Fluctuations in Thin Smectic-*A* Films

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The smectic layer displacement fluctuation profile, $\sigma(\mathbf{r})=\langle u^2(\mathbf{r})\rangle^{1/2}$, has been calculated for thin smectic-*A* films. In thin smectic-*A* films the calculated fluctuation amplitudes are only $\sigma\approx 4$ Å, compared to $\sigma\approx 8$ Å in a macroscopic sample. The fluctuations are suppressed at the two free surfaces by the surface tension, grow rapidly away from each surface, and have a parabolic profile near the center of the film. These results are in quantitative agreement (± 0.1 Å) with recent x-ray measurements.

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According to the famous Landau-Peierls[1] argument, the divergent thermal fluctuations destroy, in the thermodynamic limit, the long-range order in any periodic, one-dimensional structure (in particular, three-dimensional smectic-*A*'s). However, in practice, the logarithmic growth of the fluctuations with the size of the system is so slow that it is very difficult to directly observe the destruction of the long-range smectic order in typical experimental samples.[2] This paper addresses some of the unresolved questions about fluctuations in finite smectic systems: What are the fluctuation profiles in thin smectic systems and how do they grow with the size of the sample? How does the surface tension affect the surface fluctuations and how does it influence extend into the film? How large is the contribution due to the hydrodynamic, long-wavelength fluctuations compared to that from the short-wavelength fluctuations produced by the individual molecular motions and how do both compare to the measured fluctuations?

For a smectic-*A*, the bulk fluctuation Hamiltonian H_B in the harmonic approximation is given by[3-6]

$$H_B=\tfrac{1}{2}\int d\mathbf{r}\left[B\left(\frac{du(\mathbf{r})}{dz}\right)^2+K[\Delta_\perp u(\mathbf{r})]^2\right]. \qquad (1)$$

Here $u(\mathbf{r})$ describes the displacement of each smectic layer from its original equilibrium position $\mathbf{r}$, while B is the smectic elastic constant associated with layer compression and K is the elastic constant associated with layer bending. If the system is large, but finite, in the direction perpendicular to the smectic layers and infinite in the two transverse directions, then the fluctuations far from the sample boundaries can be calculated using Eq. (1):

$$\sigma^2(\mathbf{r})=\langle u^2(\mathbf{r})\rangle=\frac{k_BT}{4\pi\sqrt{KB}}\ln\frac{\sqrt{\lambda D}}{a_0}. \qquad (2)$$

Here D is the sample thickness, a_0 is the molecular diameter, k_BT is the thermal energy, and $\lambda=\sqrt{K/B}$ is the characteristic smectic length in the system. For typical values of the parameters appearing in Eq. (2) (i.e., $\lambda=20$ Å, $D=1$ cm, $\sqrt{KB}=5$ dyn/cm, $a_0=4$ Å, and $k_BT=4\times10^{-14}$ erg), the corresponding layer fluctuation amplitude is $\sigma=7.7$ Å. Since these fluctuations are smaller than the layer spacing, $d=30$ Å, the smectic layers in a 1-cm-thick sample are still well defined. However, these 7.7-Å fluctuations dramatically reduce the intensity of the higher-order $(00l)$ reflections from the smectic layers.[2,7]

We now consider a thin smectic-*A* film with N_A layers. The displacement fluctuations in this system are described by a Hamiltonian H with surface H_S and bulk H_B [Eq. (1)] contributions: $H=H_B+H_S$, with

$$H_S=\tfrac{1}{2}\gamma\int d\mathbf{r}_\perp[|\nabla_\perp u(\mathbf{r}_\perp,z=0)|^2+|\nabla_\perp u(\mathbf{r}_\perp,z=Nd)|^2]. \qquad (3)$$

Here γ is the smectic-*A*/air surface tension and $N_A=N+1$. Since the system consists of a finite number of layers in the z direction, it is natural to use a discrete version of this Hamiltonian with respect to z: $u(\mathbf{r}_\perp,z=nd)\equiv u_n(\mathbf{r}_\perp)$. Taking the continuous Fourier transform with respect to $\mathbf{r}_\perp$ results in a compact expression for the full Hamiltonian H:

$$H=\tfrac{1}{2}\int d\mathbf{q}_\perp\sum_{i,j=0}^{N}u_i(\mathbf{q}_\perp)M_{ij}u_j(-\mathbf{q}_\perp). \qquad (4)$$

Here the only nonzero elements of the symmetric matrix $\mathbf{M}$ are on the diagonal and in the first off-diagonal positions. They are given by the following formulas:

$$M_{00}=M_{NN}=\gamma q_\perp^2+Kdq_\perp^4+B/d\equiv a, \qquad (5)$$

$$M_{ii}=Kdq_\perp^4+2B/d\equiv b,\quad i=1,\ldots,N-1, \qquad (6)$$

$$M_{i+1i}=M_{ii+1}=-B/d\equiv c,\quad i=0,\ldots,N-1. \qquad (7)$$

The layer displacement fluctuations can now be calculated from the diagonal elements of $\mathbf{M}^{-1}$, namely,

$$\sigma_i^2(\mathbf{r}_\perp)=\langle u_i^2(\mathbf{r}_\perp)\rangle=k_BT\int\frac{d\mathbf{q}_\perp}{(2\pi)^2}(\mathbf{M}^{-1})_{ii}. \qquad (8)$$

The limits of this integration are $2\pi/W<|q_\perp|<2\pi/a_0$;

the lower limit is set by the transverse size of the film, W, and the upper limit is set by the molecular diameter since transverse modes with wavelengths smaller than the molecular diameter or larger than the film cannot be excited. For real measurements, the long-wavelength cutoff will usually be set by the instrument resolution rather than by the sample size.[8] The diagonal elements of the matrix $\mathbf{M}^{-1}$ are given by

$$(\mathbf{M}^{-1})_{ii} = A_i A_{N-i}/C_{N+1}, \tag{9}$$

where

$$C_j = a^2 T_{j-2} - 2ac^2 T_{j-3} + c^4 T_{j-4}, \quad j>2, \tag{10}$$

$$A_j = aT_{j-1} - c^2 T_{j-2}, \quad j=1,\ldots,N, \tag{11}$$

$$T_j = b^j \frac{\eta_+^{j+1} - \eta_-^{j+1}}{\eta_+ - \eta_-}, \tag{12}$$

and

$$\eta_\pm = \frac{1 \pm [1-4(c/b)^2]^{1/2}}{2} \tag{13}$$

for $i=0$, $A_0=1$.

Most of our calculations were performed assuming typical smectic parameters: $K=10^{-6}$ dyn and $B=2.5\times10^7$ dyn/cm^2 (so $\lambda=20$ Å), $d=30$ Å, $a_0=4$ Å, $\gamma=60$ dyn/cm, and $W=4\times10^5$ Å. The calculated fluctuation profiles σ_i for 7-, 11-, 21-, and 37-layer-thick films are shown in Fig. 1. The calculation shows that fluctuations at the surface are suppressed by $\sim 1-2$ Å relative to the fluctuations inside the sample and that the fluctuation amplitudes grow rapidly in the first two layers close to each surface. For thicker films (e.g., 37 layers) the fluctuation profile near the center of the film is parabolic. The maximum fluctuation amplitude occurs at the center of the film and the center fluctuations grow by ~ 1.1 Å as the film thickness increases from 3 to 37 layers. At the free surfaces, the fluctuations are strongly suppressed by the surface tension and only grow by ~ 0.13 Å between 3 and 37 layers. For infinitely thick films with a transverse cutoff, $W=4\times10^5$ Å, the layer fluctuation amplitude σ_C at the center of the film is 7.4 Å.

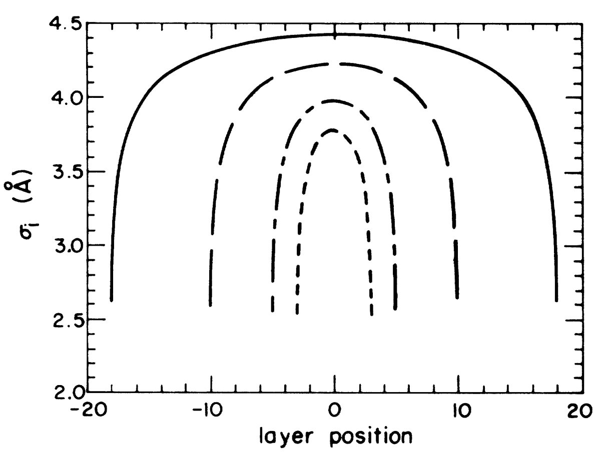

FIG. 1. The discrete layer displacement fluctuation profile $\sigma_i = \langle u_i^2 \rangle^{1/2}$ vs the layer index i. The lines connecting the discrete points have been added for visual clarity. The calculated profiles are shown for a 7-layer-thick film (short-dashed line), an 11-layer-thick film (long-dashed–short-dashed line), a 21-layer-thick film (long-dashed line), and a 37-layer-thick film (solid line).

The calculated dependence of the surface fluctuation amplitude σ_S on the surface tension is shown in Fig. 2 for a 3-layer- and a 37-layer-thick film. As γ increases from 30 to 60 dyn/cm, the surface fluctuations decrease from ~ 3.5 to ~ 2.5 Å. The asymptotic dependences of σ_S vs γ follow directly from Eqs. (4)–(13): For very large values of the surface tension ($\gamma \to \infty$), the surface fluctuations go to zero as $\sigma_S \sim \gamma^{-1}$; for very small surface tensions ($\gamma \to 0$), the surface fluctuations diverge as $\sigma_S \sim q_\perp^{-2}$ up to the limit set by the transverse cutoff, $q_\perp = 2\pi/W$. The influence of γ on the complete fluctuation profile of an 11-layer-thick film is shown in Fig. 3. The largest effects are at the surface (σ_S is reduced from ~ 2.6 to 0 Å as γ increases from 60 dyn/cm to ∞), but there is also a significant effect at the center of the film (σ_C is decreased by 0.5 Å from ~ 4 to ~ 3.5 Å). As the film thickness grows, the interior suppression becomes smaller; for example, in a 37-layer-thick film σ_C decreases by ~ 0.4 Å as γ goes from 60 dyn/cm to ∞. In all our calculations we have included a transverse cutoff W. Without it, the fluctuations diverge as $\ln W$. However, this is a very weak divergence: For a 3-layer-thick film with $W=4\times10^5$, 4×10^7, and 4×10^9 Å, we find $\sigma_S = 2.48$, 2.93, and 3.32 Å and $\sigma_C = 3.34$, 3.68, and 4.01 Å, respectively.

The dependence of the complete fluctuation profile σ_i in an 11-layer-thick film on K and B is shown in Fig. 4. It is clear from the figure that increasing either B or K suppresses the fluctuations throughout the sample. How-

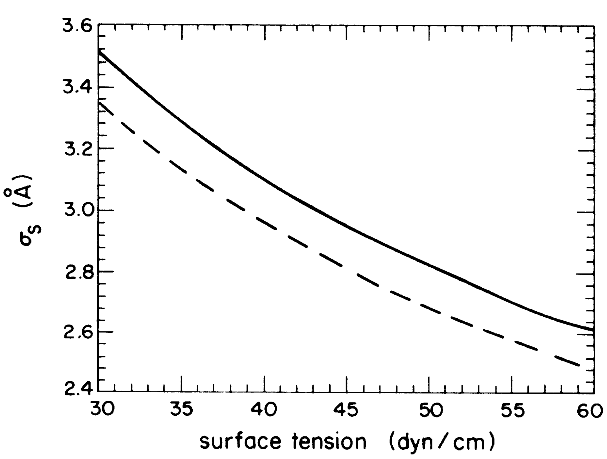

FIG. 2. The displacement fluctuation amplitude σ_S of the surface layer vs the surface tension for a 37-layer-thick film (solid line) and a 3-layer-thick film (dashed line).

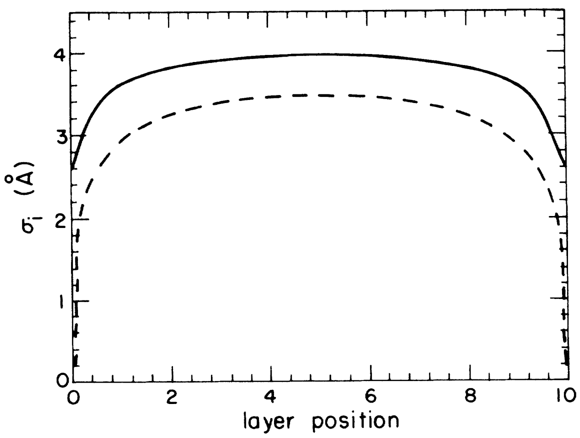

FIG. 3. The displacement fluctuation profile σ_i for an 11-layer-thick film. The solid line corresponds to the surface tension $\gamma=60$ dyn/cm and the dashed line to $\gamma=\infty$.

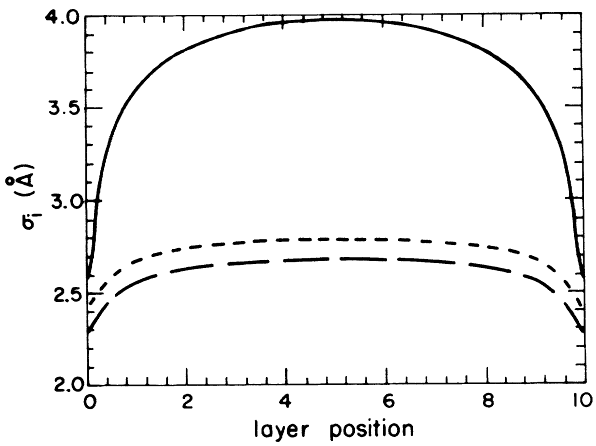

FIG. 4. The displacement fluctuation profile σ_i vs the layer index i for an 11-layer-thick film showing its dependence on the smectic elastic constants K and B. The solid line corresponds to $B=2.5\times10^7$ dyn/cm^2 and $K=10^{-6}$ dyn ($\beta\equiv\sqrt{KB}=5$ dyn/cm); the short-dashed line corresponds to $B=25\times10^7$ dyn/cm^2 and $K=10^{-6}$ dyn ($\beta\equiv\sqrt{KB}=15.8$ dyn/cm); the long-dashed line corresponds to $B=2.5\times10^7$ dyn/cm^2 and $K=10^{-5}$ dyn ($\beta\equiv\sqrt{KB}=15.8$ dyn/cm).

ever, this suppression is much stronger inside the film than at the surface. Also note from Fig. 4 that, as expected from Eq. (2), the fluctuation amplitude is more sensitive to $\beta=\sqrt{KB}$ than it is to $\lambda=\sqrt{K/B}$.

We have made the following simplifying assumptions in our theory: Although the $|\nabla u|^2$ term should, in principle, appear for each layer, because the rotational symmetry has been broken by the film holder, we have assumed that for the interior layers the contribution of this term to the Hamiltonian is very small. This assumption is supported by the experimental data.[9] We also have not included the anharmonic terms[6] in H and we have neglected the interface-interface interaction produced by the disjoining pressure.[10]

Although the theory was presented here only for smectic-A films (for simplicity), it applies to all the fluid smectics—to the 2D liquids, all the different smectic-A's and smectic-C's (e.g., $A_1, A_2, A_d, C, \ldots$) and to the 2D hexatics, hexatic-B, smectic-F, and smectic-I. In the companion Letter[9] we show that it correctly describes the layer fluctuation profiles for 7O.7 smectic films with two surface smectic-I layers and interior smectic-C layers. These experimental results indicate that β_I for the surface hexatic smectic-I layers is about twice as large as β_C for the interior liquid smectic-C layers.

In addition to the hydrodynamic, long-wavelength fluctuations which we have calculated, there are short-wavelength contributions to the total fluctuation profile that should be included before comparing the theoretical predictions with experiment. These short-wavelength contributions are due to the individual motions of the molecules. The inclusion of both contributions leads to the following formula for the combined fluctuation amplitude σ:

$$\sigma=(\sigma_E^2+\sigma_L^2)^{1/2}, \tag{14}$$

where the elastic fluctuation amplitudes calculated in this paper are σ_E and the individual molecular motion fluctuation amplitudes are σ_L. For $\sigma_E=4$ Å and $\sigma_L=1$ Å,[11] $\sigma=4.12$ Å, so the local molecular motion contributes only ~0.12 Å to the total fluctuation amplitude and the hydrodynamic, long-wavelength contribution dominates. Also note that σ_L has its own profile which cannot be studied using our phenomenological elastic theory. This profile, however, can probably be described using a microscopic mean-field density-functional theory.[12,13]

To summarize, we have presented a simple analysis of the thermally driven layer fluctuations in finite smectic systems which is in excellent agreement with recent experimental studies.[9] This analysis will be a good guide for future theoretical and experimental studies of the thickness-dependent fluctuations in freely suspended fluid smectic films and fluid smectic films deposited on solid substrates.

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