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# Temperature-induced orientational transitions in freely suspended nematic films

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We report observations of a temperature-induced orientational transition in a freely suspended nematic film of the liquid crystal 4-ethyl-2-fluoro-4′-[2-(trans-4-*n*-pentylcyclohexyl)-ethyl]-biphenyl (I52). The transition is from a high-symmetry state, where the molecules are perpendicular to the film boundaries (homeotropic alignment), to a lower-symmetry state, where the molecules are inclined (tilted alignment), and occurs as the temperature of the sample is *raised*. A previous study by Faetti and Fronzoni (1978) discovered a similar transition in freely suspended nematic films of *N*-(*p*-methoxybenzylidene)-*p*-*n*-butylaniline, except that it occurred as the temperature was *lowered*, a result that we confirm here. In order to explain both orientational transitions and the temperature-independent alignment of other nematics, we have generalized a model by Parsons (1978) that is based on competition between polar and quadrupolar contributions to the surface free energy. By considering the effects of smectic ordering and ionic impurities, we can account for all of the various observations.

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## I. INTRODUCTION

Freely suspended liquid-crystalline films have been extensively investigated since the pioneering work of Friedel [1]. These films are interesting objects to study from the point of view of surface physics. Indeed, because of the large correlation length of mesophases, the influence of the bounding surface on bulk properties can be considerable even for film thicknesses as large as several tens of microns. By contrast, the properties of micron-thick films of liquid helium or metals are indistinguishable from those of massive bulk samples.

Of particular interest are orientational transitions of the liquid-crystalline director, which can occur in nematic films when certain parameters, such as film thickness [2], impurity adsorption [3], and temperature [4,5], are changed. In this paper, we report new observations of an orientational transition in a freely suspended nematic film of the liquid crystal 4-ethyl-2-fluoro-4′-[2-(trans-4-*n*-pentylcyclohexyl)-ethyl]-biphenyl (I52). In this nematic, a transition from homeotropic to tilted alignment occurs as the sample is heated. The transition is unusual in that the more ordered state is reached upon heating, while in other orientational transitions — and indeed, in most other phase transitions — ordering increases upon cooling.

Temperature-dependent orientational transitions have been studied in several systems. For example, they have been observed in millimeter-thick nematic samples of *N*-(*p*-methoxybenzylidene)-*p*-*n*-butylaniline (MBBA) and *N*-(*p*-ethoxybenzylidene)-*p*-*n*-butylaniline (EBBA) with a single free surface [5]. As the temperature $T$ of these samples is increased, orientational transitions from an initially tilted to a homeotropic alignment are found near the nematic-isotropic transition $T_{\rm NI}$ [5]. However, only planar alignment has been observed in nematic samples with a single free surface of *p*-azoxyanisole (PAA) [6]. Orientational transitions have also been observed in 10-$\mu$m thick freely suspended MBBA films [4]; however, in this case, the transition temperature $T_0$ depends strongly on the thickness $h$ of the film. The temperature dependence of the director tilt angle $\theta$ (the angle between the director $\hat{\mathbf{n}}$ and a normal $\hat{\mathbf{k}}$ to the film boundaries as defined in Fig. 1) has also been studied experimentally in these systems. These measurements show that the transitions are second order with $\theta$ varying as $(T_0-T)^{1/2}$ [4,5].

Several partially satisfactory attempts to explain theoretically the director orientation and the temperature dependence of $\theta$ at the free surfaces of nematics have

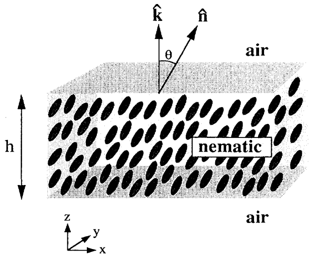

FIG. 1. A schematic diagram showing the orientation of the nematic director ($\hat{\mathbf{n}}$) with respect to the surface normal ($\hat{\mathbf{k}}$) of a freely suspended film. The film is bounded on both sides by air and has a thickness $h$.

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also been made (see, e.g., Refs. [7–10]). Because each of these models was introduced to explain a particular observation, they include only some of the relevant physical mechanisms. In this paper, in addition to studying a different material and being led to introduce another physical effect, we collect all of the other contributions that have been discussed in the literature to give a more unified presentation of orientational transitions.

## II. EXPERIMENT

Experiments were made on three liquid crystals: MBBA, I52, and 5CB (4′-*n*-pentyl-4-cyanobiphenyl). The physical properties of these materials, as well as others discussed later in the paper, are listed in Table I.

The nematic films were stretched over a supporting frame consisting of two molybdenum wires (50 $\mu$m in diameter) fixed to a plastic holder (Fig. 2). The distance $\ell$ between wires could be varied between 0.2 and 1.0 mm; most measurements were made with $\ell = 0.25$ mm. A high-frequency (29 kHz) sinusoidal ac electric voltage, slightly above the Fredericks-transition threshold, was applied to the wires in order to lift the azimuthal orientational degeneracy of the director and to eliminate topological defects in MBBA and I52 films. The films were kept in a temperature-controlled oven, which has a stability of $\pm$ 0.005 °C. In our experiments, the temperature was changed at a constant rate $dT/dt$ of 0.15 °C/min. The films were observed in a polarizing microscope using monochromatic light of wavelength $\lambda = 0.550$ mm, obtained by passing white light through a green interference filter. The transmitted light intensity was measured by a CCD camera and a video recorder. Video images were transferred to a computer, and the mean intensity $I$ of a fixed, central square portion of the film of size $145 \times 145$ $\mu$m was recorded.

The film thickness $h$, which depends on the distance $\ell$ between the wires, was measured by an interferometric method [14] on samples similar to those we used for our measurements. In general, $h$ decreases with increasing $\ell$. For $\ell = 250$ $\mu$m, the mean value of $h$ was found to be $25\pm5$ $\mu$m, independent of the liquid crystal used to form the film. These values of $h$ were verified in the films that we used for studying the orientational transition by measuring the wavelength of low-frequency electrohydrodynamic-instability domains [15] in MBBA films and by measuring the Fredericks effect threshold voltage [11] in 5CB films. The values of $h$ that we obtained were in satisfactory agreement with the interferometric data.

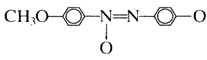
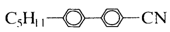
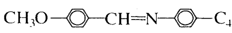
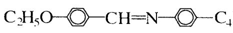
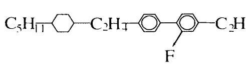
The temperature dependence of $I(T)/I_0$ [where $I_0$ is the maximum value of $I(T)$ observed] for MBBA and I52 freely suspended films, obtained as outlined above, is shown in Fig. 3. Successive maxima of the $I/I_0$ curves correspond to additional phase delays $\Delta\phi$ in the transmitted light of $\Delta\phi = \pi$. The small difference between heating and cooling curves (hysteresis) can be explained by the finite temperature scan rate. Indeed, doubling the scan rate to $dT/dt = 0.3$ °C/min approximately doubles the hysteresis.

From Fig. 3, we see that for MBBA we have an orientational transition from tilted to homeotropic alignment (when heating) at $T_0 = (22.2\pm0.15)$ °C. Our data for MBBA agree satisfactorily with the results of Faetti and Fronzoni [4]. For I52, we find, inversely, that the orientational transition from tilted to homeotropic alignment occurs when *cooling* at $T_0 = (23.6\pm0.15)$ °C.

Note that freely suspended films of 5CB exhibited homeotropic orientation of the director over the entire interval of temperature studied (15 °C $< T < T_{\mathrm{NI}}$).

It is important to realize that orientational transitions in freely suspended films are driven purely by surface effects. The boundary conditions at the film's surface (director tilted, with $\pm\theta$ being degenerate) are compatible with the uniform, undistorted nematic state shown in Fig. 1; hence, any volume distortion of the director field must have a higher free energy. Note that a number of experiments have been done where different conditions at the top and bottom of the sample imply different boundary conditions there. In these cases, the elastic bulk energy is important [11,16,17].

TABLE I. Physical parameters of nematic materials (at $T = 25$ °C, $\lambda = 515$ nm).

| Substance | Chemical formula | Phases | $\epsilon_a$ | $e$ ($10^{-4}$ dyn$^{1/2}$) | $n_o$ | $n_e$ |
|---|---|---|---|---|---|---|
| PAA [11] |  | $C \overset{117.5}{\leftrightarrow} N \overset{135}{\leftrightarrow} I$ | -0.16 [a] | | 1.565 | 1.829 |
| 5CB [11] |  | $C \overset{24}{\leftrightarrow} N \overset{35.3}{\leftrightarrow} I$ | 13 | 2.5 | 1.5616 | 1.8062 |
| MBBA [11] |  | $C \overset{16}{\leftrightarrow} N \overset{46}{\leftrightarrow} I$ | -0.7 | -4.5 | 1.5616 | 1.8062 |
| EBBA [12] |  | $C \overset{40}{\leftrightarrow} N \overset{81}{\leftrightarrow} I$ | -0.5 [b] | | 1.537 [c] | 1.745 [c] |
| I52 [13] |  | $C \overset{\overset{24}{\leftarrow} S_B \overset{13}{\leftarrow}}{\longrightarrow} N \overset{103.4}{\leftrightarrow} I$ | -0.06 | | 1.5054 [c] | 1.6533 [c] |

[a] $T = 125$ °C.
[b] $T = 60$ °C; this was estimated from data on mixtures of MBBA and EBBA [12].
[c] $\lambda = 546$ nm.

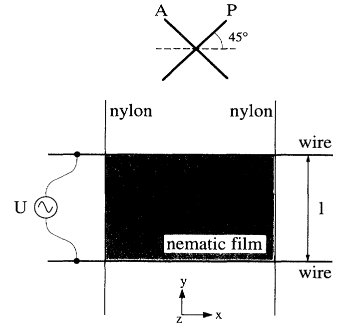


FIG. 2. A schematic diagram showing the experimental setup as viewed from above. The film is spread between two molybdenum wires spaced a distance $\ell$ apart. A voltage $U$ is applied between the wires to lift the azimuthal degeneracy of the director orientation in the plane of the film.

Thus, the temperature dependence of the film birefringence $\Delta n$ for MBBA and I52 films can be calculated simply from the $I(T)/I_0$ data. To do this, we have used the initial parts (up to the first maximum) of the $I(T)/I_0$ curves, and have extracted $\Delta n$ from these results using the following relation between the transmitted intensity and the phase delay [11]:

$$I = I_0 \sin^2[2\alpha] \sin^2[\Delta\phi/2] \ . \tag{1}$$

Here the phase delay is given by $\Delta\phi = 2\Delta n(T)\pi h/\lambda$, and the angle $\alpha$ between the wires of the frame and the polarizers was set to 45°.

The results for $\Delta n(T)$ calculated using Eq. (1) correspond to small values of $\theta$ ($\theta \ll 1$). From $\Delta n(T)$, we can obtain $\theta(T)$. Indeed, for $\theta \ll 1$, one can write for our experimental geometry [11]

$$\Delta n(T) \approx \left(\frac{n_o}{2}\right)\left(1 - \frac{n_o^2}{n_e^2}\right)\theta^2(T) \quad , \tag{2}$$

where $n_o$ and $n_e$ are the ordinary and extraordinary indices of refraction of the nematic. Values for $n_o$ and $n_e$ for the compounds studied are listed in Table I. Results for $\theta^2(T)$ are shown in Fig. 4. It is clear from this figure that $\theta^2(T) \propto T$, confirming that $\theta \propto | T - T_0 |^{1/2}$, in agreement with previous results on MBBA films [4].

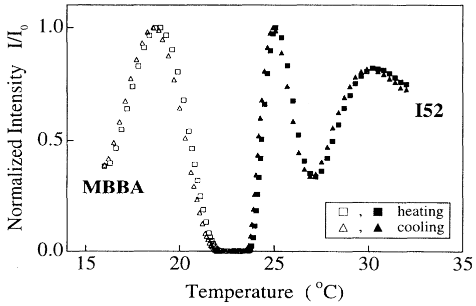


FIG. 3. Temperature dependence of the normalized transmitted light intensity $I(T)/I_0$ for MBBA (open symbols) and I52 (solid symbols) freely suspended films. The results for MBBA were obtained in the presence of a stabilizing AC voltage of 85 V, at a frequency of 29.0 kHz. The results for I52 were obtained with $U = 200$ V, also at a frequency of 29.0 kHz.

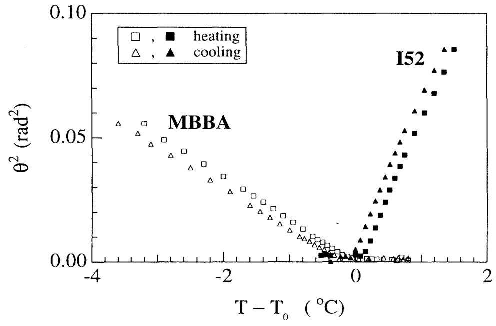


FIG. 4. Temperature dependence of the tilt angle $\theta$ for MBBA and I52 freely suspended films, calculated from the data of Fig. 3. Both sets of data are consistent with $\theta \propto (T - T_0)^{1/2}$.

As in Ref. [4], we have also found that the orientational transition temperature $T_0$ for MBBA depends upon $h$. It is lower for thinner films and higher for thicker ones and can be altered by several degrees as $h$ changes by several tens of microns. These results approach the limit observed in thick MBBA layers with only one free surface, which are characterized by $T_0 \simeq T_{\rm NI} - 1$ °C [5]. By contrast, $T_0$ is independent of $h$ for I52 films over the range of film thicknesses that we studied ($10 < h < 30$ $\mu$m). Very thin ($h \sim 1$ $\mu$m) samples of I52 and MBBA can occur in sample holders with larger wire spacing. In these films, the director remains homeotropic at all temperatures in the nematic phase, and no orientational transition is observed at all. Stable films of intermediate thickness are difficult to prepare.

We also verified that the above orientational transitions require weak anchoring: for I52 and MBBA samples between glass plates (treated with the silane compound ZLI-3124 (Merck) to ensure homeotropic ordering), the orientation is homeotropic over the temperature range 15 °C $< T < T_{\rm NI}$.

## III. DISCUSSION

### A. Models of orientational transitions

Orientational transitions and the temperature behavior of the tilt angle of MBBA freely suspended films have been discussed in terms of the following models: (1) Parsons' theory [7] takes into account the competition between quadrupolar and dipolar forces. Quadrupolar forces arise from van der Waals interactions between the anisotropic molecules of the nematic. They contribute a surface-energy term $(\hat{\mathbf{n}} \cdot \hat{\mathbf{k}})^2$ which favors planar alignment. As well, polar forces arising from an asymmetry between the two ends of the liquid-crystal molecule yield an $(\hat{\mathbf{n}} \cdot \hat{\mathbf{k}})$ surface-energy term, which generally favors homeotropic alignment. (2) The theory of Mada [8] balances the elastic torques due to a distortion of the director field near the free surface with those due to the "easy orientation" axis at the interface. (3) The model of Barbero *et al.* [9] introduces an order-electric surface polarization $\vec{P}_{\rm oe}$, which arises from the spatial variation of the nematic order parameter near the boundaries. Their approach is similar to that of Parsons; however, the presence of $\vec{P}_{\rm oe}$ implies an additional term $\propto (\hat{\mathbf{n}} \cdot \hat{\mathbf{k}})^4$ in the surface free energy. This model does not incorporate a polar term.

### B. Generalization of Parsons' model

We propose here a generalized version of Parsons' theory, which can explain satisfactorily the experimental data on the director orientation and the orientational transitions at the free surfaces of nematics.

The surface tension $\gamma_s$ of the free surface of a nematic can be expanded in powers of $\hat{\mathbf{n}} \cdot \hat{\mathbf{k}} = \cos\theta$ (see Fig. 1)

$$\gamma_s = \gamma_o - \gamma_p \cos\theta + \frac{1}{2}\gamma_q \cos^2\theta - \frac{1}{4}\gamma_{\rm oe} \cos^4\theta, \qquad (3)$$

where $\gamma_o$ is the isotropic component of the surface tension and $\gamma_p$, $\gamma_q$, and $\gamma_{\rm oe}$ are the polar, quadrupolar, and order-electric components of the surface tension, respectively, in the nematic phase [18,19]. Note that expressions analogous to Eq. (3) have been used to describe the anchoring of nematics with respect to solid surfaces [16].

### C. Physical contributions to the surface free energy

The various orientational transitions that have been observed can be described in terms of a Landau-like theory, where the coefficients $\gamma_p$, $\gamma_q$, and $\gamma_{\rm oe}$ are allowed to vary with different thermodynamic control parameters (temperature, ion concentration, etc.). Our goal will be to identify the physical mechanisms that determine these coefficients.

The polar and quadrupolar coefficients of the surface tension $\gamma_p$ and $\gamma_q$ contain contributions from a number of physical effects. We write

$$\gamma_p = \gamma_{\rm st} \pm \gamma_{\rm dp} \qquad (4)$$

and

$$\gamma_q = \gamma_{\rm vdW} \pm \gamma_{\rm sp} \pm \gamma_{\rm fe} - \gamma_{\rm sm} + \gamma_{\rm oe} \quad . \qquad (5)$$

Here, the indices st, dp, vdW, sp, fe, sm, and oe refer, respectively, to effective surface terms coming from steric forces, orientation of the surface dipole moments, van der Waals (dispersion) forces, surface polarization, gradient flexoelectricity, smectic ordering, and order-electric contributions. The + and − signs for $\gamma_{\rm dp}$, $\gamma_{\rm sp}$, and $\gamma_{\rm fe}$ correspond to longitudinal and transverse molecular dipole moments, negative and positive dielectric anisotropies $\epsilon_a$, and negative and positive flexoelectric coefficients $e$, respectively. These contributions are summarized in Table II and discussed individually below.

$\gamma_{\rm st}$: This contribution may appear when the nematic molecules have an anisotropy of form, e.g., different end groups. If one of these ends prefers to sit in the bulk of a mesophase, homeotropic alignment will be stabilized [7].

$\gamma_{\rm dp}$: This contribution appears for nematics whose molecules have constant (longitudinal or transverse) dipole moments. These molecular dipoles usually align near the surface, forming a surface layer of polarization $\vec{P}_{\rm dp}$ and thickness $l_s \sim 10^{-6}$ cm, where $l_s$ is the diffusion length [7,11].

$\gamma_{\rm vdW}$: The van der Waals interaction consists of fluctuation-induced dipole-dipole interactions. This is present even in the absence of permanent dipole moments. The interaction of an individual molecule with the surrounding medium near a surface falls off as $z^{-3}$. van der Waals forces orient the liquid-crystalline director parallel to the free surface [21].

$\gamma_{\rm sp}$: Impurity ions, which exist even in the purest samples, are adsorbed at nematic film surfaces and form a double ion layer. The double layer results in a surface ionic polarization $P_i$ and hence in an electric field perpendicular to the boundaries [22]. The strength $E_s$ of this field decreases exponentially as the distance from

TABLE II. Different contributions to the nematic surface tension. The surface free energy terms are obtained by integrating the bulk free energy over the sample thickness $h$, except in the term due to van der Waals forces where the integration is carried out over the thickness $h - 2\delta$. The strength of the van der Waals interaction is determined by the Hamaker constant $A$. In the case of surface polarization, the surface field $E_s$ is defined $E_s = (\sigma/\bar{\epsilon}\epsilon_0)\exp(-z/L_D)$, where $\bar{\epsilon}$ and $\epsilon_0$ are the average dielectric constants of the nematic and vacuum, respectively, and surface charge density $\sigma = \rho h/(2 + \rho h/\sigma_\infty)$, with bulk ion concentration $\rho$ and $\sigma_\infty = \sigma(z = \infty)$. In the smectic order term, $c_\perp$ is a Landau coefficient, and the smectic order parameter is defined by $\langle \Psi^2 \rangle = \langle \Psi_0^2 \rangle \exp(-2z/\xi_\parallel)$. In the order-electric polarization term $\epsilon_a \to 0$ and $\vec{P}_{\rm oe} = 3/2e\nabla S\ (\hat{\mathbf{n}}\hat{\mathbf{n}} - \tilde{\mathbf{I}}/3)$, where $\tilde{\mathbf{I}}$ is the Kronecker tensor and $S$ is the nematic order parameter.

| Mechanism | Ref. | Bulk free energy $F$ | Surface free energy $f$ | Coefficients $\gamma$ |
|---|---|---|---|---|
| Steric | [7] | | $\gamma_{\rm st}\cos\theta$ | $\gamma_{\rm st}$ |
| Dipolar | [7,11] | | $\gamma_{\rm dp}\cos\theta$ | $\gamma_{\rm dp}$ |
| Dispersion forces | [20,21] | $\left(A/z^3\right)\cos^2\theta$ | $\gamma_{\rm vdW}\cos^2\theta$ | $\gamma_{\rm vdW} = A/2\delta^2$ |
| Surface polarization | [22] | $\frac{1}{2}\lvert\epsilon_a\rvert\epsilon_o E_s^2\cos^2\theta$ | $\gamma_{\rm sp}\cos^2\theta$ | $\gamma_{\rm sp} = \frac{\lvert\epsilon_a\rvert L_D\sigma^2}{4\bar{\epsilon}^2\epsilon_0}$ |
| Gradient flexoelectricity | [27] | $\lvert e\rvert\left(\cos^2\theta - \frac{1}{3}\right)\frac{dE_s}{dz}$ | $\gamma_{\rm fe}\cos^2\theta + {\rm const}$ | $\gamma_{\rm fe} = \frac{\lvert e\rvert\sigma}{\bar{\epsilon}\epsilon_0}$ |
| Smectic ordering | [27–33] | $c_\perp\left\langle\Psi^2\right\rangle\cos^2\theta$ | $\gamma_{\rm sm}\cos^2\theta$ | $\gamma_{\rm sm} = \frac{c_\perp}{2}\left\langle\Psi_0^2\right\rangle\xi_\parallel$ |
| Order-electric polarization | [9,10] | $\frac{2\pi}{\bar{\epsilon}}\vec{P}_{\rm oe}^2$ | $\gamma_{\rm oe}\left(\cos^2\theta - \frac{1}{3}\right)^2$ | $\gamma_{\rm oe} = \frac{9\pi e^2 S^2}{2\bar{\epsilon}\xi}$ |

the surface increases with a characteristic decay radius $L_D$, the Debye screening length [23]. The contribution $\gamma_{\rm sp}$ to the surface tension represents the aligning effect of the surface electric field $E_s$. Depending on the sign of the dielectric anisotropy, this energy term can stabilize either planar or homeotropic alignments [22]. Note that the electric field created by surface molecular dipoles, which results in $\gamma_{\rm dp}$, can contribute to the field $E_s$ induced by the adsorbed ions, and, hence, to $\gamma_{\rm sp}$. Experiments on the electrokinetic effect in the isotropic phase of some nematic liquid crystals find for the surface-adsorbed ion charge density $\sigma \approx 10^{-12}$ C/cm$^2$ [24]. The surface polarization $P_s$ was also detected by means of optical second-harmonic generation [25] and modulation spectroscopy of light reflection at the interface between nematics and semiconductors. These last measurements gave $E_s \approx 10^4$ V/cm and $L_D \approx 10^{-5}$ cm [26]. However, neither of these methods could distinguish between the contributions to $P_s$ coming from $P_i$ and from $P_{\rm dp}$.

$\gamma_{\rm fe}$: Because the surface electric field $E_s$ created by surface adsorbed ions or molecular dipoles is spatially inhomogeneous, the gradient flexoelectric effect may be important. This results in a contribution $\gamma_{\rm fe}$. Depending on the sign of the flexocoefficient $e$ of the nematic material, this contribution can stabilize either homeotropic or planar alignments [27].

$\gamma_{\rm sm}$: The existence of smectic layers in nematics near solid substrates and at free surfaces was predicted [28–32] and has been observed experimentally for some nematic materials (e.g., cyanobiphenyl derivatives) [33,34]. Generally, these smectic layers orient themselves parallel to the boundaries, stabilizing a homeotropic orientation of the director [28–35] and leading to a surface energy term $\gamma_{\rm sm}$. The degree of smectic ordering decays exponentially away from the surface of a nematic with a characteristic decay length equal to the longitudinal smectic correlation length $\xi_{\parallel}$ [34]. Far from the nematic-smectic-$A$ phase transition temperature $T_{NA}$, $\xi_{\parallel} \sim 10^{-6}$ cm. Near $T_{NA}$, $\xi_{\parallel}$ diverges: $\xi_{\parallel} \propto (T - T_{NA})^{-\nu_{\parallel}}$, where the experimental values of the critical exponent $\nu_{\parallel}$ vary between 0.5 and 0.75 for different materials [35]. One expects considerable smectic surface ordering in nematic substances having large longitudinal dipole moments (e.g., cyanobiphenyl materials, such as 5CB) and in nematics that have a transition to some smectic phase at low temperatures (e.g., I52).

$\gamma_{\rm oe}$: As already mentioned, an order-electric polarization $P_{\rm oe}$ appears due to spatial gradients of the nematic order parameter $\nabla S$, which exist over distances from the surface comparable to the nematic correlation length $\xi \sim 5 \times 10^{-6}$ cm. This results in the contribution $\gamma_{\rm oe}$ [9,10]. This term can be important in cases where $\nabla S$ is large, e.g., at temperatures near the nematic-isotropic transition [36]. Since the experiments being considered here were done at temperatures far from $T_{\rm NI}$, $\nabla S$ should be small so that this is a small contribution ($\gamma_{\rm oe} \ll \gamma_p, \gamma_q$). As a result, only terms proportional to $\cos\theta$ and $\cos^2\theta$ need be considered in Eq. (3).

### D. Orientation transitions in Parsons' model

As discussed above, the various contributions determine the coefficients $\gamma_p$ and $\gamma_q$. Using these to find the equilibrium equilibrium orientation and neglecting the $\cos^4\theta$ term, we minimize Eq. (3) with respect to the tilt angle $\theta$,

$$\sin\theta\ (\gamma_p - \gamma_q \cos\theta) = 0, \tag{6}$$

which has two equilibrium solutions

$$\theta = 0 \qquad (\text{stable for } \gamma_p > \gamma_q), \tag{7}$$

$$\cos\theta = \frac{\gamma_p}{\gamma_q} \qquad (\text{stable for } \gamma_p < \gamma_q) \quad . \tag{8}$$

For small values of $\theta$ (near $T_0$) where $\cos\theta$ can be expanded as $\cos\theta = 1 - \theta^2/2$, the temperature dependence of $\theta$ (for $\gamma_p < \gamma_q$) can be expressed as

$$\theta = (A/B)^{1/2}, \tag{9}$$

where $A = A_0 \mid T - T_0 \mid = \gamma_p - \gamma_q$ (with $A_0$ a constant) and $B = 1/2\ \gamma_q$ are the Landau coefficients.

### E. Application to particular materials

The director orientation at the free surface of particular nematic materials can now be considered (see Tables I and III).

For PAA, $\gamma_p = \gamma_{\rm st} - \gamma_{\rm dp}$ and $\gamma_q = \gamma_{\rm vdW} + \gamma_{\rm sp} + \gamma_{\rm fe}$, where the contributions $\gamma_{\rm st}$ and $\gamma_{\rm dp}$ have opposite signs

TABLE III. Parameters of the orientational transitions as defined in Eq. (3). Type of alignment can be either planar ($P$), homeotropic ($H$), or tilted ($T$).

| Substance | Reference | $T_{\rm NI} - T_0$ (°C) | | Type of alignment initial → final (on heating) |
|---|---|---|---|---|
| PAA | [6] | | $\gamma_p \ll \gamma_q$ | $P$ |
| 5CB | This work | | $\gamma_p \gg \gamma_q$ | $H$ |
| MBBA | [5], free surface | 0.9±0.3 | $\gamma_p \simeq \gamma_q$ | $T \to H$ |
| MBBA | [4] | 12±0.3 | $\gamma_p \simeq \gamma_q$ | $T \to H$ |
| MBBA | This work | 12±0.15 | $\gamma_p \simeq \gamma_q$ | $T \to H$ |
| EBBA | [5], free surface | 1.2±0.3 | $\gamma_p \simeq \gamma_q$ | $T \to H$ |
| I52 | This work | 80±0.15 | $\gamma_p \simeq \gamma_q$ | $H \to T$ |

because the molecular dipole moment is transverse, and where the dielectric anisotropy and flexoelectric coefficient are both negative and smectic ordering effects are assumed to be negligible. One expects $\gamma_{st}$ to be small because of the symmetry of the molecule and, as a result, $\gamma_q \gg \gamma_p$. Planar alignment should always be stable, as is observed [6].

For 5CB, where $\epsilon_a > 0$ and $e > 0$, $\gamma_p = \gamma_{st} + \gamma_{dp}$ and $\gamma_q = \gamma_{vdW} - \gamma_{sp} - \gamma_{fe} - \gamma_{sm}$. Because of the longitudinal molecular dipole moment and the considerable surface smectic ordering, we expect $\gamma_p \gg \gamma_q$. This means that a homeotropic orientation will be stable, which agrees with our experimental observations.

For MBBA (or EBBA), $\gamma_p = \gamma_{st} - \gamma_{dp}$ and $\gamma_q = \gamma_{vdW} + \gamma_{sp} + \gamma_{fe}$ (transverse molecular dipole moment, $\epsilon_a < 0$, $e < 0$, no surface smectic ordering). The coefficients $\gamma_p$ and $\gamma_q$ have the same form as they do for PAA, and one would thus expect similar behavior. We can explain, qualitatively, the observed orientational transition from tilted to homeotropic upon rising the temperature as follows: First, $\gamma_{st}$ (and hence $\gamma_p$) should be larger in MBBA than in PAA since the end groups are different while in PAA they are the same. Second, the dielectric anisotropy $\epsilon_a$ is larger for MBBA (see Table I). Because $\epsilon_a$ (and hence $\gamma_{sp}$ and $\gamma_{fe}$) become small near $T_{NI}$, $\gamma_q$ should decrease significantly near $T_{NI}$. Thus, on the one hand, $\gamma_p$ is larger than it is in PAA, while on the other hand, $\gamma_q$ has a larger temperature variation near $T_{NI}$, making an orientational transition plausible.

For I52, $\gamma_p = \gamma_{st} - \gamma_{dp}$ and $\gamma_q = \gamma_{vdW} + \gamma_{sp} + \gamma_{fe} - \gamma_{sm}$ (transverse molecular dipole moment, $\epsilon_a < 0$, $e < 0$, surface smectic ordering). At higher temperatures, well above $T_{NA}$, the smectic-ordering term $\gamma_{sm}$ is negligible. One expects $\gamma_p < \gamma_q$ and a tilted director alignment. As the temperature is decreased and the smectic ordering term becomes more important, an orientational transition takes place at $T = T_0$, where $\gamma_p = \gamma_q$. For $T < T_0$, $\gamma_p > \gamma_q$ and the orientation is homeotropic. The temperature dependence of $\theta$ will have the form given in Eq. (9), $\theta \sim (T - T_0)^{1/2}$, which agrees with our experimental data.

The observed strong dependence of $T_0$ upon the film thickness $h$ for MBBA and weak dependence for I52 can be explained by the $h$ dependence of the $\gamma_{sp}$ term (which is due to the $h$ dependence of $\sigma$) (see Table II).

If in Eq. (3) we take into account $\gamma_{oe}$ and omit $\gamma_p$ (as in Refs. [9,10]), we obtain similar orientational transitions. This approach is valid for nematic films with nonpolar molecules in which there is no polar ordering at the surface (the $\hat{\mathbf{n}} \to -\hat{\mathbf{n}}$ symmetry is preserved).

Note, finally, that the orientational transitions in MBBA and I52 freely suspended films are similar in their physical mechanism (a balance between different contributions to the surface forces) to the so-called "spontaneous" [37,38] and "local" [39–41] Fredericks transitions. These are in fact orientational transitions in nematic layers (in contact with a solid substrate) due to the variation of control parameters such as the layer thickness, temperature, etc.

## IV. CONCLUSION

In conclusion, we have observed a temperature-induced orientational transition in freely suspended nematic I52 films. To explain this transition and the director orientation at the free surface of other nematics, we have generalized Parsons' phenomenological model based on the competition between polar and quadrupolar surface forces. Contributions to the surface tension coming from the surface ion adsorption, gradient flexoelectric effect, and surface smectic ordering have all been taken into account. We believe that the surface ordering that we observe to occur in I52 nematic films is induced by nearby smectic phases through the $\gamma_{sm}$ contribution to the surface free energy. This transition is remarkable in the sense that spontaneous symmetry breaking occurs as the temperature is increased, rather than decreased.

Finally, because of the large number of physical effects that are relevant to orientational transitions, we, and other workers, have only been able to make plausible hypotheses concerning the different terms relevant for particular cases. What is needed at this stage is a case where independent measurements of the relevant parameters are possible.

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[17] O.D. Lavrentovich and V.M. Pergamenshchik, Phys. Rev. Lett. **73**, 979 (1994). These authors discuss the effect of $K_{13}$ and $K_{24}$ terms on the director field. Because in our case the boundary conditions are compatible with a uniform director orientation, that will be the observed state. A lower-energy distorted state would be incompatible with the equilibrium state being a nematic.

[18] There is no $\cos^3\theta$ term in Eq. (3) for the following reason: Either the surface breaks the $\hat{\mathbf{n}} \rightarrow -\hat{\mathbf{n}}$ nematic director symmetry and the minimum of $\gamma_s$ is determined by the $\cos\theta$ and $\cos^2\theta$ terms, or the surface does not break the symmetry, and the minimum of $\gamma_s$ is determined by the $\cos^2\theta$ and $\cos^4\theta$ terms.

[19] In general, one would expand $\gamma_s$ in terms of spherical harmonics $Y_{lm}(\theta,\phi)$, but symmetry with respect to azimuthal orientations implies that only the $m = 0$ harmonic enters. The expansion then is equivalent to a power series in $\cos\theta$.

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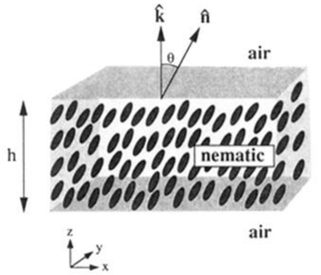

FIG. 1. A schematic diagram showing the orientation of the nematic director ($\hat{\mathbf{n}}$) with respect to the surface normal ($\hat{\mathbf{k}}$) of a freely suspended film. The film is bounded on both sides by air and has a thickness $h$.

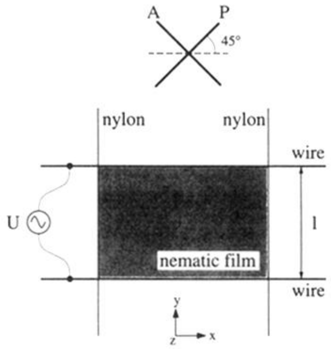

FIG. 2. A schematic diagram showing the experimental setup as viewed from above. The film is spread between two molybdenum wires spaced a distance $\ell$ apart. A voltage $U$ is applied between the wires to lift the azimuthal degeneracy of the director orientation in the plane of the film.