Wetting Phenomena at the Free Surface of the Isotropic Phase of a Smectic Liquid Crystal

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We report an ellipsometric study of the free surface of a smectic liquid crystal possessing a smectic-A–to–isotropic phase transition. Approaching the transition from above, an ordered surface layer appears at a discontinuous transition one degree above the bulk transition temperature. With decreasing temperature the thickness of the surface layer increases continuously, indicating a possible logarithmic divergence at the bulk transition. The behavior may be described as complete wetting accompanied by a prewetting transition. [S0031-9007(97)03114-1]

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The free surface of thermotropic liquid crystals exerts a pronounced ordering effect to the molecules close to the surface which becomes apparent even above the transition to the isotropic liquid phase: Beaglehole [1] has reported an ellipsometric study of the free surface of the liquid crystal 5CB [2] above its isotropic-nematic transition. The results showed the presence of a nematic layer interposing the isotropic liquid-vapor interface; the nematic coverage was found to diverge logarithmically at the bulk nematic-isotropic transition temperature thereby indicating complete wetting. Since then, a number of nematic compounds were found to show essentially the same behavior [3,4].

Whereas in the nematic phase only a long-range orientational order of the rodlike molecules exists, smectic phases show in addition a quasi-long-range positional order leading to a layered structure. Thus, above a nematic-smectic [5–9] or isotropic-smectic transition [10–13] usually the formation of smectic layers at the free surface is observed. In particular, above the isotropic-smectic-A (Sm-A) transition of the compound 12CB [14] a sequence of five successive layering transitions was observed [10,13]; since the number of surface-induced smectic layers was finite, this behavior corresponds to partial wetting of the isotropic liquid-vapor interface by the smectic phase.

In this Letter, we report a new wetting behavior above an isotropic–Sm-A phase transition. Compared to the behavior of 12CB there are two main differences: first, the thickness of the ordered surface domain grows continuously with decreasing temperature and possibly diverges at the bulk transition; second, the first appearance of an ordered surface layer on the isotropic liquid is characterized by a sharp, discontinuous transition. The corresponding layer thickness just below this transition is not that of a single smectic layer but about twice as large. Thus, our results may be described by complete wetting accompanied by a prewetting transition.

We have studied the 4-hexyloxyphenylester of 4-dodecyloxybenzoic acid, labeled in the following as $\overline{12}.\mathrm{O}.\overline{6}$ (cf. Fig. 1), the Sm-A–isotropic transition temperature T_{AI} of the bulk sample is 89.1 °C. The compound was purified by chromatography and several recrystallizations. The temperature width of the two-phase region at the Sm-A–isotropic transition, observed in a polarization micoscope, was found to be smaller than the resolution (0.1 K) of the Mettler microscope hot stage.

An approximately 1 mm thick film of $\overline{12}.\mathrm{O}.\overline{6}$ was prepared on a rough glass substrate and placed into a temperature-controlled oven possessing a temperature stability of the order of 0.02 K. We used a phase-modulated ellipsometer [15] to study the change of polarization of a laser beam ($\lambda = 633$ nm) upon reflection by the free surface of our sample film; reflection from the second (liquid crystal glass) interface was suppressed by the substrate roughness. Two quantities Δ and Ψ are determined which describe the complex amplitude ratio r_p/r_s of the p- and s-polarized components of the reflected light as $r_p/r_s = \tan\Psi \exp(i\Delta)$ [16]. Measurements of Δ and Ψ were carried out as a function of temperature T and angle of incidence θ_i.

Of particular interest is the case when θ_i equals the Brewster angle θ_B. For an ideal steplike interface, one expects Δ to jump by π and $\tan\Psi = 0$ if $\theta_i = \theta_B$ (in the

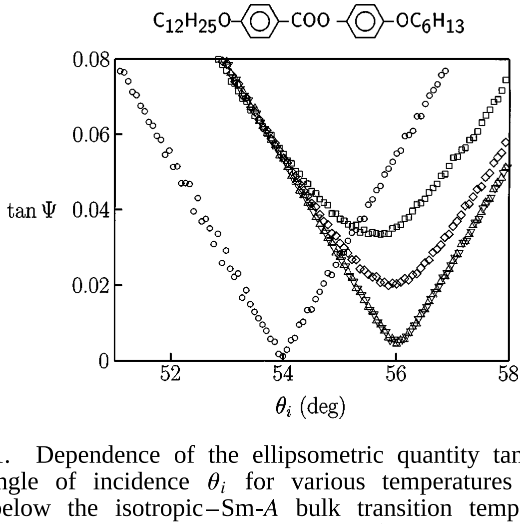

FIG. 1. Dependence of the ellipsometric quantity $\tan\Psi$ on the angle of incidence θ_i for various temperatures above and below the isotropic–Sm-A bulk transition temperature T_{AI}; △: T_{AI} + 2.9 K, ▽: T_{AI} + 1.7 K, ◇: T_{AI} + 0.7 K, □: T_{AI} + 0.2 K, ∘: T_{AI} − 0.2 K.

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following, we use the common designation $\overline{\rho}$ (ellipticity coefficient) for the value of $\tan\Psi$ at $\theta_i = \theta_B$). For a real interface, for which θ_B may be defined by the condition $\Delta = \pi/2$, $\overline{\rho}$ is finite and the deviation from zero is a measure of both the interface roughness (i.e., the deviation from a step profile) and the thickness of a layer interposing the interface between the two bulk media [17].

Figure 1 shows some $\tan\Psi$ vs θ_i curves for temperatures below and above T_{AI}. At temperatures $T > T_{AI} + 1$ K, the curves do not change with temperature and $\overline{\rho}$ and θ_B (the values of $\tan\Psi$ and θ_i at the minimum) stay constant. For $T_{AI} < T < T_{AI} + 1$ K, the curves are shifted so that $\overline{\rho}$ increases and θ_B decreases with decreasing temperature. When the temperature is shifted below T_{AI}, $\overline{\rho}$ drops down to almost zero.

The behavior described above was studied in more detail by a measurement of the complete temperature dependence of $\overline{\rho}$ and θ_B which is shown in Fig. 2. The corresponding data were taken at a constant temperature rate (0.05 K/min) while θ_i was continuously adjusted so that $85° < \Delta < 95°$. As shown in Fig. 2, the constancy of $\overline{\rho}$, which is observed for high temperatures (we did not find a significant change of $\overline{\rho}$ in the T range up to T_{AI} + 30 K), is abruptly terminated by a sharp, steplike increase at a temperature 1 K above the bulk temperature T_{AI}. On approaching T_{AI} further, $\overline{\rho}$ increases continuously until it drops down to almost zero at T_{AI}. The increase of $\overline{\rho}$ is accompanied by a simultaneous decrease of θ_B. The data shown in Fig. 2 were found to be highly reproducible in subsequent heating and cooling runs with only a minor downshift of the transition temperatures (<0.1 K in 24 h). Further, we have used different kinds of rough substrates and did not notice an influence on our data as long as the liquid crystal layer thickness was of the order of 1 mm.

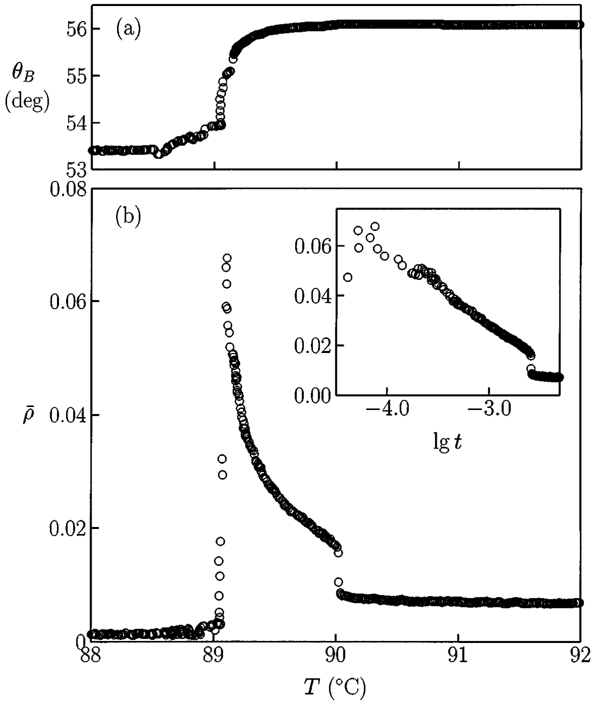

FIG. 2. (a) Temperature dependence of the Brewster angle θ_B. (b) Temperature dependence of the ellipticity coefficient $\overline{\rho}$; inset: the same $\overline{\rho}$ data on a logarithmic temperature scale, the reduced temperature $t = (T - T_{AI})/T_{AI}$ was calculated with $T_{AI} = 89.08$ °C (this value resulted from a least-mean-square fit with T_{AI} as a free parameter).

Which qualitative and quantitative properties of our experimental system can be extracted unambiguously from our data? To begin with, we can determine the values of the refractive index n_{iso} of the isotropic phase and the ordinary (n_o) and extraordinary (n_e) indices of the Sm-A phase from the corresponding values of θ_B [16]: The value of θ_B far above T_{AI} yields $n_{\mathrm{iso}} = 1.48$. If we assume that n_o and n_e must satisfy the relation $n_{\mathrm{iso}}^2 = \frac{2}{3}n_o^2 + \frac{1}{3}n_e^2$ (i.e., if we neglect the small density difference between the isotropic and the Sm-A phase), only the values $n_o = 1.446$ and $n_e = 1.545$ yield the experimentally determined value of θ_B below T_{AI}.

The most striking features of our experimental data are the discontinuity of $\overline{\rho}$ one degree above T_{AI} and the steep but continuous increase of $\overline{\rho}$ on approaching T_{AI}. We first discuss the continuous increase of $\overline{\rho}$. Since this increase is accompanied by a simultaneous decrease of θ_B, it is an indication of the presence of an anisotropic uniaxial surface layer with its optical axis parallel to the surface normal and its thickness increasing with decreasing temperature [1]. (An increase of $\overline{\rho}$ alone could be due also to an increasing roughness of the isotropic liquid-vapor interface but this cannot explain the behavior of θ_B.) Although it is easy to construct corresponding refractive index profiles which reproduce our experimental $\overline{\rho}$ values [18], it is hardly possible to prove a certain profile unambiguously. On the other hand, we can obtain a definite statement about an integral quantity, namely, the coverage $\Gamma = \int [n_e^2(z) - n_o^2(z)]\,dz$ (z being the direction along the surface normal) which is a measure of the "total amount" of the anisotropic excess surface order. As long as the characteristic lengths are considerably smaller than the wavelength of the light used for the measurements, $\overline{\rho}$ can be simply written as a sum $\overline{\rho} = \overline{\rho}_0 + \overline{\rho}_\Gamma$ where $\overline{\rho}_0$ is related to the surface roughness and $\overline{\rho}_\Gamma$ is directly proportional to Γ [1,19]. The inset of Fig. 2 shows $\overline{\rho}$ on a logarithmic temperature scale. The obtained linear dependence is consistent with a logarithmic divergence of Γ [20] at T_{AI} thereby indicating complete wetting of the isotropic liquid-vapor interface by the anisotropic, probably smectic [21], surface phase, similar to that observed above isotropic–nematic transitions [1,3,4]. The continuity of the increase of $\overline{\rho}$ indicates that the smectic layers develop continuously and not via a series of layering transitions as observed for 12CB [10]. We should note that the steep decrease of $\overline{\rho}$ at T_{AI} is not contradictory to a further increase of Γ. In fact, under ideal experimental conditions (temperature resolution better than 1 mK) one should observe a number of $\overline{\rho}$ oscillations, quenched into a very narrow temperature interval, since $\overline{\rho}$ as a function of Γ displays a nonmonotonic, oscillating behavior.

We now turn to the discontinuous onset of the surface order indicated by the $\overline{\rho}$ jump 1 K above T_{AI}. The presence of this $\overline{\rho}$ jump does not depend on the sign of the temperature rate, it appears, accompanied by a very small hysteresis, on cooling as well as on heating (cf. inset of Fig. 3). Since the $\overline{12}$.O.$\overline{6}$ compound shows a direct isotropic–Sm-*A* transition, one might think that this $\overline{\rho}$ jump indicates the formation of a single smectic layer at the surface but our results do not support this assumption: First, we can make an estimation of the thickness of the surface layer just below the $\overline{\rho}$ jump. The magnitude of $\overline{\rho}_\Gamma$ just below the $\overline{\rho}$ jump is estimated to be 0.01 or larger (cf. [20]). From this value, one obtains a thickness of 7 nm (which is about twice the length of the $\overline{12}$.O.$\overline{6}$ molecule) if we apply a simple slab model, i.e., if we assume a homogeneous layer possessing sharp boundaries and constant n_o and n_e values equal to those measured for the bulk Sm-*A* phase below T_{AI}. The uncertainty of this thickness estimation, resulting from the fact that we do not know the exact shape of the refractive index profile, is of the order of 1–2 nm. Second, we have studied the 12CB compound, which shows the formation of single smectic layers at the surface, under the same conditions. Although the smectic layer thickness of 12CB amounts to a value larger than that of $\overline{12}$.O.$\overline{6}$ [22], the layering transitions of 12CB cause $\overline{\rho}$ steps which possess only half of the height of the single $\overline{\rho}$ jump of $\overline{12}$.O.$\overline{6}$ (cf. Fig. 3). Further, the appearance of the $\overline{\rho}$ discontinuity of $\overline{12}$.O.$\overline{6}$ is considerably sharper than the $\overline{\rho}$ steps of 12CB. Thus, it seems that the anisotropic layer at the free surface of $\overline{12}$.O.$\overline{6}$ is produced by a mechanism different from that of 12CB.

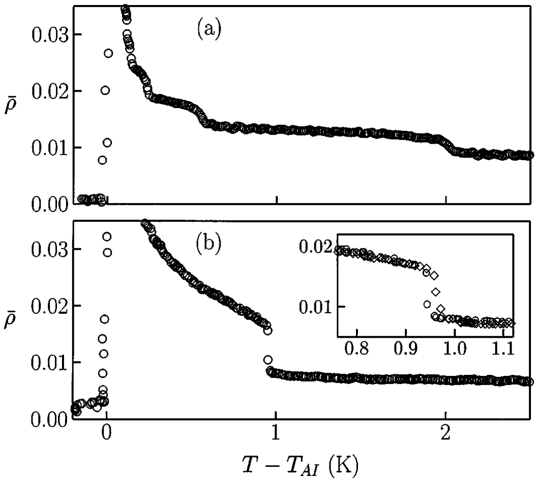

FIG. 3. Comparison of the temperature dependencies of the ellipticity coefficient $\overline{\rho}$ for 12CB (a) and $\overline{12}$.O.$\overline{6}$ (b); at least three layering transitions are clearly discernible for 12CB. Inset: Temperature dependence of $\overline{\rho}$ near the possible prewetting transition of $\overline{12}$.O.$\overline{6}$; ○: cooling run, ◇: heating run.

To summarize our experimental results, at a temperature 1 K above the bulk transition temperature T_{AI} a discontinuous change of the structure of the free surface of isotropic $\overline{12}$.O.$\overline{6}$ occurs. The ellipsometric data indicate the appearance of a uniaxial surface layer with its optical axis parallel to the surface normal. An estimation of the layer thickness just below the surface transition leads to a value of about 7 nm. On approaching T_{AI} further, the coverage Γ increases continuously. Although the data are consistent with a logarithmic divergence of Γ at T_{AI}, we have, because of the limited temperature resolution, no unambiguous proof that Γ goes to infinity. On the other hand, we can definitely state that the surface layer becomes thick: in the slab approximation the layer thickness amounts to 70 nm (about 20 molecular smectic layers) at the maximum of $\overline{\rho}$.

The discontinuous transition at which the surface layer first appears with decreasing temperature bears the characteristics of a prewetting transition which is expected for all systems showing a first-order wetting transition at coexistence. Experimentally, prewetting transitions are seldom observed [23–26] and, to our knowledge, no experimental observations of prewetting phenomena have been reported for liquid crystals. The behavior observed here at the free surface of $\overline{12}$.O.$\overline{6}$ may be thus the first example of a prewetting transition in liquid crystals.

Several theoretical studies [27–30] are concerned with the behavior near an interface above isotropic–Sm-*A* transitions. Especially suited for a free surface is the study by Mederos and Sullivan [29] who use a density functional model which yields the surface self-consistently between coexisting liquid and vapor phases without introducing external surface fields. This model predicts partial wetting and the absence of layering transitions. Our results agree with the latter prediction but the observed complete wetting, or at least a thick surface layer consisting of 20 or more smectic layers, is not predicted.

Based on [29], a more general model (which, however, concentrates on the situation near a rigid wall instead of a free surface) was presented [30] which predicts a variety of behaviors, e.g., prewetting transitions at which the surface layer thickness jumps by several smectic layers. Complete wetting, however, is obtained only in connection with an infinite number of layering transitions. On the other hand, it was proposed [30] that the layering transitions may be destroyed by roughening fluctuations leading to a single prewetting transition as observed in our study. Thus, a possible origin of the different behavior of $\overline{12}$.O.$\overline{6}$ and 12CB can consist of a different magnitude of roughening fluctuations, maybe as a result of the higher T_{AI} value of $\overline{12}$.O.$\overline{6}$ which is about 30 K above that of 12CB. Another possible origin of the different behavior may consist of a different "distance" to an isotropic–nematic–Sm-*A* triple point: for the *n*CB series (*n* gives the number of C atoms in the alkyl chain), which shows for $n < 10$ a nematic phase between the isotropic and

Sm-*A* phases, the layering transitions are found to become less pronounced with decreasing n. A reason for this may be a broadening of the interface between the smectic surface region and the isotropic bulk (e.g., because of an intermediate nematic region) leading again to roughening effects which suppress sharp layering transitions [11]. In the homologous series of the $\overline{n}$.O.$\overline{m}$ compounds, the nematic phase appears with decreasing n, m already in $\overline{11}$.O.$\overline{6}$ and $\overline{12}$.O.$\overline{4}$ [31], i.e., $\overline{12}$.O.$\overline{6}$ is close to the isotropic-nematic-Sm-*A* triple point. Finally, one should have in mind that the Sm-*A* layer structure is different in both compounds: whereas $\overline{12}$.O.$\overline{6}$ shows the classical monolayer Sm-*A* phase, the large longitudinal dipole in 12CB leads to a partial bilayer Sm-*A* structure. The free surface is known to promote polar smectic ordering [7] and may thus favor the formation of single smectic layers at the surface of 12CB.

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