Repulsive forces in thin smectic-C^* films on substrates

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X-ray reflectivity studies of spin-coated ultrathin films of smectic-C^* liquid crystals show dramatic variation of the smectic layer spacing L as a function of the number of smectic layers n. Results for three different liquid crystals suggest a long-range force between the interfaces that decays algebraically like $1/n^{\gamma}$ where $\gamma=3.0\pm0.3$. This decay is consistent with a van der Waals type of force, although its magnitude cannot be explained by the existing mechanisms. Interactions between the electric dipoles and their images as well as the formation of ferroelectric domains may provide a mechanism to explain the magnitude of the force.

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Thin and ultrathin films of smectic liquid crystals are a subject of growing interest [1–4]. The thickness and stability of such films are determined, among other factors, by long-range forces between the interfaces [5–9]. The most common force between interfaces is due to the van der Waals (vdW) type of interaction. This force, neglecting retardation effects, decays like $1/d^3$, where d is the film thickness [10,11]. Recently, several authors have demonstrated that the imposed boundary conditions at the film interfaces may change the energy associated with thermal fluctuations, leading to induced forces between the walls [6–9]. These are analogous to the "Casimir force" between parallel conducting plates which is induced by quantum fluctuations of the electromagnetic field [12]. Particularly, it has been shown that smectic fluctuations may lead to a long-range force, which decays as $1/d^2$ for smectic layers parallel to the film interfaces (to be denoted hereafter as "pseudo-Casimir" force [6–9]). There are several other long-range thermally induced forces, including the Helfrich force [13] (undulation fluctuations), which dominates in fluid membrane systems [14]. The possibility of long-range forces, decaying as $1/d^2$, between interfaces generated interesting experiments on free-standing smectic films having symmetric boundary conditions [2]. However, there is practically no information, in this respect, on ultrathin smectic films on substrates, where the forces between the interfaces are expected to be different due to the nonsymmetric walls [6,7]. Motivated by the recent theories [5–13] and experiments [2] we have carried out x-ray reflectivity measurements with the aim of exploring the nature of the forces between the interfaces of thin and ultrathin smectic-C^* films on substrates. A smectic-C^* liquid crystal is a tilted smectic phase in which the molecules are chiral [15]. The reduced symmetry (due to the absence of a mirror plane) leads to spontaneous ferroelectric polarization along the layers [15].

The forces between interfaces can be examined by detailed studies of the smectic layer spacing L as a function of the film thickness d (or equivalently as a function of the number of smectic layers n). We consider a simple phenomenological model which assumes that the film thickness is determined by the long-range forces. We then assume that the smectic layers are parallel to the interface and that L and d are commensurate, namely, $d=nL$. We define a coordinate system in which the z axis is perpendicular to the film. The free-energy per unit area f can be expressed then as the sum of two energy terms: $f=f_1+f_2$, where f_1 is the interaction energy between the interfaces due to (a) conventional vdW interaction [10,11], (b) thermally induced interactions entropic in origin [6,7,13], (c) electrostatic interaction, or (d) any other long-range interaction that depends on the film thickness d. A common feature of all these long-range interactions is the algebraic $1/d^{\kappa}$ decay. The second term f_2 is the Landau–de Gennes elastic energy [6,16]. In the first approximation, neglecting the splay contribution to the elastic energy, the various energy terms (per unit area) can be written as follows [6,7]:

$$f_1=A/d^{\kappa}=A/(nL)^{\kappa}\ , \tag{1a}$$

$$f_2=\tfrac{1}{2}\int_0^d B(\partial u/\partial z)^2 dz\cong\tfrac{1}{2}BnL[(L-L_0)/L_0]^2\ , \tag{1b}$$

where $\kappa=2$ for vdW or entropic interactions and $\kappa=1$ for the pseudo-Casimir [6] or electrostatic interaction. The parameter A in Eq. (1a) is the force constant, the parameter B in Eq. (1b) is the modules for layer compression [14,16], $u(z)$ is the layer displacement in the z direction (the $z=0$ plane coincides with the film-air interface), L is the actual smectic layer thickness, and L_0 is the layer thickness appropriate to very thick films. Minimizing the total free energy f with respect to L under the assumption that $L-L_0\ll L_0$, yields the following approximate result:

$$L=L_0+(\kappa A/BL_0^{\kappa})(1/n^{\kappa+1})=L_0+\beta(1/n^{\gamma})\ . \tag{2}$$

Equation (2) predicts a dependence of the layer spacing L on the number of layers n. The nature of the forces is determined by the parameter $\gamma=\kappa+1$. In this paper we have studied $L(n)$ at fixed temperatures with the aim of determining the parameter γ.

We have applied the specular x-ray reflectivity technique to study the thin films of three chemically different commercial ferroelectric liquid crystal (FLC) mixtures, namely, FELIX-008 (produced by Hoechst, Frankfurt) [17], ZLI-3654 (Merck, Darmstadt) [17,18], and SCE9 (British Drug House, England) [19]. These FLC mixtures

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were chosen because of (a) our ability to prepare high quality films on various substrates by the spin-coating technique; (b) the existence of a smectic-C^* phase at room temperature and smectic layering parallel to the substrate; and (c) the fact that smectic-C^* liquid crystals are commonly used in fast electro-optical cells, the so-called "surface-stabilized ferroelectric liquid crystal" (SSFLC) devices [17,20]. So, there is some information on their wetting properties on the one hand, and technological interest in the films' properties on the other hand. The phase-transition temperatures of these films are given elsewhere [17–19]. The bulk smectic-A–smectic-C^* phase-transition temperatures of these FLC mixtures are 60 °C (ZLI-3654), 70 °C (FELIX-008), and 61 °C (SCE9) [17–19]. Films were prepared by dissolving the FLC in certain solvents (tetrahydrofuran or toluene) and casting the solution onto very smooth float-glass substrates [18]. Film thicknesses (60–1100 Å) could be controlled within ±30 Å by varying the FLC concentration and the rotation speed of the coater. The film's quality in the lateral direction was checked using optical and atomic force microscopes. These studies have indicated the presence of domains in some of the samples. Samples prepared on rough substrates always show the presence of domains and liquid crystal droplets on the film surface. Films prepared on high-quality substrates exhibit remarkable stability (over more than a month in the air) and do not show any evidence for dewetting in air at room temperature and above. The specular x-ray reflectivity setup is based on a high-resolution x-ray spectrometer described elsewhere [18,21]. It used a Cu $K\alpha$ ($\lambda=1.54$ Å) beam from a narrow line source of a 12 kW Rigaku rotating anode generator. Temperature stability and homogeneity of 0.1 K was achieved using a vacuum oven.

Figure 1 exhibits typical specular x-ray reflectivity spectra of several films having different thicknesses and, therefore, a different number of smectic layers n. The data in Fig. 1 were collected after annealing for a long time to ensure an equilibrium state. This is because immediately after the coating process the films are not in an equilibrium state but approach an equilibrium by increasing their thickness d and layer spacing L. This will be described elsewhere. Kiessig oscillations [22] and quasi-Bragg peaks are clearly seen in Fig. 1. The latter suggests the formation of smectic layers parallel to the substrate. The layer thickness L is obtained by a fit to a model of Entin and others [3,18]. This model assumes that the total reflected complex amplitude is the coherent summation of beams scattered from the interfaces and from the density modulation (associated with the smectic layering). The latter is assumed to be of the following form:

$$\delta\rho(z)=\tfrac{1}{2}\rho_2[e^{-z/\xi}w\cos\{[2\pi z/L(z)]+\varphi\} + e^{(d-z)/\xi'}w'\cos\{[2\pi(d-z)]/L(z) + \varphi'\}]+\text{h.h.}\,, \quad (3)$$

where ρ_2 is the average density of the film, w and w' are the amplitudes of the density modulation, $L(z)$ is the layer thickness (which may vary slightly across the film along the z axis), φ and φ' are the phases of the electron density modulation, ξ and ξ' are the coherence lengths for the order induced by the film-substrate and film-air interfaces, and h.h. indicates higher harmonics.

The use of the modified sinusoidal electronic density in Eq. (3) requires justification, particularly in view of a recent paper by Tweet *et al* [1]. These authors have argued that the tilt angle varies slightly across the free-standing films of "70.0" liquid crystal, being smaller for the outer layers; the variation decreases with the decrease of the film thickness. For example, for $n=5$ one can estimate from their data a thickness difference of approximately 0.2 Å between an outer layer and an inner layer due to changes of the tilt angle. Tweet *et al.* [1] have calculated the electron density across their films by convoluting the "real" molecular electron density with the normalized Gaussian center-of-mass distributions of the "70.0" molecules. We found that the calculated electron density of Tweet *et al.* (Fig. 2 in Ref. [1]) deviates only slightly from the modified electron density described by Eq. (3) above; the deviations are manifested by slight changes of the density amplitudes with respect to a sinusoidal function. Furthermore, the FLC mixtures presented here consist of many components with different molecular electron densities. This may lead to some "smearing" of the electron

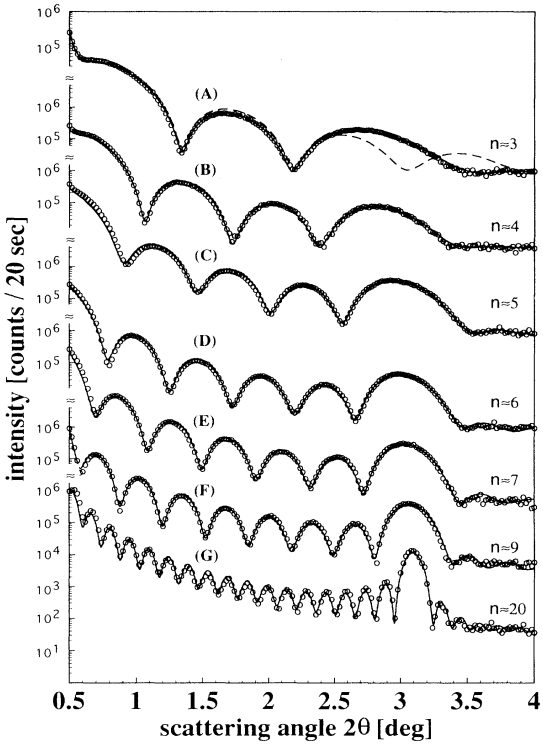

FIG. 1. Typical specular x-ray reflectivity spectra for films with different thicknesses of the SCE9 liquid crystal mixture on float glass substrates at $T=301$ K and normal air pressure. Measurements were carried out a week after spin coating to achieve an equilibrium state. The solid lines are the best fit to the model. The fit yields: (A) $d=100\pm2$ Å and $L=29.9\pm0.5$ Å; $d/L=3.3$. (B) $d=128\pm2$ Å and $L=29.5\pm0.3$ Å; $d/L=4.3$. (C) $d=153\pm3$ Å and $L=28.80\pm0.10$ Å; $d/L=5.3$. (D) $d=179\pm3$ and $L=28.68\pm0.05$ Å; $d/L=6.2$. (E) $d=210\pm3$ Å and $L=28.55\pm0.05$ Å; $d/L=7.3$. (F) $d=263\pm3$ Å and $L=28.56\pm0.05$ Å; $d/L=9.2$. (G) $d=580\pm5$ Å and $L=28.56\pm0.05$ Å; $d/L=20.3$. The dashed line is the best fit to the reflectivity of film (A) in the absence of smectic order. The number of smectic layers, n ($n\approx d/L$), is indicated.

density of the individual molecules. Indeed, the similarity of the experimental data (Fig. 2) for the three chemically different liquid crystals suggests that the results and the fitting are not very sensitive to any specific molecular electron density profile. We believe, therefore, that the modified sinusoidal-like form factor, Eq. (3), is a very reasonable assumption for these FLC mixtures. The fitting procedure involves several free parameters, including L,d, roughness parameters, the amplitude and the phase of the electronic density modulation (associated with the smectic layering), and the average electronic density [3,18,23]. The present work, however, is mainly concerned with the layer spacing L (and the film thickness d). We find excellent fits to the experiment reflectivity profiles assuming the sinusoidal-like density [i.e., $L(z)=$const] given by the Fourier series in Eq. (3). The solid lines in Fig. 1 represent the best fit of the model to the experimental data, assuming a sinusoidal form factor (i.e., assuming that ξ and ξ' are infinite or at least very large and that L is independent of z). We could also find very good fits, assuming finite values of ξ. However, these fits give the same values of L and d, and the extracted ξ values are much larger than the film thickness. In view of the excellent fits with sinusoidal-like electronic density and $L(z)=$const, we believe that if L depends on z at all, this is a very weak dependence. The excellent fits allow determination of L with a high accuracy, better than ± 0.05 Å for films of $n \geq 5$. The error in the determination of L for ultrathin films ($n \leq 5$) is significantly larger, of the order of 0.5 Å.

The extracted values of L versus the number of layers n are plotted in Fig. 2. Note the remarkable increase of L with the decrease of n for ultrathin films. This increase is too large to be explained by changes in the tilt angle alone and is attributed to other structural changes to be discussed elsewhere. Note also that the ratio $d/L \approx n$ is not always an integer number, probably due to the film's roughness. The data in Fig. 2 can be well fitted to the functional dependence: $L(n)=L_0+\beta/n^{\gamma}$ with $\gamma=3\pm0.3$ for all three chemically different FLC mixtures (solid lines in Fig. 2). The fitting parameters are $L_0=27.76$ Å and $\beta=49.6$ Å for films of ZLI-3654, $L_0=28.17$ Å and $\beta=63.5$ Å for films of FELIX-008, and $L_0=28.55$ Å and $\beta=43.2$ Å for films of SCE9. A better demonstration that indeed $\gamma \approx 3$ is obtained by a plot of $L-L_0$ versus n on a log-log scale (inset of Fig. 2) taking into consideration only ultrathin films, $n \leq 10$, for which the error in $L-L_0$ is significantly smaller. We clearly see that γ varies between $\gamma=2.7$ and $\gamma=3.1$, which suggests [Eq. (2)] that $\kappa \approx 2$. A fit assuming $\gamma=2$ (i.e., $k=1$ appropriate to a pseudo-Casimir force) or exponential function [23] is not satisfactory (inset, Fig. 2).

The observation of the power-law $1/d^3$ decay of the force for all the mixtures (Fig. 2) may indicate that the vdW type of interaction dominates. This allows an estimate of the force constant A, provided that the modulus for compression B is known. Estimates of B for a bulk smectic-C^* liquid crystal have indicated values in the range from 10^7 to 10^8 dyn/cm^2; for thin films the value of B is unknown. Under the assumption [24] that $B=10^7$ dyn/cm^2 (this assumption may be incorrect), the fitting

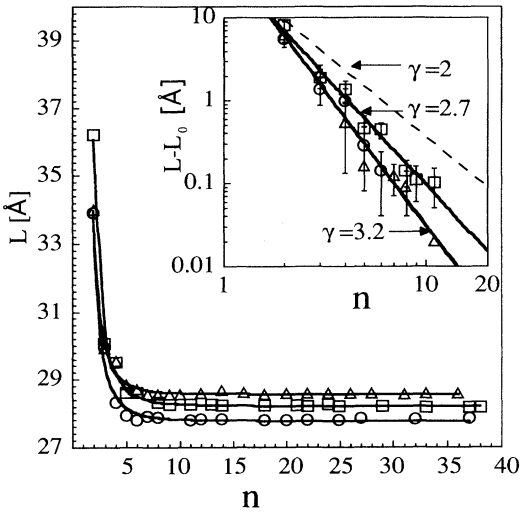

FIG. 2. Layer thickness versus the number of layers for films of three different FLC mixtures at $T=301$ K. The open symbols (□ for FELIX-008, ○ for ZLI-3654, and Δ for SCE9) indicate measurements at normal pressure. The solid lines are the best fit to the formula: $L=L_0+\beta/n^{\gamma}$, $\gamma=3$; the fitting parameters L_0 and β are given in the text. Inset: A plot of $L-L_0$ versus the number of layers n on a log-log scale for the different FLC mixtures. The solid lines are the best fits. The fits yield $\gamma=3.2\pm0.2$ for ZLI-3654 (○), SCE9 (△), and $\gamma=2.7\pm0.3$ for the FELIX-008 (□). The dashed line indicates a fit assuming $\gamma=2$.

parameter β allows the determination of the force constant to be $A=(2\pm1)\times10^{-13}$ ergs for films of both ZLI-3654 and SCE9 and $A=(2.7\pm1)\times10^{-13}$ ergs for films of FELIX-008. For larger B, A will be even larger. This gives an estimate of the Hamaker constant H ($H=12\pi A$ [6,7]) to be of the order of $H/k_BT \approx 100$. This value of H is larger by two orders of magnitude with respect to conventional Hamaker constants of simple liquids [10,11] (which are of the order of 10^{-14} ergs; i.e., of the order of k_BT). Independent estimates of the Hamaker constant for our materials using conventional models [10] and the measured refraction indices in the optical visible range [25] *cannot* explain either the magnitude or the sign of H.

We suggest a possible model associated with the interaction between the electric dipoles and their images to explain the sign and the magnitude of the Hamaker force constant in thin films of FLC. Certainly, this model is very attractive for ferroelectric smectic-C^* films. We consider the interface between the FLC film (with an average dielectric constant $\varepsilon_2=2.3$) and the air (with dielectric constant $\varepsilon_1=1$). In the first approximation the film-substrate interface is neglected because of the small dielectric contrast. In films of ferroelectric liquid crystals the ferroelectric polarization is in the plane of the film, so we shall consider a set of dipoles parallel to the interface occupying the positions $\mathbf{r}_i$ and interacting with their image dipoles at $\mathbf{r}_i'$ ($=\mathbf{r}_i-2\hat{\mathbf{k}}\hat{\mathbf{k}}\cdot\mathbf{r}_i$; $\hat{\mathbf{k}}$ is a unit vector in the z direction). A dipole $\boldsymbol{\mu}$ located at the position $\mathbf{r}$ will induce an image dipole $\boldsymbol{\mu}'$ at $\mathbf{r}'$:

$$\boldsymbol{\mu}'=[(\varepsilon_2-\varepsilon_1)/(\varepsilon_1+\varepsilon_2)](2\hat{\mathbf{k}}\hat{\mathbf{k}}\cdot\boldsymbol{\mu}-\boldsymbol{\mu}) . \quad (4)$$

The interaction energy may then be written as

$$U=\frac{1}{2\varepsilon_1}\frac{\varepsilon_1-\varepsilon_2}{\varepsilon_1+\varepsilon_2}\sum_{l,m}\frac{\boldsymbol{\mu}_l\cdot\boldsymbol{\mu}_m[R_{lm}+(2_l+2_m)^2]-3\boldsymbol{\mu}_l\cdot\mathbf{R}_{lm}\boldsymbol{\mu}_m\cdot\mathbf{R}_m}{[R_{lm}^2+(z_l+z_m)^2]^{5/2}}\ , \tag{5}$$

where $\mathbf{r}_i=\mathbf{R}_i+z_i\hat{\mathbf{k}}$, $\mathbf{R}_i=x_i\hat{\mathbf{i}}+y_i\hat{\mathbf{j}}$. The Hamaker constant is calculated as follows: let u_k denote the contribution to the interaction energy between the dipoles and their images from the kth layer. The energy for finite n layers is U_n and for an infinite number of layers is U_∞. The Hamaker constant H is defined through the following formula:

$$U_n=\sum_{k=1}^{n}u_k=\sum_{k=1}^{\infty}u_k-\sum_{k=n+1}^{\infty}u_k=U_\infty-\frac{HS}{12\pi d^2}\ , \tag{6}$$

where d ($d=Ln$) is the distance of the nth layer from the interface and S is the surface area. Assuming domains with a surface area of $M\times M$ molecules with an average distance b between the molecules, the surface area can be written as $S=(Mb)^2$. It can be shown that the Hamaker constant can be calculated using the following formula (in the limit of very large n):

$$H=[6\pi n^3L^2/(Mb)^2](U_n-U_{n-1})\ . \tag{7}$$

We apply the above formulas to the situation in which domains are formed by the dipoles. Several models with different domain size and different assumptions concerning the magnitude and direction of the dipoles have been considered. Here we emphasize a model which assumes that the domains are of size $M\times M\times 1$. All the dipoles in the domain are taken to be parallel to each other. In a neighboring domain the orientation of the dipoles is at random with respect to the original domain, so domains in adjacent layers are uncorrelated. Thus the interactions in Eq. (5) consist of an incoherent superposition of contributions from the different domains. Values used for the various parameters are $\varepsilon_1=2.3$, $\varepsilon_2=1.0$, $L=30$ Å, and $b=5$ Å. Numerical simulations using Eq. (7) show that the Hamaker constant converges to a definite value as n increases. This indicates that, indeed, the force decays as $1/d^3$. We note the following trends: the Hamaker constant scales roughly as μ^2. Also, the Hamaker constant scales as M^2, up until a value of M such that $Mb\approx nL$. The simulations indicate that for a domain size of ~ 300 Å and a typical value of μ ($\mu\sim 0.5$ D; $1D=10^{-18}$ esu cm) the Hamaker constant is of the order of $H/k_BT\approx 10$. This is lower than our experimental estimate but it is higher than the predictions of conventional mechanisms [10,11]. Unfortunately, there is no information on the domain size and the exact value of μ. However, the above model can explain the large Hamaker constant if the dipoles are large. It is possible (although highly speculative) that the magnitude of the dipole moments is enhanced due to surface interactions in thin films. A critical check of the model requires further studies in the presence of an in-plane electric field (which may affect the domain size) or on thin-smectic-A films.

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