3(A_{12} + A_{21}) + 2A_{11}]$ are the small anisotropy parameters in terms of which we will expand the Helmholtz energy. It is convenient to define

$$\gamma_l(\varphi) \equiv \Gamma_1 \cos[2(\varphi - \phi_l)] + \Gamma_2 \cos[4(\varphi - \phi_l)] \quad (14)$$

so that

$$W_l^{\text{bend}}(\mathbf{q}) = p [1 + \gamma_l(\varphi)]. \quad (15)$$

We note that the definition of p includes the ratio of elastic constants $[3(A_{12} + A_{21}) + 2A_{11}] / 8k$, which has the dimensions of the fourth power of a length. This will be a central parameter on which our results depend, and so we define this length Λ through the relation

$$\Lambda^4 \equiv [3(A_{12} + A_{21}) + 2A_{11}] / 8k, \quad (16)$$

so that

$$p = (q\Lambda)^4. \quad (17)$$

This quantity Λ , which is specific for smectic- C materials, can be related to the length λ introduced by de Gennes and Prost [14] in their discussion of layer fluctuations in smectic- A liquid crystals. In the limit of vanishing anisotropy reached just prior to the smectic- C -smectic- A transition we would have $\Lambda \sim \sqrt{\lambda d}$.

We define as D_N the part of $\det M_{ll'}(\mathbf{q})$ that is independent of Γ_1 or Γ_2 . The terms linear in Γ_1 or Γ_2 reduce to the product of two separate determinants multiplied by the factor $\gamma_l(\varphi)$, and those quadratic in Γ_1 or Γ_2 form a product of three separate determinants multiplied by the factor $\gamma_l(\varphi) \gamma_{l'}(\varphi)$, so that we may write

$$\det M_{ll'}(\mathbf{q}) = D_N + \sum_l R_l(\mathbf{q}) \gamma_l + \sum_{l>l'} S_{ll'}(\mathbf{q}) \gamma_l \gamma_{l'} + O(\gamma^3) \quad (18)$$

and

$$\begin{aligned} \ln[\det M_{ll'}(\mathbf{q})] = & \text{constant} + \sum_l \left(\frac{R_l(\mathbf{q})}{D_N} \gamma_l - \frac{R_l(\mathbf{q})^2}{2D_N^2} \gamma_l^2 \right) \\ & + \sum_{l>l'} \left(\frac{S_{l,l'}(\mathbf{q})}{D_N} - \frac{R_l(\mathbf{q})R_{l'}(\mathbf{q})}{D_N^2} \right) \gamma_l \gamma_{l'} \\ & + O(\gamma^3). \end{aligned} \quad (19)$$

We substitute this expression into Eq. (11) and note that the integration over φ that is part of the summation over \mathbf{q} eliminates the term linear in γ_l and also reduces the term bilinear in the γ_l to a function of $\phi_l - \phi_{l'}$, as we expect from rotational invariance. We find

$$\begin{aligned} \mathcal{F} = \mathcal{F}_0 - \frac{1}{4} k_B T \sum_{l>l'} f_{l,l'} \{ & \Gamma_1^2 \cos[2(\phi_l - \phi_{l'})] \\ & + \Gamma_2^2 \cos[4(\phi_l - \phi_{l'})] \}, \end{aligned} \quad (20)$$

with

$$f_{l,l'} = \sum_{\mathbf{q}} \left(\frac{R_l(\mathbf{q})R_{l'}(\mathbf{q})}{D_N^2} - \frac{S_{l,l'}(\mathbf{q})}{D_N} \right). \quad (21)$$

To evaluate the free energy we need to determine R_l , $S_{l,l'}$, and D_N , which depend on the boundary conditions of the sample. In the case of a system with rigid boundaries one finds

$$\begin{aligned} R_l^{(c)} &= p D_{l-1}^{(c)} D_{N-l}^{(c)}, \\ S_{l,l'}^{(c)} &= p^2 D_{l-1}^{(c)} D_{N-l'}^{(c)} D_{n-1}^{(c)}, \end{aligned} \quad (22)$$

where $n=l'-l$, and the superscript (c) indicates that the sample is confined. For a free-standing film, however, $R_l^{(f)}$ and $S_{l,l'}^{(f)}$ are given by

$$\begin{aligned} R_l^{(f)} &= p [D_{l-1}^{(c)} + g(p) D_{l-2}^{(c)}] [D_{N-l}^{(c)} + g(p) D_{N-l-1}^{(c)}], \\ S_{l,l'}^{(f)} &= p^2 [D_{l-1}^{(c)} + g(p) D_{l-2}^{(c)}] [D_{N-l'}^{(c)} + g(p) D_{N-l'-1}^{(c)}] D_{n-1}^{(c)}, \end{aligned} \quad (23)$$

with $g(p) = (\sigma\sqrt{p}/\Lambda^2 k) - 1$. One should note that Eq. (23) has been given in terms of $D^{(c)}$ s rather than $D^{(f)}$ s, as it is easier to give a general expression for $D_l^{(c)}$. It may be shown that $D_l^{(f)} = D_l^{(c)} + 2g(p)D_{l-1}^{(c)} + g(p)^2 D_{l-2}^{(c)}$.

The last step before calculating the free energy is to determine $D_l^{(c)}$ as a function of l and p . The recursion relation for these determinants is

$$D_l^{(c)} = (p+2)D_{l-1}^{(c)} - D_{l-2}^{(c)}, \quad (24)$$

from which

$$D_l^{(c)} = \frac{\sinh[2(l+1)\vartheta]}{\sinh 2\vartheta}, \quad (25)$$

where $\vartheta = \text{arcsinh}(\sqrt{p}/2)$. We now examine separately the cases of bulk samples, confined samples, and free-standing films.

IV. BULK SAMPLES

In this section we calculate the interaction between the two layers l and $l+n$ when they are embedded in the interior of a thick sample of N layers, with N large. The boundary conditions are unimportant in this case, and so Eq. (22) can be used to calculate $f_{l,l'}$, and hence the free energy. When l is large Eq. (25) reduces to $D_l \approx e^{2(l+1)\vartheta}/(2 \sinh 2\vartheta)$. Then $R_l/D_N = \tanh \vartheta$, which is, as expected, independent of l . One also finds $S_{l,l+n}/D_N^2 = (1 - e^{-4n\vartheta}) \tanh^2 \vartheta$, from which

$$f_{l,l+n} = \sum_{\mathbf{q}} e^{-4n\vartheta} \tanh^2 \vartheta. \quad (26)$$

We approximate the sum in Eq. (26) with an integral over the two-dimensional q -space, with an upper limit to q of π/d , with d the layer thickness. The wave number q is related to ϑ through the relation $q^2 \Lambda^2 = 2 \sinh \vartheta$, and so

$$f_{l,l+n} = (L^2/2\pi\Lambda^2) \int_0^{\vartheta_m} e^{-4n\vartheta} \sinh \vartheta \tanh \vartheta d\vartheta \quad (27)$$

with the upper limit of the integration being $\vartheta_m = \text{arcsinh}(\pi^2 \Lambda^2 / 2d^2)$.

It is now apparent that it is the length Λ that determines the strength and range of the interlayer interaction. When the ratio of Λ to the layer thickness d is small, then the factor of $e^{-4n\vartheta}$ in the integrand has little effect unless n is very large, as the upper limit of integration is reached before the exponential has been significantly reduced from unity. The range of the interlayer interaction thus becomes infinite as Λ vanishes. However, the overall strength of the interaction is reduced because even the combination of the large prefactor ($\propto \Lambda^{-2}$) and the increased range ($\propto \Lambda^{-2}$) do not compensate for the reduced magnitude of the integral ($\propto \Lambda^{-6}$). Physically, this situation corresponds to having a large bulk modulus for layer compression. Each layer is then obliged to move in unison, which causes the long range of the interaction, but the amplitude of motion is correspondingly reduced, which lowers the entropic contribution to the free energy.

At the other extreme of large Λ , which would correspond to a layer stiff against bending but soft for layer compression, the integral encompasses large values of ϑ , and is thus sensitive to the value of n . The interlayer interaction then decays rapidly with distance, weakening as n^{-3} for large n . When combined with the effects of the prefactor, which varies as Λ^{-2} , this makes the case of large Λ similarly uninteresting. Physically, the motion of adjacent layers has become uncorrelated, and so the effects of anisotropy are not communicated between layers. It thus becomes clear that it is at intermediate values of Λ that the effects of interlayer interactions mediated by fluctuations will be maximized.

It is helpful to rewrite Eqs. (20) and (27) as

$$\begin{aligned} \mathcal{F} = \mathcal{F}_0 - \left(\frac{L}{D} \right)^2 \sum_{l,n} \frac{k_B T}{8\pi} \left(\frac{D}{d} \right)^2 \{ & \Gamma_1^2 \cos[2(\phi_l - \phi_{l+n})] \\ & + \Gamma_2^2 \cos[4(\phi_l - \phi_{l+n})] \} H_n(\Lambda/d), \end{aligned} \quad (28)$$

where

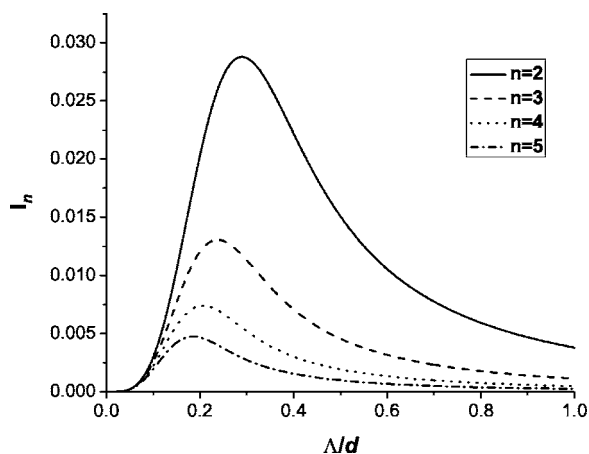


FIG. 1. This figure shows plots of $I_n(\Lambda/d)$ as a function of Λ/d for different values of the layer separation number n .

$$I_n(\Lambda/d) = \left(\frac{d}{\Lambda}\right)^2 \int_0^{\vartheta_m} e^{-4n\vartheta} \sinh \vartheta \tanh \vartheta d\vartheta. \quad (29)$$

Because $(L/D)^2$ is roughly the number of molecules per layer, the summand represents approximately the free energy per molecule of interaction due to interlayer correlations in the thermal fluctuations of layer shape. The term in braces contains the two anisotropy parameters, Γ_1 and Γ_2 . These determine, respectively, the strength of the interaction favoring parallel-or-antiparallel alignment, or alignment at some multiple of $\pi/4$ between layers. The strength of the effect is governed by the magnitude of these anisotropy parameters and by the magnitude of the integral $I_n(\Lambda/d)$. Figure 1 shows plots of $I_n(\Lambda/d)$ as a function of Λ/d for various n , beginning with $n=2$. (The case where $n=1$ is not of great interest, as this nearest-neighbor interaction will be overshadowed by the much larger steric and electrostatic forces.) We note that the maximum interlayer interaction occurs when Λ/d is around 0.29 for $n=2$ and is found at smaller Λ/d for larger n .

To predict the strength and range of the interlayer interaction for a real liquid crystal, we require an estimate of the magnitude of the ratio Λ/d , with Λ the length defined in Eq. (16) as the fourth root of a ratio of elastic constants. In our model the elastic constant k is related to the layer compression modulus B through the relation $B=kd$. The quantity $[3(A_{12}+A_{21})+2A_{11}]/8d$ is estimated to be of the same order as the Sm-A splay constant k_s , which tells us that $\Lambda^4 \sim (k_s d^2/B)$. The layer compression modulus depends on the type of material involved and on the temperature. Recent experiments [15,16] suggest that for a ferroelectric liquid crystal, B reaches its minimum value near the Sm-A–Sm-C transition, and then increases as the temperature is lowered. A typical value for the layer compression modulus for anti-ferroelectric liquid crystals is [16] 2×10^7 N/m², whereas near the Sm-A–Sm-C transition point B could be one order of magnitude smaller. Using these values for B and assuming the typical values $k_s=10^{-11}$ N and $d=3$ nm, one can conclude that $\Lambda/d \sim 0.5$ at the lower end of the smectic-C temperature range, and increases with temperature. From Fig. 1 we see that it is then likely that most systems will lie in the

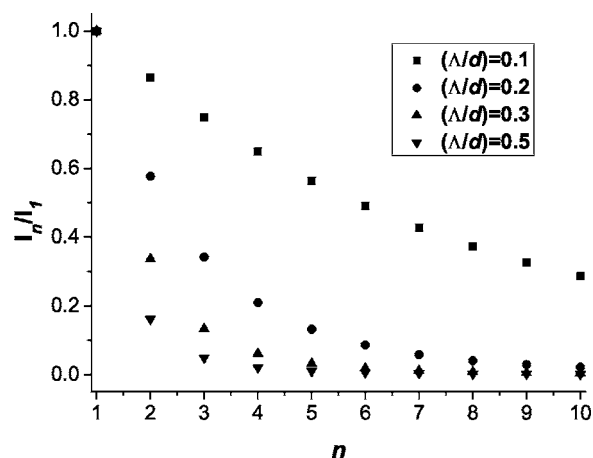


FIG. 2. The n dependence of the interlayer interaction in an infinite sample is shown in this plot of $I_n(\Lambda/D)/I_1(\Lambda/D)$ for values of the ratio Λ/D equal to 0.1, 0.2, 0.3, and 0.5.

range where the interlayer interaction is decreasing with increasing Λ/d , and hence with increasing temperature. It is, however, possible that some particular materials may have values of Λ/d below that at which the maximum of I_2 occurs. This could account for the puzzling observation [9] that in the material known as 10OHF the helical Sm- C_α^* phase unwinds on heating, while in 11OHF it tightens. These contrasting effects could be the result of a value of Λ/d that is above that where I_2 has its maximum in 11OHF, so that the interaction between next-nearest neighbors weakens with increasing temperature. The aligning forces are reduced, and the helix then tightens. For 10OHF, on the other hand, Λ/d might lie below the maximum, so that an increase in temperature, which would cause an increase in Λ/d , would lead to a strengthening of the next-nearest-neighbor interaction. This increased tendency to parallel or antiparallel alignment of c directors would cause an unwinding of the helix as the temperature is raised. A recently reported [17] phase sequence reversal in 10OHF might also be related to this possible mechanism.

The range of the interlayer interaction in a bulk sample is seen more clearly in Fig. 2, which shows how the ratio I_n/I_1 decreases with n for values of Λ/d of 0.1, 0.2, 0.3, and 0.5 and for n ranging from 1 to 10. As expected, the range of the interaction is greatest for the smallest value of Λ/d , and the interaction decays more rapidly with n at large Λ/d . The figure also indicates that the range of the interactions becomes less sensitive to change in Λ/d as this parameter is increased. In fact, for a given n , I_n/I_1 is almost independent of Λ/d when $\Lambda/d > 0.5$.

The reason for this insensitivity of I_n/I_1 to the value of Λ/d lies in the fact that the integrand in Eq. (29) has become very small at its upper limit when $\Lambda/d > 0.5$, and so the limit of integration is effectively infinite. This renders moot the discussion of how to decide the appropriate cutoff minimum wavelength permissible for layer fluctuations, since replacing Λ/d by Λ/D would have negligible effect in this regime.

V. SURFACE EFFECTS

All samples of liquid crystals are necessarily constrained by the boundaries of their containers. Even in the case of

free-standing films, the surface of the liquid crystal is subject to the forces of surface tension that tend to inhibit thermal fluctuations in the shape of the layers. Because some of the most interesting experimental results have been obtained on free-standing films of very few layers, it is necessary to consider how a free surface or substrate will modify the conclusions reached in the preceding section. In a system contained by rigid walls, thermal fluctuations of the layers nearest to the surface are suppressed, which consequently decreases the strength of interaction within these layers.

The end layers of a free-standing film have more room to oscillate than the bulk layers, and might be expected to have fluctuations of a larger amplitude than in the bulk. However, surface tension tends to suppress these fluctuations at the two surfaces. The amplitude of the interlayer interaction close to the surface is then determined by the relative strength of these two competing effects. Because the restoring forces due to surface tension vary as the square of the wave number, while those due to layer stiffness vary as the fourth power of the wave number, the effects of surface tension will be felt most strongly by fluctuations of low wave number, and hence low frequency.

The presence of the boundaries changes both the strength and range of the interactions. For an indication of how the boundaries affect the strength of the interlayer interactions, one may calculate the interaction between the first layer and its nearest neighbor in a system comprising N layers. This can be done by using Eq. (21) with $l=1$ and $l'=2$, with the sum once again replaced by an integral. To calculate $f_{l,l'}$ in the case of a free-standing film one needs an estimate for the dimensionless combination $\tilde{\sigma} \equiv \sigma/\Lambda^2 k$ that appears in Eq. (23) in the guise of the function $g(p) = (\sigma\sqrt{p}/\Lambda^2 k) - 1$. Using Eq. (16), one can write $\tilde{\sigma} = \sigma^*(\Lambda/d)^2$ with $\sigma^* = 8\sigma d^2/[3(A_{12}+A_{21})+2A_{11}]$. With the typical value $\sigma = 10^{-2}$ N/m [18] and the previously estimated values of other parameters, we find $\sigma^* \sim 3$.

In order to examine the effects of the surfaces, we compare the interaction between adjacent layers in the bulk to that between the surface layer and its immediate neighbor, as this will show the strongest influence of the surface. In the bulk the contribution to the free energy from one adjacent-layer interaction will be given by a single term in the sum in Eq. (28), this term having $n=1$ and arbitrary l . For the surface layer and its adjacent companion in a free-standing film, the factor $I_1(\Lambda/d)$ will be replaced by a term $J_{12}^{(f)}(\Lambda/d, N, \sigma^*)$, as the interaction now depends on the surface tension and the total number N of layers. For the case of a sample confined by a rigid substrate, $I_1(\Lambda/d)$ will be similarly replaced by a term $J_{12}^{(c)}(\Lambda/d, N)$. The relationship of these quantities to the originally defined functions $f_{l,l'}$ are then $2\pi(d^2/L^2)f_{1,2}(\Lambda/d, N, \sigma^*) \equiv J_{12}^{(f)}(\Lambda/d, N, \sigma^*)$ for free-standing films and $2\pi(d^2/L^2)f_{1,2}(N, \Lambda/d) \equiv J_{12}^{(c)}(\Lambda/d, N)$ for rigid substrates. We should note that while it is a comparatively simple matter to generate free-standing films with parallel surfaces and few defects, this is by no means the case for material held between rigid substrates; these results are thus reported as an illustration of the effects to be expected were such a system feasible.

The results of numerical calculations of $J_{12}^{(f)}(\Lambda/d, N, \sigma^*)$ are shown in Figs. 3(a)–3(c) for three different values of σ^* .

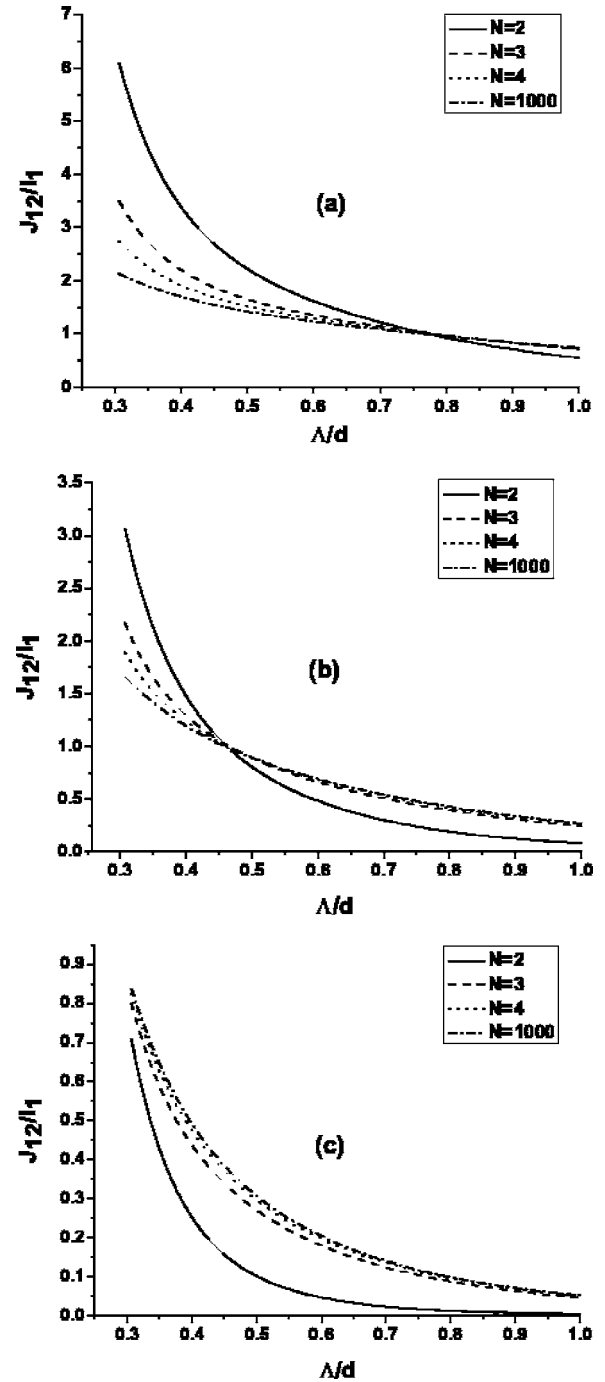


FIG. 3. The ratio $J_{12}^{(f)}/I_1$ of the interlayer interaction strength in an N -layer free-standing film to its value in a bulk sample is shown as a function of Λ/d for (a) $\sigma^* = 1$, (b) $\sigma^* = 3$, and (c) $\sigma^* = 10$.

For cells with rigid boundaries, the results are shown in Fig. 4. In these figures the ratios of $J_{12}^{(f)}$ and $J_{12}^{(c)}$ to the value $I_1(\Lambda/d)$ that would be found in the bulk have been plotted as functions of Λ/d for systems consisting of different numbers of layers. In Fig. 4, we see that the plots corresponding to $N=4$ and $N=1000$ are very close, suggesting that for a system with fixed boundaries $J_{12}^{(c)}$ is independent of the number of layers except when the cell is extremely thin.

From Fig. 3, the same conclusion can be drawn about a system with free surfaces except when Λ/d is very small, in

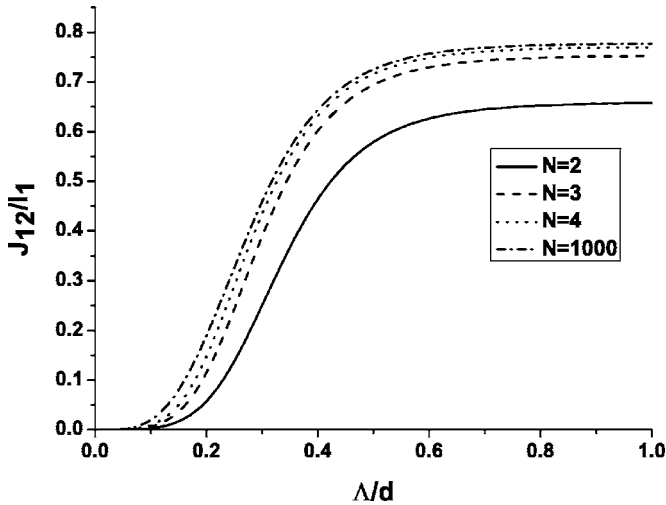


FIG. 4. The ratio $J_{12}^{(f)}/I_1$ of the interlayer interaction strength in an N -layer sample with rigid boundaries to its value in the bulk.

which case $J_{12}^{(f)}$ no longer vanishes in the limit of small Λ/d , but remains dependent on the number of layers. This is very different from the behavior of near-neighbor interactions in an infinite system shown in Fig. 1. In fact, in two- and three-layer free-standing films $J_{12}^{(f)}(\Lambda/d, N, \sigma^*)$ has its maximum at $\Lambda/d=0$. With an increasing number of layers, however, $J_{12}^{(f)}(\Lambda/d, N, \sigma^*)$ decreases and vanishes as N approaches infinity. This behavior can be understood in terms of the relative size of the elastic constants. When Λ/d is small the layer compression modulus is large, and so the layers move in unison. The entropy due to this motion is shared equally between many layers in the bulk, and so makes a negligible contribution to the free energy per layer. For a system of small N , on the other hand, the entropy is shared among only a handful of layers, and thus can have a significant effect on the phase structure of the system.

Because the interlayer interaction in confined samples depends on so many parameters, it is hard to characterize the behavior comprehensively. An illustration of how the presence of surfaces affects the range of the interaction is shown in Figs. 5 and 6, which show the strength of the interaction between the two outside surfaces of a thin film as a function of the thickness of the film. In Fig. 5 we see the variation of the ratio $r^{(f)}(N) \equiv J_{1N}^{(f)}(\Lambda/d, N, \sigma^*)/J_{12}^{(f)}(\Lambda/d, N, \sigma^*)$ with N in a free-standing film for various values of Λ/d and for $\sigma^*=1, 3, 10$, while in Fig. 6 the equivalent ratio is shown for a film held between rigid substrates. The decay in the strength of the interaction with distance again does not follow any simple power law.

The effect of the surfaces in modifying the range of the interactions is seen most clearly in Figs. 7 and 8, where the quantity plotted is the interaction between layers separated by $N-2$ intervening layers, expressed as the ratio of the value when these two layers lie on opposite surfaces of a thin sample to the value in the bulk. Thus in Fig. 7 we see the variation of the ratio $R^{(f)}(N) \equiv J_{1N}^{(f)}(\Lambda/d, N, \sigma^*)/I_{N-1}(\Lambda/d, N)$ with N in a free-standing film for various values of Λ/d and for $\sigma^*=1, 3, 10$. Two points can be noted here. First, the fact that the curves tend

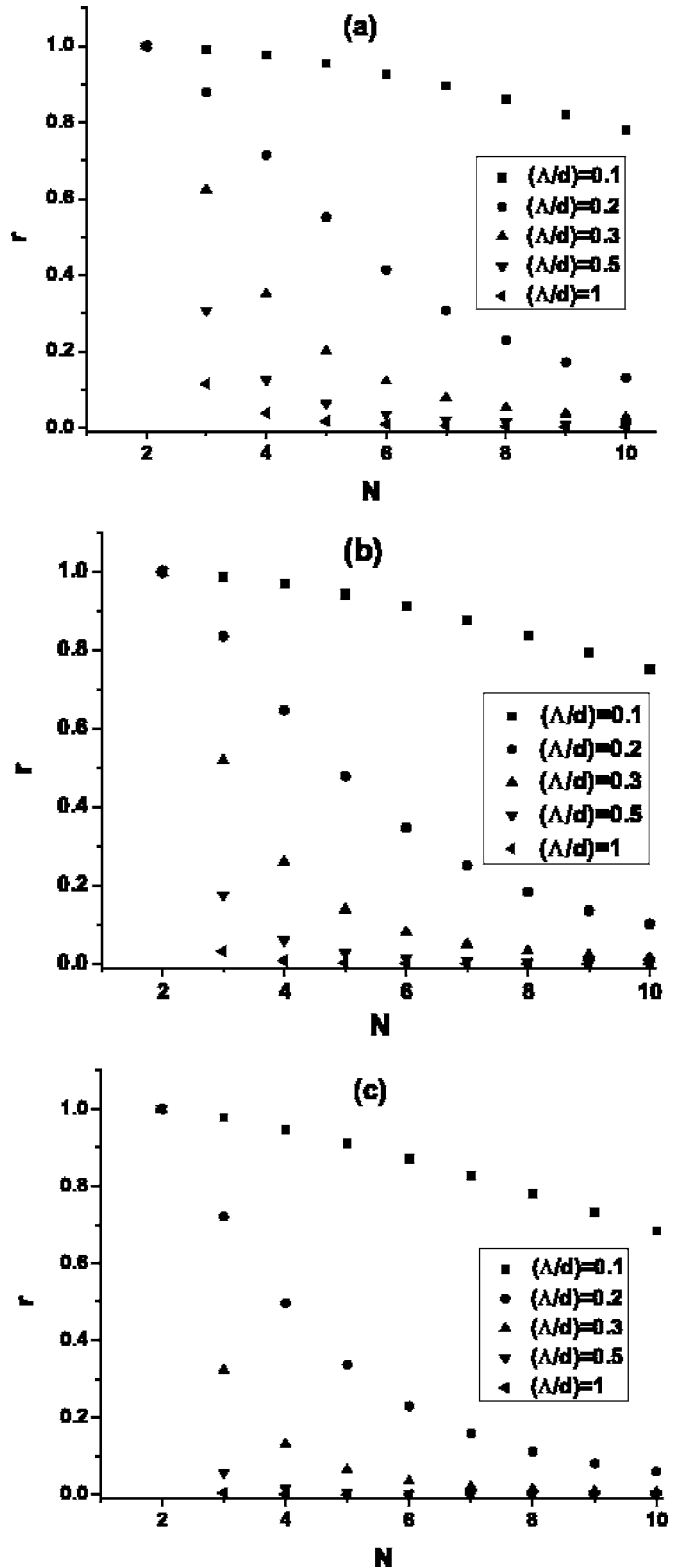


FIG. 5. The interlayer interaction between opposite surfaces of an N -layer free-standing film is shown as a fraction r of its value for a 2-layer film for various values of Λ/d when (a) $\sigma^*=1$, (b) $\sigma^*=3$, and (c) $\sigma^*=10$.

to a constant at large N shows that the manner in which the interaction decays with distance is unaffected by the surfaces for large N . Second, the relative magnitude of the interaction

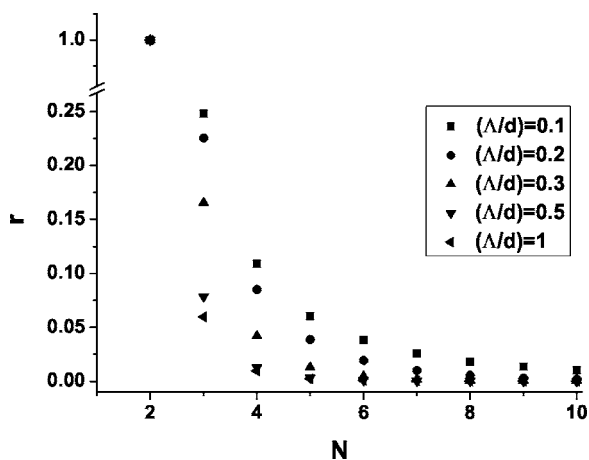


FIG. 6. As in Fig. 5, but for an N -layer film between fixed substrates. The interaction decays rapidly with N .

depends crucially on Λ/d , with a very significant enhancement of the interaction when Λ/d is small. This is to be expected, as the free surface permits fluctuations of larger amplitude when the layer compression modulus is large while the resistance to bending is small. In contrast, a rigid substrate strongly inhibits such fluctuations and reduces the interaction to insignificant values, as seen in Fig. 8.

VI. CONCLUSIONS

In this paper we have attempted to explore the nature of the interlayer interactions in smectic liquid crystals that arise from correlations in the thermal fluctuations of the shape of the layers. We have found that within a bulk sample, the range of this interaction depends principally on the ratio of a characteristic length Λ , defined in terms of a ratio of elastic constants, to the layer thickness. The way in which this interaction decays with distance does not follow any simple power law except at large separations. For samples in the form of free-standing films, the picture is more complex, as the surface tension adds an additional parameter, and there are opposing effects of the absence of neighboring layers and the confining effect of surface tension, the latter being most prominent for fluctuations of large wavelength. As would be expected, the presence of rigid confining substrates always reduces the strength of the interaction by suppressing fluctuations.

The absolute strength of the interaction that we have calculated can be expressed as a free energy per molecule that is equal to the product of $k_B T$ with three other factors, all of which are less than unity. Of these, the most important is an anisotropy parameter that describes the difference in elastic constants for bending a layer around an axis parallel or perpendicular to the c director. A second factor is approximately the square of the ratio of molecular diameter to its length. The third factor is a function of the layer thickness and the ratio of the average bending elastic constant to the layer compression modulus, and has its maximum at intermediate values of this ratio.

In order to compare the magnitude of our predicted interaction with the amount required to influence the phase dia-

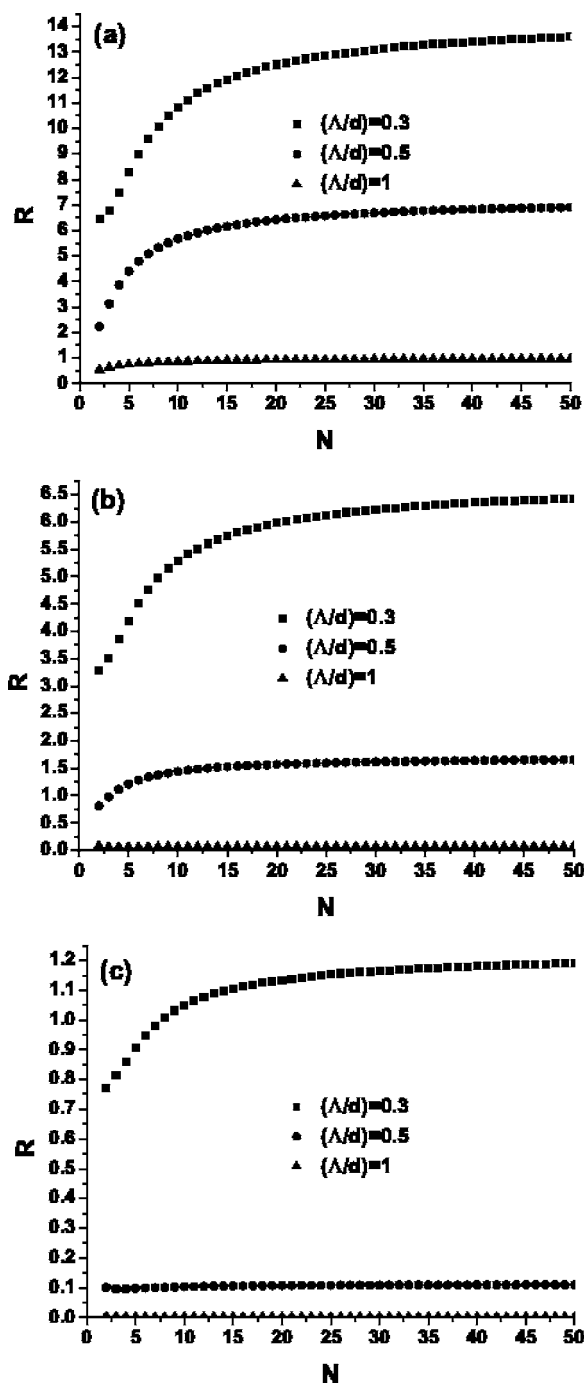


FIG. 7. The interlayer interaction between opposite surfaces of an N -layer free-standing film is shown as its ratio R to the interaction when these layers lie in a bulk sample. For small reduced surface tension σ^* the interaction is enhanced. (a) $\sigma^* = 1$, (b) $\sigma^* = 3$, and (c) $\sigma^* = 10$.

gram, we approximate Eq. (28) to write the change in free energy per unit volume as

$$\frac{\Delta \mathcal{F}}{NL^2 d} \approx \frac{k_B T}{8\pi d^3} \Gamma_1^2 \sum_n I_n(\Lambda/d). \quad (30)$$

For a layer thickness d of 3 nm, the energy density $k_B T / 8\pi d^3$ will be about 7 kJ/m³ at 60 °C. To estimate the

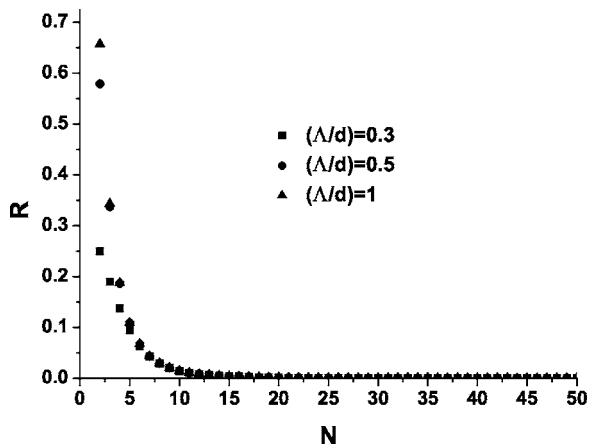


FIG. 8. As in Fig. 7, but for layers in contact with fixed substrates.

anisotropy parameter Γ_1 , we note that if the tilt angle θ could approach $\pi/2$, then the director would lie in the layer plane along the axis x_l . There would then be no elastic resistance to bending a layer about this axis, and consequently A_{21} would vanish, A_{11} would be small, and we would have $\Gamma_1 \geq 1$. If we suppose Γ_1 to vary as $\sin^2 \theta$, then for a typical tilt angle of 18° we would have $\Gamma_1 \sim 0.1$ and $(\Gamma_1)^2 \sim 0.01$. The remaining factor, which is a sum over n of $I_n(\Lambda/d)$, has a maximum possible value of about 0.14 when the term with $n=1$ is included in the sum, but a little less than one-half of that when the first term in the sum, which represents interactions between adjacent layers, is excluded. The product of these factors yields an effective interaction strength per unit volume of about 10 J/m^3 when nearest-neighbor layers are included.

It might at first be thought that such a perturbation would be too small to modify the phase diagram. However, it turns out that the differences in free energy between the various phases of antiferroelectric liquid crystals are very small indeed. One can appreciate just how small they are by calculating the difference $\Delta\mathcal{E}$ between the free energies of the ferroelectric and antiferroelectric phases in a typical material far from its transition temperature. We obtain this number by considering the electric field strength E_0 necessary to switch a material from its antiferroelectric phase, which has no net dipole moment per unit volume, to a ferroelectric phase having a dipole moment per unit volume P_0 . The electrostatic energy per unit volume, $P_0 E_0$, will then be equal to $\Delta\mathcal{E}$. The switching field is of the order of 0.3 MV/m [19], and the dipole moment per unit volume is probably around $700 \mu\text{C/m}^2$ [20], making $\Delta\mathcal{E} \sim 200 \text{ J/m}^3$.

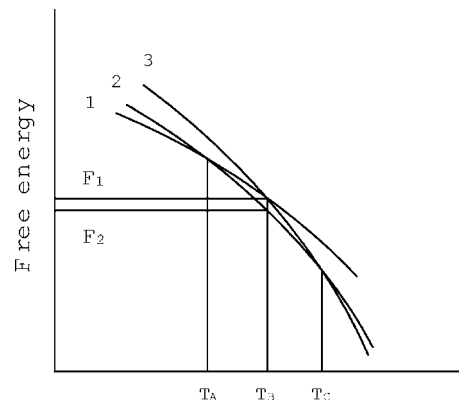


FIG. 9. The free energy difference between phases is roughly the product of two small factors, namely the entropy difference between phases and the temperature extent of the intermediate phase.

While this value of 200 J/m^3 is somewhat larger than the 10 J/m^3 cited earlier, the free energy difference between the helical phases is likely to be much smaller than the 200 J/m^2 estimated for the free energy difference between the Sm-C_A^* and Sm-C^* phases. To see this we consider the case of a system that has three phases, 1, 2, and 3, with successive transitions at temperatures T_A and T_C , as illustrated in Fig. 9. We are concerned with the difference in free energy, $F_1 - F_2$, between phase 2 at some intermediate temperature T_B and the free energy that phase 1 or 3 would have, were it stable, at T_B . The order of magnitude of this difference will be the product of the small temperature difference $T_B - T_A$ with the difference in slopes of lines 1 and 2 at T_A . This difference in slope is just the latent heat of transition between phases 1 and 2 divided by T_A , making $F_1 - F_2$ two orders of magnitude smaller than the latent heat of transition at T_A . If we accept that the free energy difference between the Sm-C_{FI1}^* and Sm-C_{FI2}^* helical phases is just one order of magnitude less than the free energy difference between the antiferroelectric Sm-C_A^* and the ferroelectric Sm-C^* , then we arrive at a figure comparable to our calculated 10 J/m^3 . The magnitude of the effect that we have studied is thus in the right range to have a significant effect. Nevertheless, a definitive identification of the effects of correlations in layer fluctuations may have to await experimental measurements of the actual dynamics of layer motion.

ACKNOWLEDGMENT

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