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Smectic ordering in nematic and smectic liquid-crystalline films probed by means of surface light scattering

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We present the first results of experiments that measure the intensity of light scattered by capillary waves on the surface of free-standing liquid-crystalline thin films. The intensity of the scattered light provides information about the surface tension of the liquid-air interfaces and, more interestingly, about the interactions between the surfaces as a function of the film thickness. Light scattering experiments performed on 4-*n*-octyl-4′-cyanobiphenyl (8CB) in the nematic phase show the sudden onset of a strong interaction between the interfaces when the film thickness is decreased. The range of this interaction increases with decreasing temperature. The suppression of the out-of-phase capillary waves coincides with the point where the range of surface-induced smectic ordering becomes comparable to the film thickness. We argue that these experiments probe the growth of the interlayer elasticity modulus *B*.

I. INTRODUCTION

Of all the phase transitions involving liquid-crystalline phases the nematic–smectic-A (N–Sm-A) transition is probably the one that has been studied the most extensively.[1,2] Nevertheless, a fully consistent theoretical picture is still lacking. One particularly interesting class of experiments to probe the onset of smectic ordering in the nematic phase involves the study of surface-induced smectic order.[3]

These experiments have shown how, for certain liquid-crystalline materials, a smectic layer may form at the nematic-air interface. The thickness of the smectic layer grows as the N–Sm-A transition is approached. As shown by Als-Nielsen *et al.*,[4] the range of this surface-induced order is equal to the longitudinal correlation length $\xi_{\parallel}$.

In this paper we report experiments on free-standing nematic films in the temperature range around the N–Sm-A transition. On the basis of the earlier experiments on a single surface,[4] we expect smectic ordering to grow in from both interfaces. However, the present experiments allow us to study in detail how these smectic surface layers interact.

To measure the interaction between two liquid-air interfaces we carried out light scattering experiments. In these experiments we measure the intensity of light scattered by the capillary waves on both fluid-air interfaces as a function of film thickness. Dynamic light scattering due to propagating waves yields information about the surface tension γ. The results of the latter experiments have been reported elsewhere.[5] Here we concentrate on the analysis of the static light scattered by thin nematic films. Such experiments probe the mean-square amplitude of the surface waves. For thin films the interaction between the two surfaces becomes important and the surface modes become coupled. For symmetry reasons it is useful to distinguish the in-phase (bending) and out-of-phase (squeezing) modes of the two surfaces. It is the latter mode that provides information about the interaction between the two surfaces.

In Sec. II we briefly review the main results of the classical theory of light scattering by thin liquid films. In Sec. III we describe the experiments on thin films of 8CB. Section IV contains an analysis of our light scattering data.

II. LIGHT SCATTERING BY THIN FILMS

A perfectly flat interface will reflect an incident light beam, but will not give rise to light scattering. However, due to the presence of thermally excited surface waves, the surface of a fluid will scatter light in all directions. The intensity of this scattered light is related to the mean-square amplitude of the capillary waves. For a single surface this relation was derived in the early years of this century by Andronow and Leontowiez[6] (see also Ref. 7). The theory was later extended to thin films by Vrij.[8] Here we briefly review the main results of the latter paper. For more details the reader is referred to Ref. 9.

We start our description by assuming that the amplitude of surface waves is small. If we choose our undistorted surfaces parallel to the xy plane at $z=+h/2$ and $z=-h/2$. Then the assumption that the amplitude of the waves is small implies that the deviation $u^{\pm}(x,y)$ at $z=\pm h/2$ is a single-valued function of x and y, and $|u^{+}-u^{-}| \ll h$, where h is the thickness of the film. With this (fairly minor) restriction we can expand the amplitude of the surface waves in a two-dimensional Fourier series:

$$u^{\pm}\left[z=\pm\frac{h}{2},x,y,t\right]=\sum_{\mathbf{q}} u_{\mathbf{q}}^{\pm}(t)e^{i\mathbf{q}\cdot\mathbf{s}} ,$$

with $\mathbf{s}=(\mathbf{x},\mathbf{y})$, and $|\mathbf{q}|=2\pi/\Lambda$, where Λ is the wavelength of a particular surface mode. In the following it is convenient to define two new amplitudes that are linear combinations of the surface modes, viz.,

$$b_q=(u_q^{+}+u_q^{-})/2, \quad s_q=(u_q^{+}-u_q^{-})/2 ,$$

where b and s stand for bending and squeezing, respectively. In terms of these symmetry-adapted amplitudes, the expression for the light scattering becomes

$$I_s=\frac{\pi^2(n^2-1)^2}{4\lambda_0^4}(K^2\langle|b_q|^2\rangle+L^2\langle|s_q|^2\rangle)\mathcal{S} , \tag{1}$$

where I_s is the scattered intensity defined as the energy flow scattered per unit area, per unit solid angle divided by the energy flow per wave-front area of the incident beam, n is the refractive index, λ_0 is the wavelength of the incident light in vacuum, $\langle|b_q|^2\rangle$ and $\langle|s_q|^2\rangle$ are the mean-square amplitudes of the bending and squeezing mode, and $\mathcal{S}$ is the film area. The factors K^2 and L^2 (see appendix, Ref. 9) are dimensionless optical factors that take the interference in a thin film into account. They depend only on the film thickness h, the refractive index n, the scattering angle θ, and the angle of incidence θ_0. Figure 1 gives an illustration of the thickness dependence of the optical factors L^2 and K^2.

Vrij *et al.*[8,9] have given the following expressions for the mean-square amplitudes of the bending and squeezing mode for (isotropic) liquid films:

$$\langle|b_q|^2\rangle=\frac{2k_BT}{\gamma q^2\mathcal{S}}, \quad \langle|s_q|^2\rangle=\frac{2k_BT}{(\gamma q^2+2V'')\mathcal{S}} , \tag{2}$$

where γ is the surface tension, q is the surface wave vector, k_B is Boltzmann's constant, $\mathcal{S}$ is the film surface area, and T is the absolute temperature. For soap films,[9] $V''=\partial^2F/\partial h^2$ is the second derivative of the free energy per unit area with respect to the film thickness h. As can be seen from the above expressions, all the information about the interaction between two interfaces is contained in the intensity of the squeezing mode. Actually, for *nematic* films the situation is somewhat different if there is strong anchoring of the director at the air-liquid interface. In that case a surface wave will induce a deformation of the director pattern. This distortion is purely a "splay" deformation for the bending mode, but for the squeezing mode it is a combined "splay-bend" deformation. For thin nematic films ($qh \ll 1$),

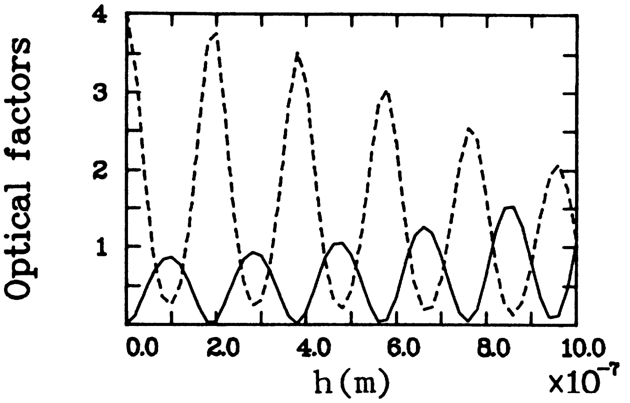

FIG. 1. Thickness dependence of the dimensionless optical factors K^2 and L^2 calculated with the values $n=1.5$, at the scattering angle $\theta=80°$, and an angle of incidence $\theta_0=30°$ and $\lambda_0=514.5$ nm, where K^2 is marked with a solid line and L^2 with a dashed line.

$$\begin{aligned}\langle|b_q|^2\rangle_N&=\frac{2k_BT}{(K_1hq^4+\gamma q^2)\mathcal{S}}\\ \langle|s_q|^2\rangle_N&=\frac{2k_BT}{[\frac{4}{3}K_1hq^4+8K_3(q^2/h)+\gamma q^2]\mathcal{S}} ,\end{aligned} \tag{3}$$

where K_1 is the splay elastic constant, K_3 is the bend elastic constant, and γ is the surface tension.

For the present experiments the values of K_1, h, γ, and q are such that the splay contribution is always negligible compared to the term containing the surface tension. A rough estimate for a typical 8CB film used in the experiments yields $K_1=2\times10^{-12}$ N,[10] $\gamma=25\times10^{-3}$ N/m,[4] $q\approx3\times10^{6}$ m^{-1} and $h\approx5\times10^{-7}$ m. It follows that, indeed, $K_1hq^2(\approx10^{-4})\ll\gamma$. For the bend deformation the situation is more subtle because K_3 (unlike K_1) is expected to diverge at the N–Sm-A transition. In addition, the effect of the bend deformation becomes larger for thinner films.

If smectic ordering of the film takes place, the description of surface fluctuations becomes quite different, but as before, the main effect is that, for thin films, the squeezing mode is affected by the surface-induced order, whereas the bending mode is not. We shall return to this point in more detail in Sec. IV.

III. EXPERIMENTAL PROCEDURE

A. Sample

The liquid crystal used in the present study was 4-n-octyl-4'-cyanobiphenyl (8CB). This compound has a (continuous[2]) N–Sm-A transition in a temperature range that could be conveniently studied in our light scattering cell. The material was obtained from British Drug House (BDH) and was used without further purification. The phase transition temperatures of the bulk material were obtained using a polarization microscope. We found the *I-N* transition at a temperature of 313.6 K and the *N*–Sm-*A* transition at 306.6 K. Both transition temperatures should be compared to those reported in literature,[2] i.e., $T_{NI}=313.95$ K and $T_{N\text{-Sm-}A}=306.921$ K. Before a free-standing film was prepared, the sample was degassed under vacuum for several hours in the isotropic phase in order to remove any air bubbles that might be trapped in the fluid.

B. Experimental setup

In Fig. 2 a schematic drawing of the experimental setup is shown. The scattering cell consists of a double-walled stainless-steel vessel, the temperature of which is regulated by a temperature-controlled water bath (Heto 02PT623). Using this thermostat the temperature of the scattering cell was stable to within 0.05 K over longer periods of time (days). On a shorter time scale the temperature was stable to within 0.1 K. The temperature was measured using a copper-constantan thermocouple which was mounted in the sample holder, close to the liquid-crystalline film. A more detailed description of the scattering cell can be found in Ref. 11.

The free-standing liquid-crystalline films were prepared by dipping a copper frame with a hole of 1 cm diameter into a small vessel containing 8CB. The copper frame was coated with an antireflection layer. We observed that films in the isotropic phase rapidly drained and ruptured. However, nematic films were more stable and, after initial rapid draining, could be kept for weeks. We observed that the application of a weak (0.028 T) transverse magnetic field greatly facilitated the formation of stable nematic films. However, the magnetic field was too weak to have any measurable effect on the properties of the nematic film.

The film was illuminated by a Spectra Physics 165 Ar laser ($\lambda_0=514.5$ nm). The polarization was perpendicular to the scattering plane. The intensity of the incident laser beam was monitored using a photosensitive cell (Siemens BPX79) which was illuminated via a beam splitter placed in the incident beam. The intensity of the light that was specularly reflected off the liquid-crystalline film was also monitored using a photo diode. The light scattered by the film was passed through an analyzer that transmitted only the component of the scattered light that was polarized perpendicular to the scattering plane. The intensity of this scattered light was measured with a photomultiplier (EMI 9863 KB/100). The signal from the photomultiplier tube was fed to a digital multimeter (Keithley DMM196), as was the signal of the diode monitoring the specularly reflected beam. Both multimeters were connected to a microcomputer (Apple II) using an IEEE interface.

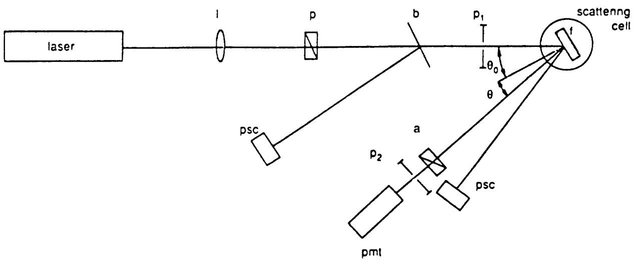

FIG. 2. Experimental setup used to measure surface light scattering; *l*, lens $f=0.5$ m; *p*, polarizer; *b*, beam splitter; p_1,p_2, pinholes ($\Phi_1=1$ mm and $\Phi_2=0.2$ mm); *f*, liquid-crystal film; psc, photosensitive cells; *a*, analyzer; pmt, photomultiplier; $\theta_0=30°$; θ, scattering angle.

C. Analysis of the measurements

The signal from the photo diode monitoring the intensity of the reflected beam could be used to measure the thickness of the liquid-crystalline film. If we assume that the film is of uniform thickness, then we can use the Airy formula[12] to relate the intensity of the reflected light to the film thickness *h* and to the refractive index *n*:

$$\frac{I_R}{I_0}=R\frac{(2-2\cos\delta)}{1+R^2-2R\cos\delta}\ , \tag{4}$$

where $R=(\cos\theta_0-n\cos\theta_0')^2/(\cos\theta_0+n\cos\theta_0')^2$, θ_0 is the angle of incidence, θ_0' the angle of refraction, and δ the phase difference between the successive multiply reflected beams: $\delta=(4\pi/\lambda_0)nh\cos\theta_0'$. Since nematic liquid crystals are birefringent, the refractive index *n* in the above expression depends both on the alignment of the nematic director in the film and on the polarization of the incoming beam. In the liquid-crystal films we used, the nematic director was aligned perpendicular to the plane of the film (homeotropic alignment). This observation is supported by the fact that the film appeared to be optically isotropic when illuminated between crossed polarizers. Actually, we found that for freshly prepared (and hence rapidly draining) films, the Airy formula, Eq. (4), failed to describe the measured reflectivity. The observed behavior can be easily understood if it is assumed that a vertically mounted film, when draining, must be wedge-shaped rather than flat. In fact, we have very direct evidence for this effect, because in the early stages of the film preparation we observed two distinct reflected spots, rather than one. From the separation of these spots we could deduce that the maximum wedge angle α is less than 1.6×10^{-3} (5.5′). As the film becomes thinner the angle α rapidly decreases and, as the two spots merge, the full modulation of the reflected intensity is recovered. In our analysis of the data we took this initial deformation of the film into account, for the computation of both the reflected and scattered intensity. However, in the range of film thicknesses where we observe interesting changes in the light scattering intensity, the liquid-crystal film is flat and no corrections are needed. Near the *N*–Sm-*A* transition the thickness changes in discrete steps during the drainage. These steps are very well resolved as soon as the thickness of the film is reduced to about 200 nm and the drainage becomes slower, see Fig. 3.

In order to analyze the scattering data, we make use of the expression relating the mean square amplitude of the bending and squeezing modes of the surface waves (see

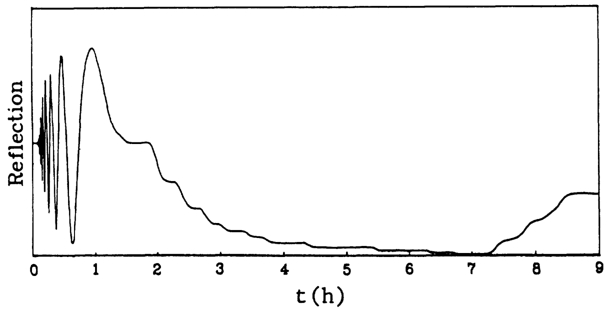

FIG. 3. A typical interference pattern of a draining film $\theta = 30°$, $T - T_{N\text{-Sm-}A} = 0.53$ K.

Sec. II) to the intensity of the scattered light, Eqs. (1) and (2),

$$I = \frac{\pi^2 k_B T (n^2 - 1)^2}{2\lambda_0^4} \left[\frac{K^2}{\gamma q^2} + \frac{L}{2V'' + \gamma q^2} \right] . \qquad (5)$$

In Eq. (5) we have used the fact that the bending mode is not affected by surface interactions. To stress the analogy with earlier work[8,9,11] we have denoted the interaction term which reduces the intensity of the squeezing mode by V''. However, in the present case the interpretation of this term may be rather different than for soap films. The scattered intensity is measured by means of a photomultiplier; the output current i of the photomultiplier is proportional to the scattered intensity I_s, i.e.,

$$i = \frac{\pi^2 k_B T (n^2 - 1)^2}{2\lambda_0^4} \left[\frac{K^2}{\gamma q^2} + \frac{L^2}{2V'' + \gamma q^2} \right] f . \qquad (6)$$

The factor f is a calibration factor which has still to be determined. The standard procedure to determine this factor[13] is to carry out a measurement of i for a thick film where V'' is negligible. Under those conditions all quantities in Eq. (6), except f, are known (note that the surface tension γ can be measured by dynamic light scattering, see Ref. 5), and hence f can be determined. In practice, the calibration is complicated by the fact that it is precisely for these thick films that the analysis of the light scattering experiment is difficult because we have to correct for the fact that the film is wedge shape.

We also measured the angular dependence of the scattered light at constant film thickness. These measurements provide, in principle, an additional means to estimate the calibration factor f which relates the photomultiplier current i with the surface scattering ratio I_s [see Eq. (5)]. However, in the experimental setup used for the current measurements the latter method to determine the calibration factor proved to be unreliable due to large statistical errors in the data.

D. Results

During the drainage of a nematic film, we measured both the reflected and scattered light. The scattered light could be measured over two ranges of angles $10° < \theta < 70°$ (around the reflected beam) and $110° < \theta < 130°$. After letting the film drain for several hours we find that the reflected intensity changes increasingly slowly, even though the film still has a thickness of several hundreds of nanometers. In fact, we observe that the film thickness changes with small steps of ~ 3 nm (see Ref. 5), but these steps become increasingly infrequent and after a day the film thickness is effectively constant. We have no reason to believe that this "final" thickness is in fact the equilibrium thickness of the film, because we would expect the van der Waals forces between the constituent molecules to cause a continued thinning of the film until it ruptures. Hence we believe that the final thickness of the film is determined by kinetic factors. This assumption also explains why we could not form stable films at temperatures higher than 2 K above N–Sm-A transition. Furthermore, if we started our experiments at lower temperatures, i.e., less than about 1 K above N–Sm-A transition, the viscosity was such that virtually no drainage took place on the time scale of our experiments. Hence we were rather limited in the temperature range over which we would carry out free drainage experiments. However, once the film thickness had reached its final value, we could cool the film down, at constant thickness, into the smectic phase. Figure 4 shows the result of a series of measurements of a freely draining nematic film of 8CB at a temperature of 307.6 K, i.e., 1.0 K above $T_{N\text{-Sm-}A}$. We note that for a film thickness larger than 400 nm, no interaction between the two interfaces is observed. However, below $h \approx 300$ nm, the interaction is seen to rise precipitously. In order to see how the range of this interaction depends on temperature, we have collected in Table I the film thickness at which the interaction sets in as a function of temperature. These values for the interaction range can be derived from a least-squares fit of the logarithm of V'' as a function of the film thickness (see Fig. 5), as will be explained later on.

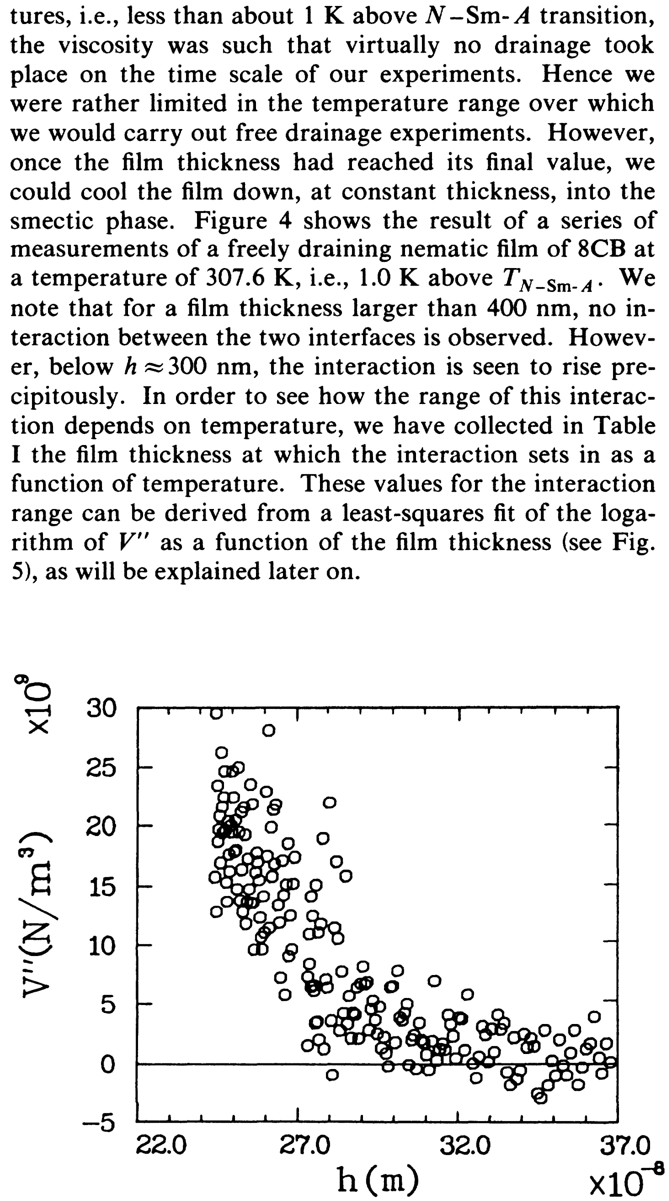

FIG. 4. Interaction parameter V'' as a function of the film thickness derived from a drainage experiment at $T = 307.6$ K, measured at a scattering angle $\theta = 35°$, $\theta_0 = 30°$.

TABLE I. The range of the surface interactions as derived from a free-drainage experiment at different temperatures.

T (K)	ξ (nm)
307.5	374
307.6	325
308.0	216
308.5	204

As can be seen from Table I, the range of the surface interactions appears to increase from 200–220 nm at 308.5 K to 375 nm at the lowest temperature ($T=307.5$ K). At lower temperatures, free drainage experiments could not be performed. However, it was still possible to measure the light scattering of the liquid-crystalline film at lower temperatures, where its thickness is effectively frozen. Figure 6 shows the behavior of V'' found in this cooling experiment. In this figure, the film has been cooled through the N–Sm-A transition (at $T=306.6$ K) down to the point where it crystallizes. As can be seen from this figure, the surface interaction in the smectic phase is at least a factor 1000 larger than in the nematic phase.

In the smectic phase, V'' changes only slowly with temperature. The behavior of V'' in the smectic phase can be understood if we start from the simplest expression for the distortion free energy in a smectic-A phase:[14]

$$\mathcal{F}=\int d\mathbf{r}\left[\frac{1}{2}B\left[\frac{\partial u}{\partial z}\right]^2+\frac{1}{2}K_1\left[\frac{\partial^2 u}{\partial x^2}+\frac{\partial^2 u}{\partial y^2}\right]^2 + \text{higher-order terms}\right] .$$

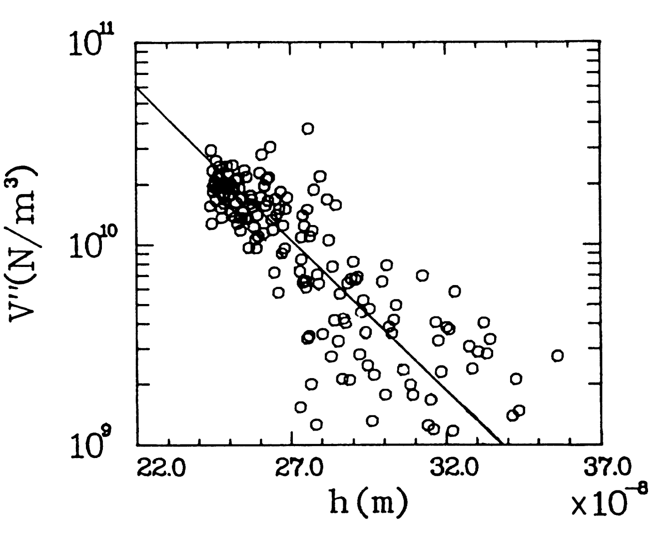

FIG. 5. A logarithmic plot of V'' as a function of the film thickness under the same experimental conditions as in Fig. 4.

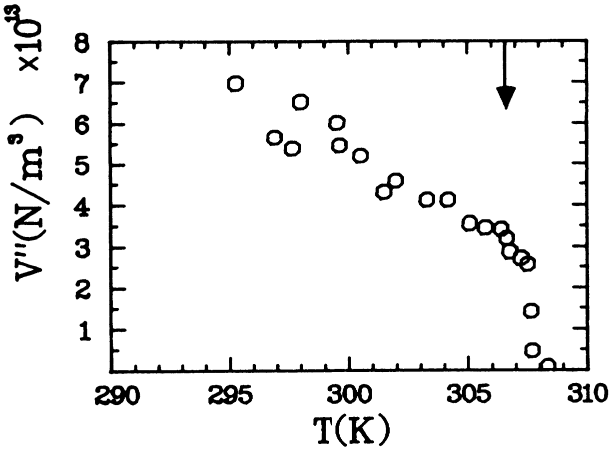

FIG. 6. Values for V'' obtained from a cooling experiment at scattering angle $\theta=130°$; the bulk nematic–smectic-A phase transition temperature is marked with an arrow.

In this equation, u describes the displacement of smectic layers from their equilibrium position, B is the interlayer elasticity modulus, and K_1 is the Frank elastic constant for splay deformations. Starting from this expression, it is easy to show that the free-energy per unit area of a symmetric (i.e., squeezing) surface wave with amplitude u_0 and transverse wave vector q is given by

$$F=\frac{1}{2}u_0^2\frac{B}{\xi}\frac{\sinh(h/\xi)}{[\sinh^2(h/2\xi)]}+u_0^2\gamma q^2 ,$$

where $\xi=q^{-2}\sqrt{(B/K_1)}$. In the limit $\xi \gg h$, this expression reduces to

$$F=u_0^2\left[\frac{2B}{h}+\gamma q^2\right] . \tag{7}$$

Hence, in the smectic phase, V'' can be identified with B/h if $\xi \gg h$. We can easily estimate if the latter condition is fulfilled. In our experiments we use a film thickness of order $h \approx 10^{-7}$ m, whereas in the smectic phase of 8CB, $K_1 \approx 8\times10^{-12}$ N,[10] $B \approx 10^6$–10^8 N/m²,[15,16] and $\gamma=25\times10^{-3}$ N/m (see Ref. 5). If we take for q a typical value of 3×10^6 m^{-1}, we obtain $h/\xi \sim 10^{-3} \ll 1$. From our data we can estimate the dependence of B on temperature or film thickness with a relative error of 2%. However, the absolute value of B is determined with a lower accuracy due to the problem in measuring the calibration factor for thick films [see discussion below Eq. (6)]. As a consequence the absolute value of B is only accurate to within a factor of 2. A typical value for B obtained from the present experiments is $B \sim 2\times10^6$ N/m². Note that the present experiments provide, in principle, a direct method of measuring B in the smectic phase. In contrast, bulk light scattering measures B/K_1,[17] and with x-ray scattering one can determine BK_1. The only other technique to probe B directly is to study acoustically induced surface waves.[15,16]

Above the N–Sm-A transition the preceding picture cannot be used. One might expect that in that case the bend elastic deformation of the nematic director becomes the dominant interaction mechanism. We recall that, according to Eq. (3), the mean-square amplitude of the squeezing mode in a nematic film should be proportional to

$$(4/3K_1hq^4+8K_3q^2/h+\gamma q^2)^{-1}\ .$$

However, the measured magnitude and thickness dependence of V'' is not compatible with the assumption that $V''=4K_3q^2/h$. First of all, the thickness dependence of V'' at constant T is much steeper than $1/h$, and secondly the observed magnitude of V'' can only be explained if it is assumed that K_3 is some 10^2 times larger then K_1. It is true, of course, that K_3 diverges at the N–Sm-A transition, while K_1 does not, but a ratio of $K_3/K_1\approx 10^2$ (Ref. 10) is only expected very close to the transition, and not in the temperature range under consideration. We are therefore led to consider the possibility that surface-induced smectic ordering is the main cause of the observed steep increase in V'' as the thickness of a nematic film is decreased. It should be noted that smectic surface ordering does not in itself tend to stabilize thick films and, in fact, consideration of the effect of the free energy associated with surface-induced smectic order in a nematic film leads to the prediction of a negative V''. Rather we must look for an explanation of the observed effect in the rapid growth of the interlayer elasticity modulus B in a nematic film as soon as, its thickness becomes comparable to the correlation length for longitudinal smectic order-parameter fluctuations. The absolute value of the V'' derived from the experimental data is not yet sufficient to make a quantitative comparison with theory meaningful. However, the qualitative features of V'' are easily understood from the form of the free-energy density of smectic precursor fluctuations in the nematic phase first proposed by de Gennes:[18]

$$F=F_0+F_N+\alpha\left|\psi\right|^2+\frac{\beta}{2}\left|\psi\right|^4+\frac{1}{2M_\perp}|(\partial_x+iq_ln_x)\psi|^2+\frac{1}{2M_\perp}|(\partial_y+iq_ln_y)\psi|^2+\frac{1}{2M_\parallel}|\partial_z\psi|^2\ , \tag{8}$$

where ψ is the complex smectic order parameter $\psi=|\psi|e^{iq_lu}$, and α and β are the leading coefficients in the Landau expansion of the free-energy density in powers of the order parameter ψ. The coefficients $M_\perp$ and $M_\parallel$ are phenomenological coefficients determining the free energy associated with smectic order-parameter distortions parallel and perpendicular to the nematic director. Finally F_N is the free-energy density associated with deformations of the detector ($\mathbf{n}$) pattern:[19]

$$F_N=\tfrac{1}{2}[K_1(\nabla\cdot\mathbf{n})^2+K_2(\mathbf{n}\cdot\nabla\times\mathbf{n})^2+K_3(\mathbf{n}\times\nabla\times\mathbf{n})^2]\ .$$

The above expression for the free-energy density associated with smectic order-parameter fluctuations was introduced by de Gennes,[18] who exploited the analogy between the complex order parameter in superfluid helium and the smectic order parameter. The de Gennes "Hamiltonian" provides a convenient framework for a discussion of precursor effects in the vicinity of the N–Sm-A transition. It should be noted, though, that there is now a large amount of experimental data which cannot be accounted for within this picture.[20]

For simplicity we limit ourselves to the description of long-wavelength surface modes. In this limit we may ignore all transverse distortions and all deformations of the director pattern. We are left with a simplified form of Eq. (8) for the free-energy density

$$F=\alpha|\psi|^2+\frac{\beta}{2}|\psi|^4+\frac{1}{2M_\parallel}|\partial_z\psi|^2\ . \tag{9}$$

In the nematic phase, the average value of the smectic order parameter is zero. In a simple (i.e., not renormalized) description, this corresponds with the situation $\alpha,\beta>0$.

In the following we shall neglect the quartic term altogether. This amounts to the assumption that $|\psi|\ll 1$. Actually, as we shall see, this condition is not satisfied at the surface of the film. However, the introduction of the quartic terms would make little difference to our argument. Hence the neglect of quartic terms is mainly a matter of convenience.

Let us first consider the order parameter profile in a thin film in the case where $u=0$ (no layer fluctuations). We assume that at the surface of the film the smectic order is fixed at a value ψ_0, which is close to 1. Inside the film the smectic order will decay exponentially. This follows directly from a minimization of the free-energy density given in Eq. (9) taken to order ψ^2.

The Euler-Lagrange equation becomes

$$\frac{\partial^2\psi}{\partial z^2}=2M_\parallel\alpha\psi$$

and hence (10)

$$\psi(z)=\psi_0\frac{\cosh(z/\xi)}{\cosh(h/2\xi)}\ ,$$

where we have used the fact that the order-parameter profile is symmetric. We have defined the (longitudinal) smectic correlation length ξ by $\xi=(2M_\parallel\alpha)^{-1/2}$. Next we look at what happens if a long-wavelength, symmetric surface mode is present. In that case we have to consider the full smectic order parameter $\psi=|\psi|e^{iq_lu}$, where $u(z)$ is the deviation of a smectic layer at z, from its equilibrium position, and $q_l=2\pi/d_l$ with d_l the smectic layer thickness. We assume that the presence of a surface wave affects the phase of ψ, but not the amplitude. The free energy (per unit area) associated with a given deformation $u(z)$ is then

$$\Delta F=\frac{1}{2M_\parallel}\int_{-h/2}^{h/2}\psi^2(z)q_l^2\left[\frac{\partial u}{\partial z}\right]^2dz$$

$$=\frac{q_l^2\psi_0^2}{2M_\parallel}\int_{-h/2}^{h/2}\left[\frac{\psi(z)}{\psi_0}\right]^2\left[\frac{\partial u}{\partial z}\right]^2dz\ . \tag{11}$$

We now define a layer compressibility modulus B_0 as $q_l^2\psi_0^2/M_\parallel$. B_0 is the compressibility modulus that the film would have if the smectic order parameter were equal to ψ_0 throughout the film. We can solve Eq. (11) for $u(z)$ by minimizing ΔF. This yields

$$\frac{\partial}{\partial z}\left[\left[\frac{\psi(z)}{\psi_0}\right]^2\frac{\partial u}{\partial z}\right]=0 \quad\text{or}\quad \left[\frac{\psi(z)}{\psi_0}\right]^2\frac{\partial u}{\partial z}=c\ , \qquad (12)$$

where c is a constant which remains to be determined by the boundary conditions $u(z=h/2)=u_0$ and $u(z=-h/2)=-u_0$. Using Eq. (12) we can write

$$\frac{\partial u}{\partial z}=c\frac{\cosh^2(h/2\xi)}{\cosh^2(z/\xi)}\ , \qquad (13)$$

from which we find

$$u=c\cosh^2(h/2\xi)\xi\tanh(z/\xi)\ .$$

Using the boundary conditions, we find

$$c=u_0/[\xi\cosh(h/2\xi)\sinh(h/2\xi)]\ .$$

Using Eqs. (9)–(13), we can now compute the free energy per unit area with these deformations:

$$\Delta F=\frac{B_0}{2}\int_{-h/2}^{h/2}c^2\left[\frac{\psi_0}{\psi(z)}\right]^2dz=\frac{2B_0u_0^2}{\xi\sinh(h/\xi)}\ .$$

In this integration we assume that the smectic order is homogeneous in the plane of the film. The total free energy also includes the contribution due to the surface tension γ:

$$\Delta F_T=u_0^2\left[\frac{2B_0}{\xi\sinh(h/\xi)}+\gamma q^2\right]$$

and hence

$$\langle u_0^2\rangle=\frac{k_BT/\mathcal{S}}{2[2B_0/\xi\sinh(h/\xi)+\gamma q^2]}\ .$$

In this equation $\mathcal{S}$ is the scattering surface area. The intensity of the light scattered by the squeezing mode is proportional to $\mathcal{S}\langle u_0^2\rangle$. The interaction term then becomes $V''=B_0/[\xi\sinh(h/\xi)]$.

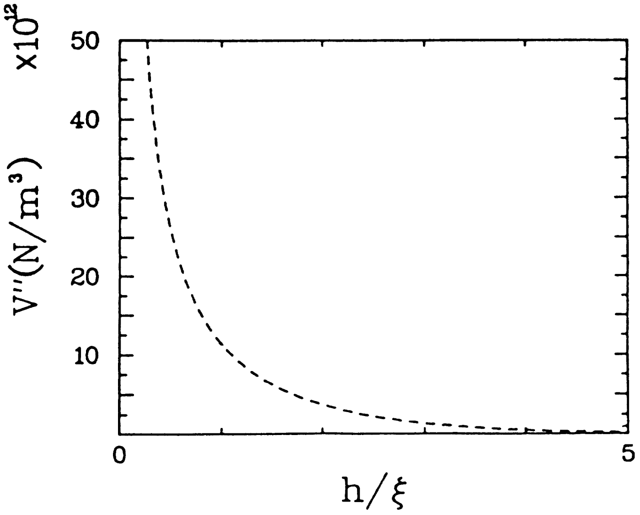

FIG. 7. Dependence of V'' on the dimensionless parameter h/ξ as derived from Eq. (11). In this figure we assumed the following values for the parameters: $\xi=300$ nm and $B=4\times10^6$ N/m^2.

Let us consider the behavior of V'' in two limiting cases. First of all, $h\ll\xi$. In that case, the smectic order persists throughout the film and we find $V''=B_0/h$, which is the result we obtain in a smectic film. In the other limit, $h\gg\xi$, V'' reduces to $V''=B_0\xi^{-1}\exp(-h/\xi)$. Hence in this limit V'' decreases exponentially with film thickness. The dependence of V'' on h/ξ is shown in Fig. 7. Note that this figure has the same overall features as the experimental V'' (Fig. 4).

Although the present preliminary results are not sufficiently detailed for us to make a more quantitative analysis we stress that future experiments could provide us with unique information about the order-parameter profile and the layer elasticity modulus in nematic films with surface-induced smectic order.

IV. CONCLUSIONS

Measurements of the intensity of light scattered by the surface of liquid-crystalline films provide information about interactions V'' between the smectic layers which develop near the liquid-air interfaces. We analyze our data within the framework of the de Gennes theory for smectic fluctuations in a nematic medium The thickness dependence of V'' can be considered in two limiting cases. In the case where the thickness h is much less than the smectic correlation length, i.e., if the smectic ordering persists throughout the film, then V'' is proportional to the layer elastic modulus and the light scattering data directly measures this elastic modulus. In the limit of $h\gg\xi$, the measured V'' is expected to decrease exponentially with h. Our static light scattering experiments follow the trends of the simple model.

The present measurements of light scattered by capillary waves on the surface of liquid-crystalline films show that the static light scattering can be used to obtain unique information about the order-parameter profile and the layer elasticity modulus in nematic films with surface-induced smectic ordering.

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APPENDIX

The dimensionless optical factors L^2 and K^2 which take account of the interference of the scattered light, calculated in Ref. 9, are given by

$$L^2=G_0G_3\ ,$$

$$K^2=2G_1G_0-G_0G_2\ ,$$

with

$$G_0=\frac{t^2t_0^2}{(1+r^4-2r^2\cos2\alpha)(1+r_0^4-2r_0^2\cos2\beta)}\ ,$$

$$G_1=(1+r^2-2r\ \cos2\alpha)(1+r_0^2-2r_0\cos2\beta)+2t^2t_0'^2\ ,$$

$$G_3=G_1-2t'^2t_0'^2\cos\alpha\ \cos\beta+2tt't_0t_0'\sin\alpha\ \sin\beta\ ,$$

where r_0 and t_0 are the reflection coefficients and the transmission coefficients of the incoming light beam whereas r and t are the transmission coefficients of the scattered light at the air-film interface; t_0' and t' are the transmission coefficients at the film-air interface. The phase differences between the successive multiply diffracted light beams is $\alpha=h2\pi n\ \cos\theta'/\lambda_0$ and the phase difference between multiply reflected beams is given by $\beta=h2\pi n\ \cos\theta_0'/\lambda_0$, where n is the refractive index, h is the film thickness, θ' is the scattering angle, θ_0' is the angle of reflection, and λ_0 is the wavelength of the light in vacuum.

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