

Atomic force microscope evidence for the existence of smecticlike surface layers in the isotropic phase of a nematic liquid crystal

K. Kočevar,¹ R. Blinc,^{1,2} and I. Muševič^{1,2}

¹*J. Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia*

²*Faculty of Mathematic and Physics, University of Ljubljana, Jadranska 19, 1000 Ljubljana, Slovenia*

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Using a temperature controlled atomic force microscope we have observed presmectic layering in the isotropic phase of 4-cyano-4'-*n*-octylbiphenyl (8CB) on silanated glass. The first molecular layer shows a smecticlike compressibility modulus of $B \approx 10^7$ N/m² and is stable more than 20 K beyond the bulk clearing point. It is followed by a presmectic modulation that increases when cooling towards the isotropic-nematic transition. In the bulk isotropic phase, the layers cover approximately 70% of the glass surface, indicating a clusterlike organization.

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It is well known that the breaking of a continuous translational symmetry by a flat surface induces stratification and oscillations in the translational and orientational order of matter [1]. It is also well known, since the pioneering work of Sheng and Miyano [2], that surfaces may induce significant surface *orientational order* even in the disordered, isotropic phase of liquid crystals. This pretransitional surface *orientational order* was observed, for example, by optical birefringence [2], ellipsometry [3], second harmonic generation (SHG) [4], nuclear magnetic resonance (NMR) [5], x-rays [6], and specific-heat [7]. Whereas most of these methods cannot discriminate between the positional and orientational ordering of liquid crystal molecules, some of them observe the structure of the interface in a reciprocal space and imply fitting of the spectra to the model interface. Direct space observations of the solid-liquid crystal interface were reported using a scanning tunneling microscope (STM) [8] and surface force apparatus (SFA) [9]. Unfortunately, these experiments were performed either at ambient temperature [8], or at some selected temperatures [9]. This has motivated us to perform temperature-controlled atomic force microscope (AFM) experiments. These can be performed in much smaller samples than in standard SFA, have a much smaller time constant and can be performed with a resolution of 10 mK.

Here we present direct structure of the liquid crystal-solid interface, as observed by measuring the interfacial forces with an atomic force microscope over a large temperature interval. We find that the interface of the nematic liquid crystal 4-cyano-4'-*n*-octylbiphenyl (8CB) on a silanated glass is formed of (i) clusters of smectic layers with a smectic amplitude of $\Psi_1 \approx 0.3$ that do not change significantly with increasing temperature and are stable more than 20 K above the bulk isotropic-nematic phase transition T_{IN} , and (ii) weak and strongly temperature dependent presmectic modulation, which follows this first molecular layer and decays exponentially into the isotropic bulk. This presmectic modulation is typically observed in a 10 K interval above T_{IN} . Our experiment is an unambiguous confirmation of what was previously conjectured: the interaction of the first layer of liquid crystalline molecules with a solid boundary is responsible for the aligning action of the solid surface [10].

The experiments were performed in the isotropic phases of 8CB on silanated glass surface. Glass substrates (Donnelly PD5005/5088) were thoroughly cleaned in acid, rinsed, and coated with a monolayer of (*N,N*-dimethyl-*N*-octadecyl-3-aminopropyltrimethoxysilyl chloride (DMOAP), as described elsewhere. This gave an excellent homeotropic alignment of liquid crystals in the nematic and smectic phases, as checked with a polarizing microscope on extra samples. In the experiments, we have used a Nanoscope III AFM, equipped with a double-temperature controlled microstage [11]. The silane-treated glass was attached to the hot surface of the microstage. The standard Si₃N₄ AFM tips (Park Scientific Microlevers) were used in the experiments, with force constants from 0.1 to 0.01 N/m and a typical tip radius of 20 nm. In other experiments, a glass microsphere coated with DMOAP was attached to the cantilever, thus measuring the force between a flat silanated glass surface and a silanated glass sphere, in the presence of a liquid crystal in between.

The AFM was used in the so-called force plot mode of operation, where the piezo scanner of the AFM and the substrate perform time-periodic linear movements in the direction of the AFM tip. The speed of approach is several nm per second and at the same time, the deflection of the AFM cantilever is monitored. Figure 1 shows an example of the force-separation plots for the 8CB-DMOAP silanated glass interface 8 K above the bulk isotropic-nematic phase transition. At large separations, the force on the AFM tip is nearly zero, as can be seen from the far-right part of the graph. At a tip-surface separation of 5–10 nm, the cantilever is suddenly attracted towards the surface (jump from point *A* to *B*). The attractive force is of the order of 10^{-10} N and the tip comes to force equilibrium at a distance of 1–2 molecular lengths away from the surface. After that, the cantilever starts to compress the material between the tip and the surface, until it reaches point *C*, indicated in Fig. 1. Here, the tip suddenly penetrates the surface-adsorbed molecular layer and comes in close contact with the surface, indicated by *D*. This happens at a tip-surface separation of typically 2 nm, which is close to the length of a single liquid crystal molecule.

Let us consider the compression of surface-adsorbed molecular layer from point *B* to the point of rupturing. For small

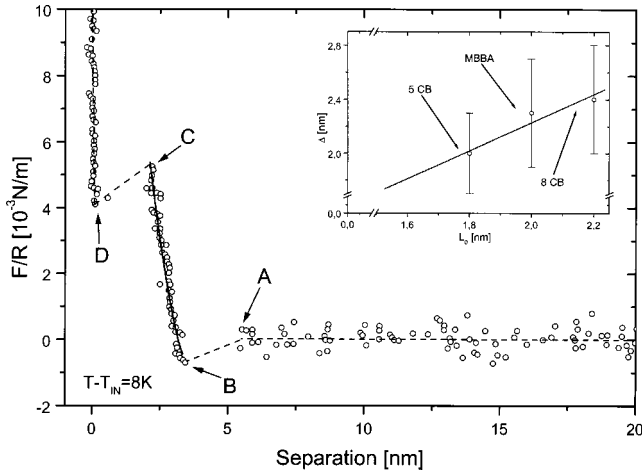


FIG. 1. Force on the Si_3N_4 AFM tip, normalized to the tip radius $R=20$ nm, as a function of separation between the tip and the DMOAP silanated glass surface in the bulk isotropic phase of 8CB. The solid line is the fit to the Hertz theory with compressibility modulus $E=1.6 \times 10^7(1 \pm 0.15)$ N/m² and a small van der Waals attractive force (Hamaker constant $A=5 \times 10^{-21}$ J) between the tip and the glass. The inset shows the thickness Δ of a fully compressed first layer as a function of length of fully extended liquid crystal molecule, which were also used in the experiments, i.e., 4-cyano-4'-*n*-pentylbiphenyl (5CB), 4-cyano-4'-*n*-octylbiphenyl (8CB), and *p*-methoxy benzylidene *p*-*n*-butylaniline (MBBA).

force loads, the thickness of this layer is ≈ 3 nm. By increasing the force of the AFM tip, the layer compresses to ≈ 2 nm and then ruptures at a force load of ≈ 60 pN. By performing trace-retrace experiments, we have observed that the compression of this layer is purely elastic, with no hysteresis indicating plastic deformation. We have also made sure that this layer cannot be attributed only to the silane monolayer by performing the same force experiment using hexane instead of liquid crystal. At a hexane-DMOAP interface we have observed an interfacial force that decayed exponentially with separation. The decaying length was typically ≈ 2.5 nm, and we could not observe any rupturing of the silane-hexane layer. This clearly indicates that: (i) silane molecules are strongly positionally anchored to the glass and contribute a small, polymer-entropic-like repulsive force; (ii) the rupturing is definitely attributed to the surface-adsorbed layer of liquid crystalline molecules. We have followed the temperature stability of this layer deep into the isotropic phase, as it can be observed more than 20 K above the T_{IN} . In this temperature range the layer shows no change of compressibility modulus or thickness, which is a clear indication of a very strong coupling of the first layer of liquid crystalline molecules to the substrate.

The compression of the first layer of liquid crystal molecules was analyzed using Hertz theory for the indentation of a flat surface of a soft material by the spherical AFM tip of radius R [12]. The depth of indentation is $\delta = \sqrt[3]{(9F^2)/(16RE^{*2})}$, where F is the force applied to the spherical tip and $E^*=E/(1-\nu^2)$, where E is the Young's elastic modulus of the surface layer and ν is the corresponding Poisson's number. The solid line in Fig. 1 shows the fit to the Hertz theory including a small van der Waals attraction between the tip and the glass. The elastic modulus of the

first molecular layer is in all cases of the order of $E=1 \times 10^7(1 \pm 0.15)$ N/m², which is typical for a smectic liquid crystal [13]. The continuum approach in the analysis of indentation of a thin adsorbed layer is justified, if the fluctuation contributions to the compressibility is small. In view of extremely strong thermal stability of the first adsorbed layer, we conclude that it is strongly adsorbed to the surface. Hence, the fluctuations are expected to be small and the mean-field description is legitimate. The constitution of the first molecular layer of 8CB on DMOAP silane-treated glass surface is therefore similar to smectic. The same was observed in separate experiments on 5CB and MBBA, which also showed the presence of the first molecular layer with similar properties. As shown in the inset to Fig. 1, the thickness of fully compressed first layer depends linearly on the molecular length, which indicates that the first layer is indeed formed of strongly adsorbed liquid crystalline molecules.

In the experiments with a sharp AFM tip, we have also investigated lateral coverage of silanated glass surface with smectic layers of 8CB. By performing numerous force-plots (i.e., 1700 curves in 30 experiments on different samples) we have observed that typically 70% of the interface is covered with clusters of smectic layers. As we could not directly image these clusters, we can only estimate their radius to $10 \text{ nm} < R_c < 100 \text{ nm}$. There are two possible explanations for this clusterlike adsorption of the ordered phase: (i) macroscopic inhomogeneities of the glass surface, and (ii) partial wetting of silanated glass by the ordered smectic phase in the presence of an isotropic melt. We presume that (i) is more likely the reason for the appearance of smectic clusters, as the AFM image of glass surface shows irregularities on the same scale as the cluster size. However, one should also keep in mind the possibility (ii) which is well known in the theory of growth of solid crystals [14]. The observed clusterlike growth of smectic layers in the presence of isotropic melt indicates Wolmer-Weber or island growth mode. This kind of growth can appear if the surface free energy of silanated glass w_{sub} is lower than $w_{\text{ad}} + \gamma$, where w_{ad} is the surface free energy of the adsorbed smectic phase and γ is the energy of the silanated glass-smectic interface. As silanated surfaces are indeed low-energy surfaces, this could be a realistic mechanism responsible for the clusterlike structure of liquid crystal interface.

The interfacial forces on the sharp AFM tip are too small to detect presmectic surface modulation following the first adsorbed layer, if any is present. We have therefore also measured the separation dependence of the interfacial forces using a silanated glass sphere of $R=6.2 \mu\text{m}$, attached to the AFM cantilever. The results are shown in Fig. 2, together with results for the sharp AFM tip at a temperature 0.05 K above the bulk nematic-isotropic transition. One can clearly see the periodic structural force due to presmectic, surface induced modulation, which was first discussed by de Gennes [15] and observed in lyotropic liquid crystals by Moreau, Richetti, and Barois [16]. In the DeGauguin approximation, this structural force is [16]

$$F = 2\pi R \alpha \xi_{\parallel} \rho_s \left(\tanh[(d-d_a)/2\xi_{\parallel}] + \frac{1 - \cos[\Phi]}{\sinh[(d-d_a)/\xi_{\parallel}] - 1} \right). \quad (1)$$

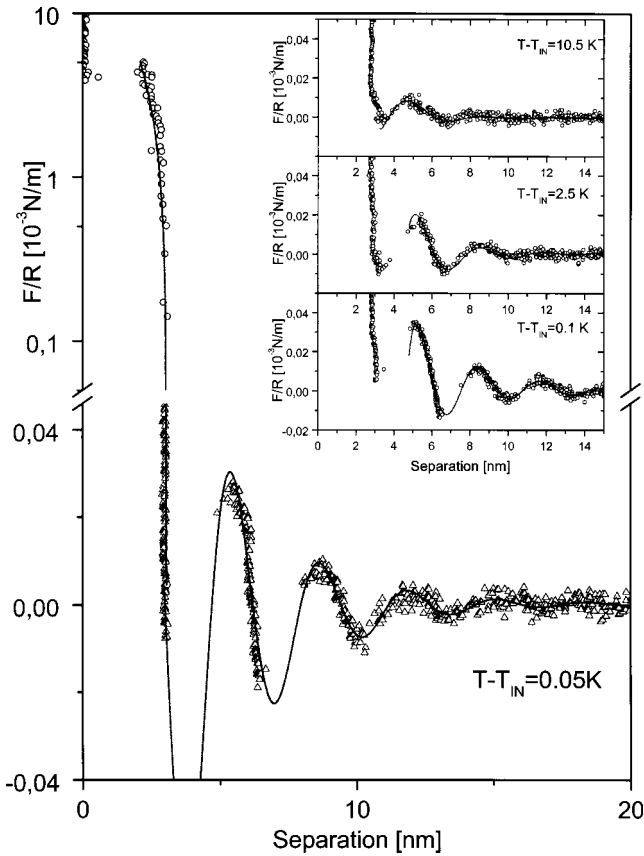


FIG. 2. Normalized structural force as a function of separation between a $6.2 \mu\text{m}$ silanated glass sphere and flat silanated glass surface in the bulk isotropic phase of 8CB, $T - T_{\text{IN}} = 0.05 \text{ K}$. The data at small separations, shown by circles, are obtained by a sharp AFM tip and the scale is here logarithmic. The solid line is the best fit to the Eq. (1) with $\psi_s = 0.04(1 \pm 0.05)$, $d_a = 3.2(1 \pm 0.015)$, and $\xi_{\parallel} = 2.9(1 \pm 0.15)$. The compression of the first layer is fitted to the Hertz theory with $E = 2.9 \times 10^7(1 \pm 0.15) \text{ N/m}^2$ and a small van der Waals attractive force with $A = 5 \times 10^{-21} \text{ J}$. The inset shows sequence of interfacial force profiles at different temperatures in the bulk isotropic phase.

Here d_a is zero-stress separation without any smectic layer in between. $\Psi = \psi e^{i\Phi}$ is the smectic order parameter, ψ measuring the amplitude of modulation, and $\Phi = (2\pi/a_0)u$ is the phase related to layer displacement u and smectic periodicity a_0 . $[\Phi] = \Phi(d/2) - \Phi(-d/2) = 2\pi(d - na_0)/a_0$, is the phase difference that gives rise to strain when the distance d between the surfaces is not an integral multiple of a_0 . $\rho_s = \psi_s^2$ is the smectic density at the surface. ξ_{\parallel} is the smectic correlation length and $\alpha = a(T - T_0)$ is the coefficient of the harmonic term of the Landau expansion, driving the *nematic-smectic-A* transition. The modeling force is in remarkable quantitative agreement with experiments and allows for an unambiguous determination of: (i) the smectic order ψ_s at the surface, (ii) the smectic correlation length ξ_{\parallel} , (iii) the smectic periodicity a_0 . By taking $a = 1.3 \times 10^5 \text{ JK}^{-1}\text{m}^{-3}$ [17], we obtain from data in Fig. 2 the smectic amplitude at the surface $\psi_s = 0.04(1 \pm 0.05)$, smectic correlation length of $\xi_{\parallel} = 2.9(1 \pm 0.15) \text{ nm}$, zero stress separation of $d_a = -0.8(1 \pm 0.2) \text{ nm}$ and smectic periodicity of

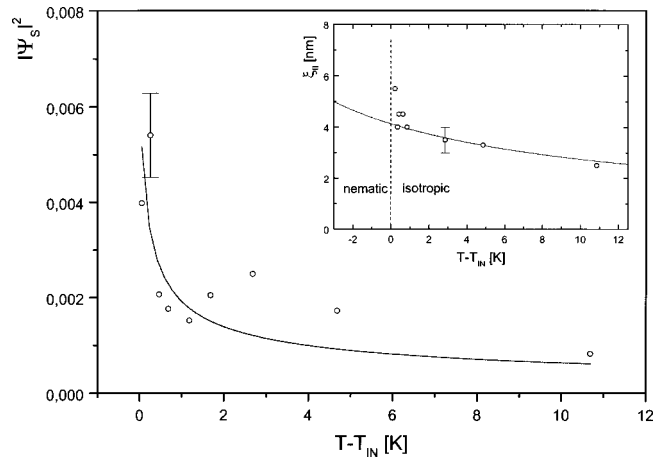


FIG. 3. Temperature dependence of the surface smectic amplitude ψ_s , calculated from the data in Fig. 2. The inset shows the temperature dependence of the smectic correlation length. Solid line represents x-ray measurements of Davidov *et al.* [18].

$a_0 = 3.2(1 \pm 0.015) \text{ nm}$. This is in excellent agreement with bulk values [18] and indicates bilayer presmectic ordering.

We can notice from Fig. 2 that the stiffness of the first molecular layer is nearly *two orders of magnitude larger* than the stiffness of the second, i.e., pre-smectic layer. The first layer is therefore too stiff to be ruptured by a micron sphere. As we find from our experiments, a linear dependence of the rupturing force on the smectic density, we can estimate the smectic order in the first molecular layer to $\psi_1 \approx 0.3$, which is similar to the results of Ocko on 12 CB [6]. We have also measured the structural force due to the presmectic modulation at different temperatures of the bulk isotropic phase of 8CB, which is shown in the inset to Fig. 2. One can clearly see, that the amplitude of the presmectic modulation increases continuously, as we approach the nematic phase from above and there is no discrete layer-by-layer growth, characteristic for 12 CB [6]. Finally, we show in Fig. 3 the temperature dependence of the presmectic surface order parameter ψ_s , together with the smectic correlation length. Surprisingly, the smectic order parameter at the surface increases rather significantly at the bulk phase transition into the nematic phase, whereas the smectic correlation length changes only slightly. This behavior is in fact expected due to the coupling between the nematic and smectic order parameters and due to the fact that in this system the surface nematic order parameter increases at the transition [3]. On the other hand, the smectic correlation length remains nearly unaffected when crossing this transition, and seems to be predominantly related to the bulk properties of a liquid crystal and to a lesser extent to the surface action.

In conclusion, we have observed smectic ordering of nematic liquid crystal 8CB at a solid interface, which persists deep into the bulk isotropic phase. We have shown that the first adsorbed molecular layer is a smectic layer, followed by a weak presmectic modulation that decays exponentially into the isotropic bulk. The amplitude of this presmectic order is nearly an order of magnitude smaller than the smectic order in the first layer. Equally important, we have observed in our AFM experiments that the surface-induced smectic order ap-

pears in surface clusters that cover approximately 70% of the surface. This clearly shows that the nature of the surface-induced orientational order of liquid crystals on real surfaces is at least in some cases much more complex than previously

believed and considered. In particular, our observation of the first molecular layer, which is always adsorbed to the solid surface, opens new questions relevant for the wetting behavior of liquid crystals and other complex fluids in general.

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