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Anchoring transition in a nematic liquid crystal composed of centrosymmetric molecules

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A temperature-driven anchoring transition strongly influenced by ionic impurities appears in a nematic liquid crystal composed of centrosymmetric molecules. Two anchoring parameters, the tilt angle and the anchoring strength, were measured. The observed phenomena are explained as a result of a balance between the orienting tendencies of electric double layers and direct molecular interactions at the interface.

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A spatial bounding of ordered media breaks the symmetry of the system and results in a rich variety of interesting phenomena. An exciting example is the possibility of reorientation (or anchoring) phase transitions. These transitions manifest themselves in experiments with ferromagnetics [1] and liquid crystals [2–11] as a surface reorientation of the vectorlike order parameter. The transitions should occur as a result of a changing balance between antipodal surface-alignment tendencies and, therefore, are of prime importance both for a fundamental understanding of surface alignment and for device applications.

In liquid crystals the situation is especially interesting since the number of possible factors influencing the surface phenomena seems to be larger than in other ordered media. Consider, for example, a simple situation where a nematic liquid crystal is in contact with an amorphous substrate. The surface free energy depends only on the polar angle θ between the director **n** and the surface normal **k**. Transitions between homeotropic ($\theta=0$), tilted ($0<\theta<\pi/2$) and tangential ($\theta=\pi/2$) orientation were observed [2–9] as a result of temperature changes. A few important conditions met in the experiments [2–9,11] inspired the associated explanations.

First, the transitions were observed only for liquid crystals with molecules possessing dipole moments [12]. The substitution of the asymmetric molecules by their symmetric dimers with zero average dipole resulted in disappearance of the transition [6]. At first glance the transitions can be explained according to the Parsons model [13] of competition between dipole and quadrupole interactions. Second, most experiments use surfactant coatings. Surfactant molecules such as lecithin or fatty acids have relatively long aliphatic tails whose polymorphism may drive the transition [3,7,11]. Third, some transitions occur in the vicinity of the melting point T_{NI} and therefore may result from the growth of an isotropic wetting film [2,14]. Other factors that may influence such transitions are balance of steric and dispersive forces [15], flexo- [16] and order-electricity [17], surface elasticity [18], impurities, etc. A reference system that allows one to discern the most relevant mechanisms is obviously needed. It might be a nematic liquid crystal composed of centrosymmetric molecules placed on a flat substrate.

We report on the observation of anchoring phenomena and, in particular, a temperature-driven anchoring transition in such a "reference" system. Given the liquid crystal and substrate employed, many of the above-mentioned models of the transition are not applicable. The Parsons model [13] is ruled out because the liquid-crystal molecules $C_7H_{15}(C_6H_4)N_2(C_6H_4)C_7H_{15}$ (p,p'-di-n-heptylazobenzene, DHAB) have zero dipole moments [19,20]. Second, the surface coating was provided by dimethyldichlorosilane, $(CH_3)_2SiCl_2$, with short methyl groups that have no degree of freedom for polymorphism. Third, the temperature of the anchoring transitions was well separated from T_{NI}. Finally, the most important result of the study is that the anchoring properties are strongly influenced by ions.

The glass substrates (Thomas Scientific, 72% SiO_2) were washed in an ultrasound bath using soap water (30 min), acetone (10 min), ethanol (10 min), and distilled water (12 h). Clean plates were dipped in a 10% hexane solution of dimethyldichlorosilane for 15 min to provide the coating. The resulting plates were strongly hydrophobic, which indicates that the surface was covered with CH_3 groups.

After coating, the plates were divided into three sets. The first set (denoted as "0" plates) was used as obtained for sample preparation (no additional washing). The "5" plates were washed over a period of 5 h, one by one, in 80 ml of distilled water using an ultrasound bath and then dried. The "24" plates were washed over a period of 24 h.

The cells "0," "5," and "24" were prepared from the corresponding plates with a spacing $h=19$ μm. The samples were cooled from the isotropic phase with temperature control better than 50 mK. The isotropic-nematic and nematic-crystal transitions were located at $T_{NI}=320.4$ K and $T_{NCr}=305.9$ K, respectively.

Viewed under the polarizing microscope the cells showed completely different orientation of the director **n**. Cells "0" show only homeotropic alignment, $\theta=0$, for $T_{NCr}\leq T\leq T_{NI}$. Cells "24" show only tilted orientation; θ changes with T but never becomes zero. Note that cells

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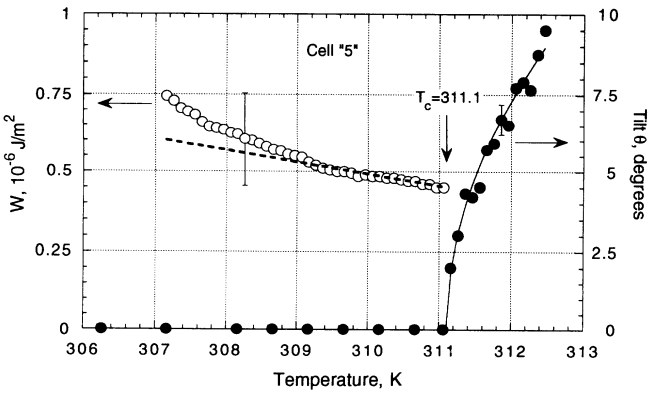

FIG. 1. Temperature dependencies of the tilt angle θ (closed circles) and the anchoring strength W (open circles) during the anchoring transition in the cell "5" that occurs at $T_c=311.1$ K. Lines correspond to the fit $\theta(T)=(180°/\pi)\xi\sqrt{T/T_c-1}$, Eq. (10), with $\xi=2.37$, and the calculated $W(T)$ as defined by Eq. (11) with parameters indicated in the text.

composed of uncoated glass plates also show tilted alignment. Finally, cells "5" exhibit a tilted to homeotropic anchoring transition (THT) at $T_c=310$–312 K (depending on the cell and the particular region of the cell) which is well separated from both T_{NI} and T_{NCr}.

The behavior of $\theta(T)$ was measured by a magnetic null method [21] using the "5" cell with plates gently rubbed in antiparallel directions to provide a uniform tilt (Fig. 1). We rotated the cell between the poles of an electromagnet (Varian, maximum field ~ 11 kG with 65 mm gap between the poles) until we found the orientation where the intensity of the He-Ne laser beam (4 mW) passing through the cell and polarizer behind it did not depend on the field strength [21]. The tilt angle was defined from the orientation of the sample since in the null position **n** is oriented along the magnetic field [21]. It does not appear that $\theta(T)$ has a discontinuity at $T=T_c$ (Fig. 1); thus the transition should be classified as a second-order transition.

An anchoring strength W (the work one needs to spend in order to deviate **n** from the equilibrium orientation) was defined from measurements of the equilibrium width d of the domain walls that occur during the THT and provide a reorientation of **n** between two regions of the sample with $\theta=0$. Balancing the anchoring and elastic forces leads to the formula [2]

$$W=\pi^2 K_{22} h/2d^2 , \tag{1}$$

where K_{22} is the twist elastic constant (known from Ref. [19]). W monotonically decreases with T, but remains nonzero at $T=T_c$ (Fig. 1). The $W(T)$ data should be considered indicative only since they correspond to the edge of validity of the wall method defined by [1] as $h<2K_{22}/W_a \sim 20$–25 μm.

The difference in the anchoring properties of the cells "0," "5," and "24" is evidently brought about by the difference in their preparation. The plate coating is a result of chemical reaction between the molecules $(CH_3)_2SiCl_2$ and the glass surface containing Si—OH groups. The chemical bonding occurs via links "Si—O—Si—$(CH_3)_2$" [22,23]. Such a reaction releases hydrogen chloride, HCl (Fig. 2). Since the HCl molecules dissociate into ions H^+ and Cl^-, the liquid crystal is doped with an electrolytic compound. The concentration of accumulated ions should be highest on the nonwashed "0" plates and lowest on the carefully washed "24" plates, as we verified in the following procedure. The plates from each set, with total surface area ~ 100 cm^2, were dipped in vessels filled with 25 ml of deionized water which has pH=7.0. The dipping of the "0" plates resulted in significant decrease of pH, down to 5.9; the "5" plates showed pH=6.6 while the "24" plates showed pH=6.9. This means that the concentration of H^+ ions in the vessel increased by ~ 13 times because of the release of ions from the "0" plates, the "5" plates increased the concentration by ~ 2.5 times, and the "24" plates only by ~ 1.1 times. Despite the fact that the measurements were performed for a water solution rather than for the nematic cells, they show that the concentration of ions is maximal in the "0" and minimal in the "24" cells.

If two adjacent nonidentical phases, one of which is electrolyte, are in contact, an electric double layer develops at the boundary between them; the driving force is often the accumulation of ions of a given kind on the boundary [24]. A resulting normal surface field $\mathbf{E}_S$ acts within a thickness equal to the Debye screening length L_D. As predicted by Barbero and Durand [25], the dielectric coupling between $\mathbf{E}_S$ and **n** contributes to the surface free energy:

$$f_{\mathrm{EDL}}=-\frac{\varepsilon_a L_D}{4\varepsilon_0\varepsilon^2}\sigma^2(\mathbf{n}\cdot\mathbf{k})^2 , \tag{2}$$

where $(\mathbf{n}\cdot\mathbf{k})^2=\cos^2\theta$, σ is the surface charge density, ε_0 is the electric constant, $\varepsilon_a=\varepsilon_\parallel-\varepsilon_\perp$ is the relative dielectric anisotropy ($\parallel$ and $\perp$ refer to the director **n**) and $\varepsilon=\varepsilon_\parallel\cos^2\theta+\varepsilon_\perp\sin^2\theta$, or, in terms of the averaged constant $\bar{\varepsilon}=\varepsilon_\parallel/3+2\varepsilon_\perp/3$ and ε_a:

$$\varepsilon=\bar{\varepsilon}+\varepsilon_a[(\mathbf{n}\cdot\mathbf{k})^2-1/3] . \tag{3}$$

For $\varepsilon_a>0$, which is the case for DHAB [19], $\mathbf{E}_S$ orients **n** *normally*. One of the consequences of Eq. (2) is that f_{EDL} depends on the cell thickness, because $\sigma=\sigma(h)$ [25].

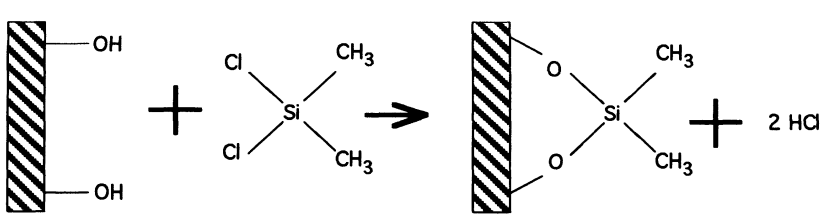

FIG. 2. Scheme of a reaction between the coating material and the glass substrate that releases HCl.

Thus data from experiments where the anchoring strength [26] or tilt angle [27] are thickness dependent can be explained by $\mathbf{E}_S \neq 0$ [25,16]. As discussed below, the electric double layers can be equally involved in the mechanism of the temperature-induced anchoring transitions when $\mathbf{E}_S$ competes with an opposite orientational tendency that sets tangential or tilted orientation.

An obvious orientational force at the interface different from $\mathbf{E}_S$ is due to direct molecular (e.g., the van der Waals) interaction between the nematic and the substrate. This net surface energy f_q can be represented in terms of the Landau–de Gennes theory as an expansion up to second order in the nematic scalar order parameter S [28]. For an amorphous substrate and a nonpolar nematic the only angular parameter entering the coefficients of the expansion is $(\mathbf{n}\cdot\mathbf{k})^2$ [28,29,14]:

$$f_q = (\beta_1 S - \beta_2 S^2)(\mathbf{n}\cdot\mathbf{k})^2 + \beta_3 S^2 (\mathbf{n}\cdot\mathbf{k})^4 \; ; \tag{4}$$

β_i are constants and S depends only on temperature. Even without the electric double layer term, only because $S = S(T)$, Eq. (4) predicts a rich variety of anchoring transitions as analyzed by Sluckin and co-workers [28,24] and Barbero, Gabbasova, and Osipov [29]. If $\beta_1 S - \beta_2 S^2 > 0$, Eq. (4) predicts *tangential* orientation. Note that a molecular theory of the nematic-vapor interface [30] resulted in $\beta_1 S - \beta_2 S^2 > 0$ for molecules which, to the lowest order, possess a quadrupole moment. The case $\beta_1 S - \beta_2 S^2 > 0$ might be close to the situation with "24" cells: tilted orientation in the cells "24" clearly indicates that in the absence of the electric double layers the equilibrium orientation is either tilted or tangential. However, we do not restrict ourselves by this inequality and consider Eq. (4) only a source of an alignment tendency *different* from the homeotropic orientation provided by $\mathbf{E}_S$.

The total surface energy density $f = f_q + f_{\mathrm{EDL}}$ follows from Eqs. (2)–(4) and the condition that $\varepsilon_a/\bar{\varepsilon}$ is small (≤ 0.2 for DHAB [19]) as

$$f = \left[\beta_1 S - \beta_2 S^2 - \left[1 + \frac{\varepsilon_a}{3\bar{\varepsilon}}\right] W_{\mathrm{EDL}}\right](\mathbf{n}\cdot\mathbf{k})^2 + \left[\beta_3 S^2 + \frac{3\varepsilon_a}{2\bar{\varepsilon}} W_{\mathrm{EDL}}\right](\mathbf{n}\cdot\mathbf{k})^4 \; , \tag{5}$$

where $W_{\mathrm{EDL}} = \varepsilon_a L_D' \sigma^2 / 4\varepsilon_0 \bar{\varepsilon}^2$ and $L_D' = L_D(\varepsilon/\bar{\varepsilon})^{1/2}$. To describe the temperature-driven transition, the temperature dependencies of ε_a, $\bar{\varepsilon}$, L_D', σ, and S should be considered.

For a nematic with zero molecular dipoles $\bar{\varepsilon} \approx \mathrm{const}$ while the dependency $\varepsilon_a(T)$ is close to that of $S(T)$: $\varepsilon_a(T) = \alpha S(T)$ [20]; therefore the form that one uses to represent $S(T)$ [29] can also be used for $\varepsilon_a(T)$:

$$S(T) = \varepsilon_a(T)/\alpha = \Delta \tau^{1/2} \; ; \tag{6}$$

here $\tau = (T_0 - T)/T_0 \ll 1$, $T_0 (> T_{NI})$, Δ and α are constants. L_D' grows with T, $L_D' \sim T^{1/2}$ [24], while $\sigma \sim [1 - \exp(-G/k_B T)]^{-1}$ [25]; $G > 0$ stands for the free energy of the adsorption and is supposed to be temperature independent for $T_{NCr} \leq T \leq T_{NI}$, and k_B is the Boltzmann constant.

Neglecting terms of order S^3 and higher, one has

$$f[S(T)] = (\beta_{11} S - \beta_{12} S^2)(\mathbf{n}\cdot\mathbf{k})^2 + \beta_{22} S^2 (\mathbf{n}\cdot\mathbf{k})^4 \; , \tag{7}$$

which is Eq. (4) with coefficients renormalized by the surface electric field:

$$\begin{aligned} &\beta_{11} = \beta_1 - \beta_{\mathrm{EDL}} \; , \quad \beta_{12} = \beta_2 + \alpha\beta_{\mathrm{EDL}}/2\bar{\varepsilon} \; , \\ &\beta_{22} = \beta_3 + 3\alpha\beta_{\mathrm{EDL}}/2\bar{\varepsilon} \; , \\ &\beta_{\mathrm{EDL}} = \alpha L_D'(T_0)\sigma^2(T_0)/4\varepsilon_0(\bar{\varepsilon})^2 \; . \end{aligned} \tag{8}$$

Note that $\beta_{22} \neq 0$: with $\beta_{22} = 0$ only first-order transitions are possible.

The equilibrium surface orientations θ are found from Eq. (7) using the conditions $\partial f/\partial\theta = 0$, $\partial^2 f/\partial\theta^2 > 0$. To provide a basic agreement with the fact that $\theta = 0$ in the low-temperature region, one should make $\beta_{11} > 0$, $\beta_{22} > 0$, and $\beta_{12} > 2\beta_{22}$. The minimizing of $f[S(T)]$ with $S(T)$ defined by Eq. (6) predicts that $\theta = 0$ when $T < T_c$, $\theta = \pi/2$ when $T > T_c'$, and $0 < \theta < \pi/2$ for $T_c < T < T_c'$; here

$$\begin{aligned} T_c &= T_0 \left[1 - \frac{\beta_{11}^2}{\Delta^2(\beta_{12} - 2\beta_{22})^2}\right] , \\ T_c' &= T_0 \left[1 - \frac{\beta_{11}^2}{\Delta^2 \beta_{12}^2}\right] , \end{aligned} \tag{9}$$

are the temperatures of the two second-order anchoring transitions, $T_c < T_c'$. Close to T_c, where $T - T_c \ll T_0 - T_c'$, one finds a simple power law for $\theta(T)$:

$$\begin{aligned} \theta &= \xi \left[\frac{T - T_c}{T_c}\right]^{1/2} , \\ \xi &= \left[\frac{\beta_{12}}{4\beta_{22}} - \frac{1}{2}\right]^{1/2} \left[\frac{T_c}{T_0 - T_c}\right]^{1/2} = \mathrm{const} \; . \end{aligned} \tag{10}$$

The model allows us to find also $W(T)$. Assuming that the wall contains pure twist deformation $\theta = \pi x/d$ along the transversal x axis,

$$\begin{aligned} W(T) &= \frac{2}{d} \int_0^d [f(\theta = 0) - f(\theta = \pi x/d)] dx \\ &= [\Delta^2(\beta_{12} - \tfrac{5}{4}\beta_{22})\tau - \Delta\beta_{11}\tau^{1/2}] \; . \end{aligned} \tag{11}$$

At $T = T_c$

$$W(T = T_c) = \frac{3\Delta^2}{4} \left[1 - \frac{T_c}{T_0}\right] \beta_{22} \; . \tag{12}$$

The model agrees fairly well with the experiment: (a) when $\beta_{\mathrm{EDL}} \gg |\beta_i|$, the equilibrium predicted by Eq. (7) is $\theta = 0$, which is the case of homeotropic orientation in the "0" cells with high concentration σ of ions and, consequently, large β_{EDL}; (b) the decrease in σ and β_{EDL} shifts the tilted state towards lower T, see Eq. (9), again as observed experimentally when one proceeds from cells "0" to cells "24"; (c) the experimental dependency $\theta(T)$ in cells "5" follows Eq. (10) very closely with a slope $\xi = 2.37$ (Fig. 1); (d) the monotonous decrease of $W(T)$, seen in Fig. 1, is in agreement with Eq. (11).

Experimentally we can estimate β_{11}, β_{12}, and β_{22} if Δ and T_0 are known. Using the results of $\varepsilon_{\parallel}(T)$ and $\varepsilon_{\perp}(T)$ for DHAB [20], $\varepsilon_a(T)$ is approximated by Eq. (6) with $T_0=340$ K and $\Delta\alpha=1.4$ for the interval of interest, $306<T<318$ K. Since in this range $\varepsilon_a\approx0.4$ [20] and S is supposed to be ≈0.6, Eq. (6) gives $\alpha\approx0.7$ and $\Delta\approx2$. From Eq. (12) and the result $W(T=T_c)=0.45\times10^{-6}$ J/m^2 one finds $\beta_{22}\approx1.7\times10^{-6}$ J/m^2. Furthermore, Eq. (10) with $\xi=2.37$ leads to $\beta_{12}\approx4.1\times\beta_{22}\approx7.2\times10^{-6}$ J/m^2. Finally, from the definition of T_c, Eq. (9), and the estimated β_{12} and β_{22}, it follows that $\beta_{11}=2.2\times10^{-6}$ J/m^2. The dependence $W(T)$ calculated from Eq. (11) using these values of $\beta_{11},\beta_{12},\beta_{22}$ is in good agreement with the experimental data, Fig. 1.

It is reasonable to assume that β_{EDL} is of the order of β_{11}, β_{12}, and β_{22}. Taking $\alpha=0.7$, $\bar{\varepsilon}=2.5$, and $\beta_{\mathrm{EDL}}\sim10^{-5}$–$10^{-6}$ J/m^2 one finds $\sigma^2L_D\sim(4$–$0.4)\times10^{-4}$ J/m^2. For comparison, given $\sigma\sim10^{-5}$–10^{-4} C/m^2 and $L_D\sim1$–0.1 μm [31,32], σ^2L_D is expected to range between 10^{-4} and 10^{-7} J/m^2, in agreement with our estimations.

The initial purpose of the experimental design was to eliminate the most obvious mechanisms as causes of the anchoring transitions: dipole-quadrupole balancing, surfactant polymorphism and surface melting. The results exceed the expectations and indicate that many other rather intrinsic liquid-crystalline factors (such as temperature dependency of S and the surfacelike elasticity) taken alone do not explain the observed anchoring phenomena, especially the drastic difference in orientation on the "0" and "24" plates. It turned out that the type of the orientation strongly depended on the concentration of ions accumulated on the plates during cell preparation. In the nematic cells these ions create the surface electric field which orients **n** normally to the plates. When the concentration of ions is high (cells "0") the orientation is always homeotropic. When the concentration is low (cells "24") the orientation is always tilted, indicating that in the absence of the electric double layers an equilibrium orientation is either tilted or tangential. A simple model of balance between the two opposite alignment tendencies provides a good agreement with the experimental findings, including the most interesting case of the cells "5" where the balance results in the temperature-driven anchoring transition. Work is presently underway to measure explicitly the tilt angle and the anchoring strength as a function of ion concentration.

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