

Surface Triple Points and Multiple-Layer Transitions Observed by Tuning the Surface Field at Smectic Liquid-Crystal–Water Interfaces

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We present an ellipsometric study of the interface between a smectic liquid crystal and water in the presence of a nonionic surfactant. The surfactant concentration serves as a handle to tune the surface field. For sufficiently large surfactant concentrations, a smectic phase is present at the interface in the temperature range above the smectic-*A*–isotropic bulk transition; when the bulk transition is approached, the thickness of this surface phase grows via a series of layer-by-layer transitions at which single smectic layers are formed. At lower surfactant concentrations, transitions appear at which the thickness of the surface phase jumps by multiple smectic layers, thereby implying the existence of triple points at which surface phases with different smectic layer numbers coexist. This is the first experimental demonstration of such surface triple points which are predicted by theoretical models.

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Understanding the behavior of soft matter at interfaces is essential for numerous topics in fields like nanotechnology, biophysics, colloids, emulsions, etc. Phase transitions at interfaces are also important from a fundamental viewpoint because of the great influence of fluctuations, new types of critical behavior, and novel ordering phenomena related to surface melting, surface freezing, adsorption, and wetting [1–4]. In many cases, theoretical models are more elaborate than corresponding experimental systems. One example is the surface-induced smectic order in the isotropic phase of thermotropic liquid crystals (LCs), for which theoretical models predict several features which have experimentally not been observed so far.

It is well known that thermotropic LCs exhibit surface-induced order at temperatures where the bulk phase is isotropic. As the bulk transition temperature T_b is approached from above, a large variety of growth processes of the thickness of the ordered surface phase is observed which has been discussed in terms of wetting (for reviews see [5,6]).

Above a smectic-*A*–isotropic transition, many LC compounds show a smectic surface phase which grows, as T_b is approached from above, via a series of discrete single-layer transitions, at which the thickness of the surface phase jumps by a single smectic layer. This behavior has been observed in numerous LCs at plane interfaces to air [7–12] or to solid substrates [13] as well as in cylindrical pores [14,15]. However, theoretical models [16–20] predict, depending on the magnitude of an effective surface field V , a richer variety of experimental behaviors than just a simple layer-by-layer growth. In the (T, V) plane, lines of first-order single-layer transitions are predicted which end in the high- V region at critical points and, at lower V values, at triple points at which single-layer transition lines merge to multiple-layer transition lines. When crossing such a multiple-layer transition line, the thickness of the surface phase should jump by several smectic layers. Whereas it

has already been shown experimentally that single-layer transitions can change from first order to continuous [9,15], the occurrence of multiple-layer transitions and the corresponding surface triple points has not been demonstrated so far. To the best of our knowledge, this applies as well to the related phenomenon of multilayer adsorption of simple molecules on solid substrates like graphite, which proceeds also in a layer-by-layer mode as the chemical potential of the adsorbate is increased (see, e.g., [21] and references therein). However, a recent adsorption study of acetone on graphite has indicated that several layers may be adsorbed simultaneously whereas a layerwise removal is observed on desorption [22].

A problem for systematic experimental studies of LC interfaces is the control of the surface field V . At an air interface, V is fixed for a given LC; at solid interfaces, suitable substrate modifications enable a certain control of V [6,15,23] but require considerable experimental efforts. At LC-water interfaces, the alignment of nematic LC phases can be influenced by surfactants [24–26]. Studies at alkane-water interfaces [27,28] have shown that surfactants can induce a surface freezing behavior which is analogous to that at bare alkane-air interfaces. Stimulated by these experiments, we have recently demonstrated that the effective surface field at LC-water interfaces, which might induce LC surface phases in the isotropic temperature range, can be controlled by varying the concentration of a suitable surfactant [29]; for the case of a nematic surface phase, the value of V was shown to vary linearly with the amount of surfactant adsorbed at the interface. In the present study, we apply this concept to a LC possessing a smectic-*A*–isotropic transition and explore the behavior at low surfactant concentrations. Our results directly demonstrate the existence of lines of first-order surface transitions in the (V, T) plane, at which the thickness of the surface phase jumps by multiple smectic layers. These multiple-layer transition lines split off at triple points at

which three surface phases with different smectic layer numbers coexist. We determine the surface phase diagram and compare it with theoretical predictions.

The compound under investigation, 12CB (4-dodecyl-4'-cynaobiphenyl, Synthron Chemicals, Germany) was recrystallized from ethanol and hexane; its smectic-A–isotropic bulk transition temperature T_b is 331 K. The surfactant, mono-olein (1-oleoylglycerol, Fluka) was used as received. For each measurement, about 300 mg 12CB were mixed with the appropriate amount of mono-olein by stirring the mixture 30 min at 243 K; we studied samples with the value of the surfactant mol fraction in the bulk LC phase, x_s , ranging from 0 to 0.03.

The presence and thickness of the smectic interface phase is determined by ellipsometry. The LC sample is placed into a Teflon tube (diameter 7 mm) which dips into a water reservoir. The thickness of the liquid-crystal sample amounts to several mm, so that the liquid-crystal–air interface is well separated from the liquid-crystal–water interface. Since the aqueous phase does not intrude between the LC and the Teflon surface, it is possible to tune the curvature of the liquid-crystal–water interface by adjusting the immersion depth of the Teflon tube. In this way, a planar interface, suitable for ellipsometric measurements, can be prepared. The interface is located in the center of a spherical glass container which is placed in a copper oven allowing for optical access of the incident and reflected laser beam of the ellipsometer. The temperature of the sample is controlled with a resolution of ≈ 0.02 K. A phase-modulated ellipsometer is used to determine the temperature dependence of the ellipticity coefficient $\bar{\rho}$ and the Brewster angle θ_B . More experimental details can be found in [30].

Figure 1 gives examples of the measured temperature dependence of the ellipticity coefficient $\bar{\rho}$ in the vicinity of the smectic-A–isotropic bulk transition for different surfactant mol fractions x_s . For $x_s > 7 \times 10^{-3}$, $\bar{\rho}$ increases with decreasing temperature via a series of several steps possessing approximately the same height; i.e., we observe a similar layer-by-layer growth of a smectic surface phase as in many other systems. The behavior of the Brewster angle θ_b , which shows a marked decrease as $T \rightarrow T_b$, clearly indicates that the optical axis of the smectic phase is oriented perpendicular to the interface (homeotropic anchoring), which is expected in the presence of surfactants possessing the usual structure with a polar head and a nonpolar tail [24]. The temperatures of the single-layer transitions, especially that of the $0 \leftrightarrow 1$ -layer transition, increase with increasing surfactant concentration. Three single-layer steps are clearly observed, in most runs an indication of a fourth step appears very close to T_b . The height $\Delta\bar{\rho}$ of the steps amounts to 0.023 ± 0.001 . The refractive indices of the smectic surface phase at an air interface of 12CB have been estimated as $n_o = 1.49$ and $n_e = 1.63$ [12]. Applying these values to the simplest possible model, in which the surface phase corresponds

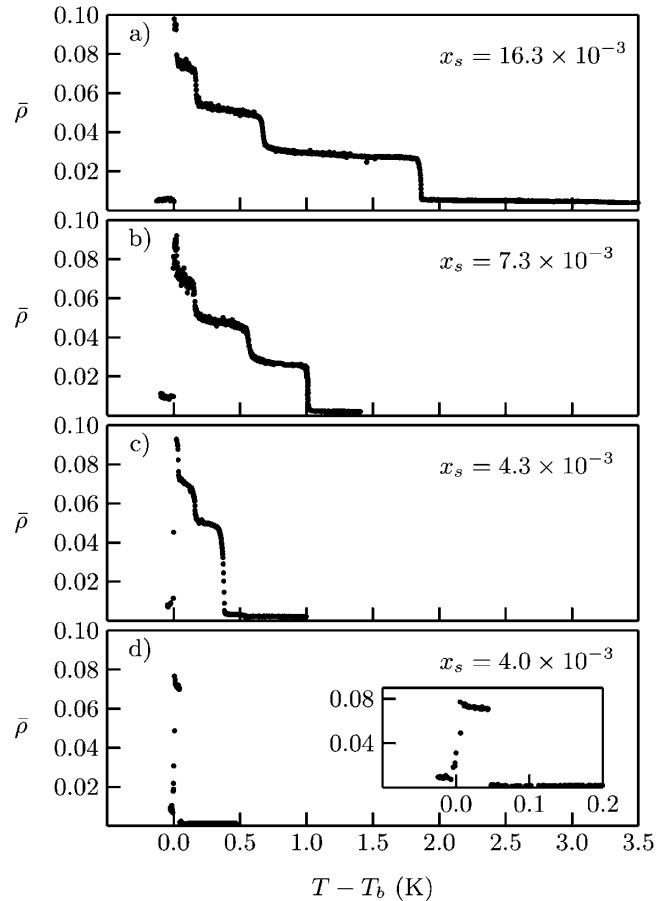


FIG. 1. Ellipticity coefficient $\bar{\rho}$ as a function of the temperature difference to the smectic-A–isotropic bulk transition temperature T_b at 12CB/water interfaces. The values x_s give the surfactant content (mol fraction) of the bulk 12CB phase. The data for $x_s = 4.3 \times 10^{-3}$ indicate a $0 \leftrightarrow 2$ -layer transition and for $x_s = 4.0 \times 10^{-3}$ a $0 \leftrightarrow 3$ -layer transition (the inset displays the same data on an expanded temperature scale).

to a homogeneous birefringent layer in which the refractive indices are constant and the optical axis is perpendicular to the interface, the steps $\Delta\bar{\rho}$ correspond to thickness changes of the surface phase of 4.0 ± 0.2 nm. This coincides well with the smectic layer thickness of 12CB which amounts to 3.9 nm according to x-ray diffraction measurements [31]; thus, there is no doubt that the $\Delta\bar{\rho}$ steps shown in Figs. 1(a) and 1(b) correspond to the formation of single smectic layers.

Figure 1(c) shows the results for $x_s = 4.3 \times 10^{-3}$. It is obvious that the two $\Delta\bar{\rho}$ steps located in Figs. 1(a) and 1(b) at the largest temperature differences to T_b have merged to a single step with double the height. Thus, instead of the two individual $0 \leftrightarrow 1$ -layer and $1 \leftrightarrow 2$ -layer transitions we observe for this lower surfactant concentration a single $0 \leftrightarrow 2$ -layer transition. At a slightly lower surfactant concentration, all three $\Delta\bar{\rho}$ steps have merged to a single step: for the sample with $x_s = 4.0 \times 10^{-3}$, a $0 \leftrightarrow 3$ -layer surface transition is observed just 50 mK above the bulk

transition [cf. Fig. 1(d)]. A further decrease of x_s changes the anchoring of the LC from homeotropic to planar and a smectic surface phase above T_b is no longer observed.

To further explore the nature of these new smectic surface transitions, we have performed subsequent heating and cooling runs with rates of 5 mK/min. As shown in Fig. 2, a clear thermal hysteresis of the order of 0.1 K is obtained, thereby indicating that we observe first-order transitions at which the thickness of the surface phase jumps by two or three smectic layers.

The multiple-layer as well as the single-layer transitions show a sharp appearance and occur within a narrow temperature interval of <50 mK. This suggests that the surfactant molecules form at the interface an isotropic 2D liquid or gas phase leading to a homogeneous surfactant coverage of the interface. The observed homeotropic anchoring of the LC director also supports this assumption since more condensed 2D mesophases of surfactants may lead to nonhomeotropic anchoring conditions [26].

Figure 3(a) shows the surface phase diagram resulting from our study of several samples with surfactant bulk mol fractions x_s between 4.0×10^{-3} and 32.8×10^{-3} . We have recently shown that the surfactant coverage Γ of the interface is, at least for a nematic surface phase, a linear measure of the effective surface field V [29]. The relation between Γ and the bulk surfactant concentration x_s is, for $x_s \ll 1$, described in the simplest case by the Langmuir adsorption isotherm: $\Gamma = Kx_s/(1 + Kx_s)$, with K being a constant. At present, we cannot directly measure the values of Γ in the system under investigation. However, we can make an estimation, if we assume that the temperature shift of the $0 \leftrightarrow 1$ -layer transition is proportional to Γ , if we are not too close to the $(0,1,2)$ -layer triple point. From the values of $T_{0 \leftrightarrow 1}$ determined in the samples with the four largest x_s values, we obtain $K \approx 70$. The Γ vs T diagram based on this K value is shown in Fig. 3(b), which can be considered as a qualitative (V, T) surface phase diagram.

Our surface phase diagram closely resembles a theoretical (V, T) surface phase diagram obtained by Pawlowska *et al.* [16] as far as the locations of the triple points and the relative positions of the different layer transitions are con-

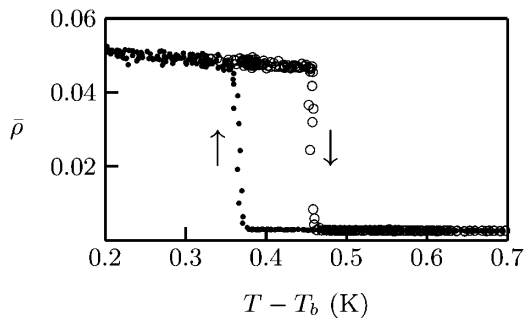


FIG. 2. Temperature dependence of the ellipticity coefficient $\bar{\rho}$ in the vicinity of a $0 \leftrightarrow 2$ -layer transition, determined at a slow heating (\circ symbols) and cooling (small dots) rate.

cerned. As observed by us experimentally, the model of [16] predicts with decreasing temperature either a sequence of single-layer transitions or a multiple-layer transition followed by one or more single-layer transitions. The predictions of [16] are based on a lattice model in which the influence of the surface is described by an ordering potential of the form $-VP_2(\cos\theta)$ acting only on the first surface layer (P_2 denoting the second Legendre polynomial and θ the angle between the long molecular axis and the surface normal).

A different model by Somoza *et al.* [20] is based on density functional theory. The influence of the surface is described, apart from confining the liquid into one-half space, basically by the same ordering potential as in [16], supplemented by a factor resulting in a continuous decrease with z^3 (z being the distance from the surface). The main feature of [20] is a prewetting line (consisting of multiple-layer transitions), from which several single-layer transition lines split. This prewetting line is not observed experimentally in the system of the present study. However, for a certain set of parameter values, the model [20] predicts off-prewetting $0 \leftrightarrow 2$ -layer transitions and a

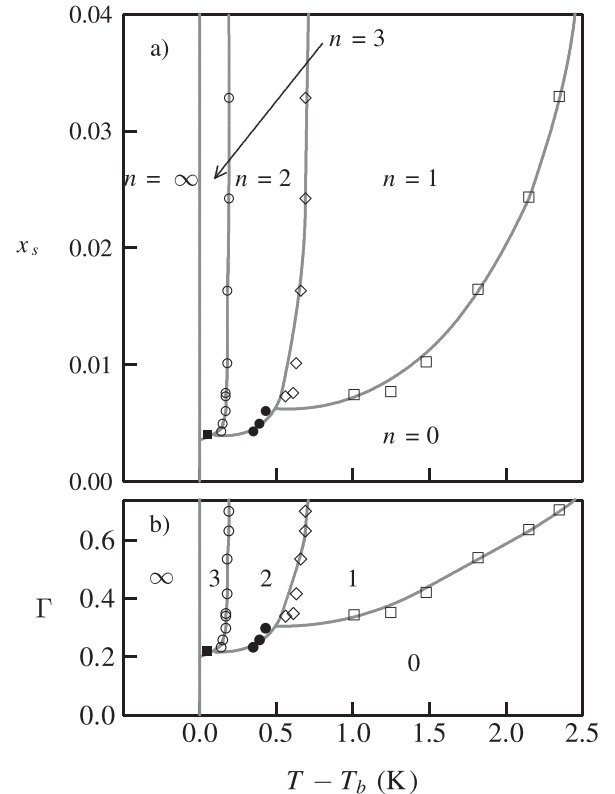


FIG. 3. (a) Surface phase diagram in the (x_s, T) plane. The values of n give the number of smectic surface layers. Open symbols: single-layer transitions; \bullet : $0 \leftrightarrow 2$ -layer transitions; \blacksquare : $0 \leftrightarrow 3$ -layer transition; T values are taken from cooling runs; lines are guides to the eye. (b) Same surface phase diagram after conversion of x_s (surfactant bulk mol fraction) to Γ (surfactant coverage of interface, see text).

(0,1,2)-layer triple point as observed in the present study. Thus, our experimental results may correspond to a special case of [20] with parameter values leading to a very short (experimentally unobservable) prewetting line.

Besides at interfaces separating two half-infinite volume phases, smectic-*A* layer-by-layer transitions have also been observed in more confined systems such as freely suspended smectic films [32] and smectic Langmuir films on water [33,34]. Freely suspended smectic-*A* films of compounds with fluorinated alkyl tails show above the bulk transition to the isotropic phase a series of irreversible thinning transitions at which the film thickness decreases by a single smectic layer. In thicker films, multiple-layer thinning steps were observed. The thinning transitions are probably initiated by the nucleation of defects [35] and result thus from a mechanism which is different from the transitions of the present study.

Some smectic LC compounds can be spread as Langmuir monolayers on water. On lateral compression, the inherent smectic phase structure permits the layerwise formation of stable multilayer structures. In these systems, only single-layer steps were observed. When the compressed Langmuir films are formed by polar LC compounds, which possess smectic-*A* phases consisting of interdigitated bilayers, the bilayer structure of the smectic volume phase is destroyed at the bare water surface where a polar monolayer is formed [34,36]. This is not the case in the present study where the volume smectic bilayer structure of 12CB is retained at the surfactant-laden water interface.

In conclusion, we have presented an ellipsometric study of the interface between water and the smectic liquid crystal 12CB doped with small amounts of the surfactant mono-olein. The variation of the surfactant concentration offers a handle to control the magnitude of the effective surface field. For surfactant mol fractions in the bulk 12CB phase larger than 0.007, a smectic surface phase is present at $T > T_b$ which grows in thickness via a series of single-layer transitions when the temperature is decreased toward T_b . With decreasing surfactant concentration, single-layer transitions merge first to a $0 \leftrightarrow 2$ -layer and then to a $0 \leftrightarrow 3$ -layer transition. The resulting surface phase diagram resembles the (V, T) diagram predicted by the lattice model of Pawlowska *et al.* [16].

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