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Atomic force microscope study of presmectic modulation in the nematic and isotropic phases of the liquid crystal octylcyanobiphenyl using piezoresistive force detection

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Using a temperature controlled atomic force microscope (AFM), we have studied surface induced presmectic order in the nematic and isotropic phases of 4-cyano-4′-*n*-octylbiphenyl. A modified AFM head with piezoresitive cantilevers has been used to measure the structural force between a flat BK7 glass plate and a 10 μm glass sphere, both being treated to induce homeotropic alignment of the confined liquid crystal layer in between. We have observed surface-induced presmectic force not only in the isotropic, but also in the nematic phase. We have measured the temperature dependencies of the presmectic force, the smectic correlation length ξ and the smectic order parameter ψ at the surface. The correlation length $\xi(T)$ shows a power-law temperature dependence with a critical exponent of $\nu=0.67\pm0.03$ and the bare correlation length of $\xi_0=(0.39\pm0.08)$ nm, in good agreement with x-ray data. The smectic density at the surface is $\psi_S^2=0.4$ in the nematic phase and decreases in the isotropic phase.

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I. INTRODUCTION

When a smectic liquid crystal undergoes a phase transition from the smectic phase to a less ordered one, such as the nematic or the isotropic phases, the long-range one-dimensional (1D) positional order is lost and the liquid crystal phase recovers a complete translational symmetry of the isotropic liquid [1–4]. When such an isotropic liquid is confined between two flat and orienting surfaces, a layering of the molecules is induced close to the wall due to the breaking of the translational symmetry. As a result, a presmectic order is created at the surface, that decays into the isotropic bulk, the thickness of this interfacial region being of the order of the smectic correlation length. The presmectic layering at a solid wall can most straightforwardly be observed via a presmectic structural force, which is generated between two closely spaced surfaces with a pre-smectic film in between [5–10]. The surface-induced layering is not only characteristic of liquid crystal materials with tendency to form smectic phases, but is a much more general phenomenon, observable also for simple (even spherical) molecules, forming ordinary isotropic liquids [11].

The nature of the structural force between two surfaces separated by d and confining a thin presmectic film was first addressed by de Gennes [5]. He treated such a system in terms of the complex smectic order parameter $\Psi=\psi e^{-\phi}$, where the amplitude ψ is a local degree of the smectic order. The phase $\phi=2\pi u/a_0$ describes the local elastic deformation of the smectic layers and is related to the layer displacement u through the thickness a_0 of an uncompressed layer.

The first measurements of the structural force due to confined presmectic film were performed by Horn *et al.* [8] using surface force apparatus (SFA) in the thermotropic liquid crystals and later by Moreau *et al.* and Richetti *et al.* [9,10] in the lyotropic liquid crystals. Due to experimental limitations, the forces between the confining surfaces were measured only at room temperature.

Recently, Kočevar *et al.* [7,12–14] have used a temperature controlled atomic force microscope (AFM) to study the surface-induced nematic and smectic order in the isotropic phase of a 4-cyano-4′-*n*-octylbiphenyl (8CB) liquid crystal. By performing the force measurements at different temperatures, they could follow the temperature evolution and also characterized quantitatively the structural presmectic force in the isotropic phase of 8CB. However, due to experimental limitations, the force experiments could be performed in the optically isotropic phase only [15]. The strong scattering of light by collective molecular rotations in the nematic phase prevented the measurements in the nematic phase.

In this work, we extend the AFM force experiments to optically anisotropic and disordered fluids by introducing a force-detecting system, based on the piezoresistive AFM cantilevers [16]. The normalized force sensitivity of this AFM is directly comparable to the sensitivity of an SFA. This enabled us to perform a systematic characterization of the temperature dependence of the presmectic surface induced order in the nematic phase. We show that the smectic order is significant in the nematic phase of 8CB, confined in a thin layer between homeotropic orienting surfaces covered with N,N-dimethyl-N-octadecyl-3-aminopropyl trimethoxysilyl chloride (DMOAP). We analyze the force measurements using a Landau–de Gennes mean field theory for the presmectic force and determine the temperature dependence of the smectic correlation length and smectic order parameter at the surface. The results are in remarkable agreement with x-ray data [17] and show an extremely strong influence of the DMOAP surface anchoring.

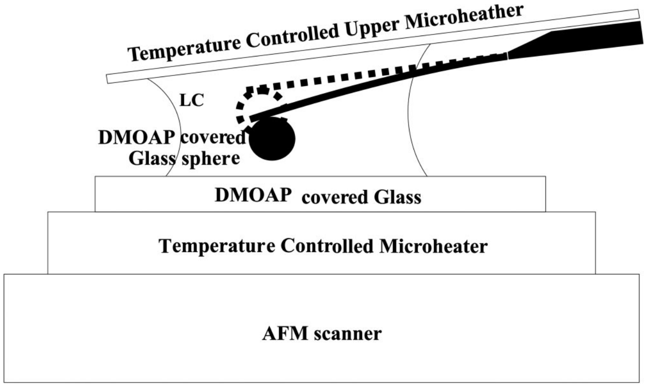

FIG. 1. Setup: The liquid crystal fills the space between a flat, DMOAP-covered glass substrate, mounted on the AFM scanner, and a thin glass plate rigidly mounted above the cantilever. The cantilever and the sphere are totally immersed in a liquid crystal.

II. EXPERIMENT

In order to overcome the experimental limitations of optically detected cantilever deflection in a standard AFM, we have replaced the optical head of our AFM (Digital Instruments Nanoscope III) by a homemade AFM head designed to operate with piezoresistive cantilevers, as described elsewhere [18]. The piezoresistive cantilevers used for our experiment (Veeco-Park Scientific Contact Piezolevers PLCT-SAMT) have an elastic constant of $k=1N/m$ and a RMS noise level of typically 300 pN. This is much worse than the noise level of several *pN* of an optical AFM, but is directly comparable to SFA noise level.

A temperature controlled hot stage was mounted on the AFM scanner and another temperature controlled hot stage was mounted above the piezoresistive cantilever [18]. Both were temperature controlled to better than 2 mK, and the temperature gradient inside the LC sample was smaller than 1.4×10^{-4} K/μm. The experiments were performed by confining 8CB liquid crystal (Merck) between a flat BK7 glass plate and a micrometer sized glass sphere, mounted to the piezoresistive cantilever, as described before [13]. Both confining surfaces were first cleaned in an ultrasonic detergent bath for 1 h. Then they were rinsed using a distilled water. After drying, the surfaces were cleaned in oxygen plasma at 100 °C with a RF power of 300 W for 1 h, in order to remove all organic substances adsorbed to the surface. Finally they were coated with a monolayer of DMOAP, that is known to give a good hometropic alignment of LC. The DMOAP monolayer was obtained by dipping the glass plate and the glass sphere in a DMOAP water-alcohol solution for several minutes. In order to wash out the excess of DMOAP, the DMOAP-covered surfaces were thoroughly rinsed with a distilled water, and the glass plate was dried at 110 °C in order to evaporate the solvent. The glass plate was mounted on the hot surface of the hot stage, that was put on top of the AFM scanner. The micron-sized glass sphere was glued on the free end of the AFM cantilever by means of a thermoplastic glue. In order to avoid the influence of capillary force due to air-liquid crystal interface, all measurements where performed having both the sphere and the cantilever totally immersed in the LC, using the scheme depicted in Fig. 1.

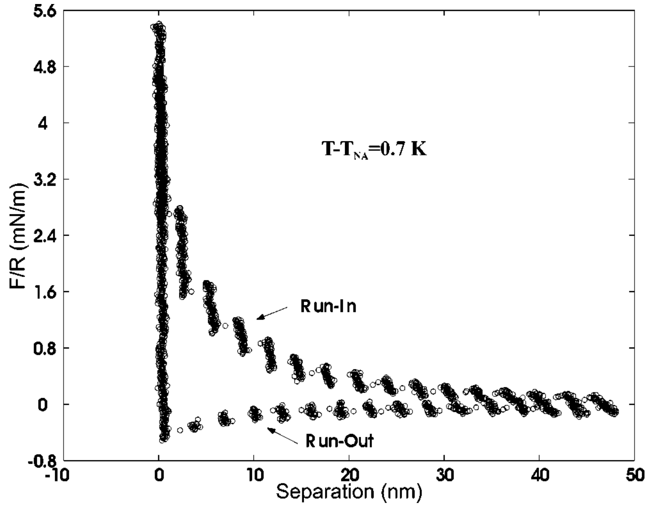

FIG. 2. The force as a function of surface separation, measured in the nematic phase of 8CB ($T-T_{NA}\approx 0.7$K). The LC is confined between a flat glass plate and a glass sphere, both covered with a DMOAP monolayer to induce homeotropic alignment. The radius of the sphere is $R\approx 10$ μm and the sphere is attached to the AFM cantilever that has an elastic constant of $k\approx 1$ N/m. The measurement shows an oscillating force, typical of a layered structure, that decays exponentially with increasing separation. Due to the mechanical instability of the cantilever, the regions in which $\partial F/\partial z > k$ are inaccessible to force spectroscopy.

The AFM was used in the force spectroscopy mode [12,13], where the surface separation was continuously changed at a constant speed, while the force between the surfaces was monitored. The speed of surface approach was 10 nm/s, which was low enough to prevent viscous drag forces.

III. RESULTS AND DISCUSSION

Figure 2 shows a typical force measurement obtained in the nematic phase of 8CB. The oscillations in the structural force are clearly related to the layering of the LC molecules at the interface. The layering is obviously promoted by the ordering effect of the surface and decays exponentially with separation from the wall [5]. The presence of discontinuities in the force-vs-separation measurements is due to the mechanical instability of the cantilever. This appears whenever the spatial gradient of the force on the cantilever $\partial F/\partial z$ is larger than the elastic constant of the cantilever k [15,20]. As a side effect of this mechanical instability, the maxima of the oscillating force appear only in the run-in, and, on the other hand, only the run-out force plot contains all the minima of the force.

Using the Derjaguin approximation [11], the presmectic force acting on the confined surfaces is [5]

$$\frac{F(d)}{R} = 2\pi\frac{L_A\psi_S^2}{\xi}\left[\tanh\left(\frac{d-d_0}{2\xi}\right) + \frac{1-\cos(2\pi(d-d_0)/a_0)}{\sinh(d/\xi)} - 1\right]. \tag{1}$$

Here R is the radius of the sphere, L_A is the smectic elastic constant, describing the free-energy increase when the smectic order varies in space. ψ_S and ξ are the smectic order at the surface and the smectic correlation length, respectively, d is the separation between the sphere and the flat surface, d_0 is the residual gap when the hard contact is reached, and a_0 is the thickness of an uncompressed smectic layer.

Making a large number of force measurements in different experimental runs, we noticed that the force measurements performed by compressing the confined LC (run-in) were extremely reproducible. On the other hand, in the force plots, performed by increasing the separation between the confining surfaces (run-out), the values of the first minima were not reproducible. This is most probably due to the perturbation caused on the first molecular layer by the hard contact, where the surface order might be partially disturbed. When increasing the separation, the local surface order may be recovered differently in different experimental runs. Because of their high reproducibility, only the run in of the force plot will be considered.

Figure 3 shows the force measurements performed in the nematic phase at different temperatures. One can clearly observe that by increasing the temperature, the number and the amplitude of the oscillations decrease. In general, we find that the experimental data can be well described by de Gennes equation for the presmectic force [Eq. (1)]. This allows us to determine, for each temperature, the values of (i) the thickness a_0 of an uncompressed layer, (ii) the smectic correlation length ξ, (iii) the residual gap at the hard contact d_0, and (iv) the smectic density at the surface ψ_0^2. In the analysis we have considered the value of $L_A = 5\text{pN}$ found in the literature [6]. The thickness a_0 of a single uncompressed smectic layer was found to be independent of temperature and its value $a_0 = (3.2 \pm 0.1)$ nm is in excellent agreement with the smectic period measured in the bulk by x rays [21]. Also the residual gap at the hard contact $d_0 = (6.1 \pm 0.3)$ nm does not show any temperature dependence. This value strongly suggests that a monolayer of LC is adsorbed on each DMOAP-covered surface, and that during the hard contact they cannot be expelled by the walls. This is quite reasonable and consistent with previous measurements of the presmectic force in the isotropic phase. The values obtained for the smectic density ψ_S^2 at the surface and for the smectic correlation length ξ will be discussed later.

When the LC was heated up into the isotropic phase, the force plots still show an oscillating behavior, but the number and the amplitude of the oscillations strongly decrease. In addition, an attractive component of the force becomes evident (see Fig. 4). We think that this attractive component is a mean-field contribution due to the spatial gradient of the nematic order. Including such a contribution, the total interaction reads [7]

$$\frac{F}{R}(d) = 2\pi \frac{L_A \psi_S^2}{\xi}\left[\tanh\left(\frac{d-d_0}{2\xi}\right) + \frac{1-\cos(2\pi(d-d_0)/a_0)}{\sinh(d/\xi)} - 1\right] + 2\pi\left[-\frac{w_1^2 \xi_N}{w_2\xi_N + L_N \tanh((d-d_0)/2\xi_N)} + \frac{w_1^2\xi_N}{w_2\xi_N + L_N}\right]. \tag{2}$$

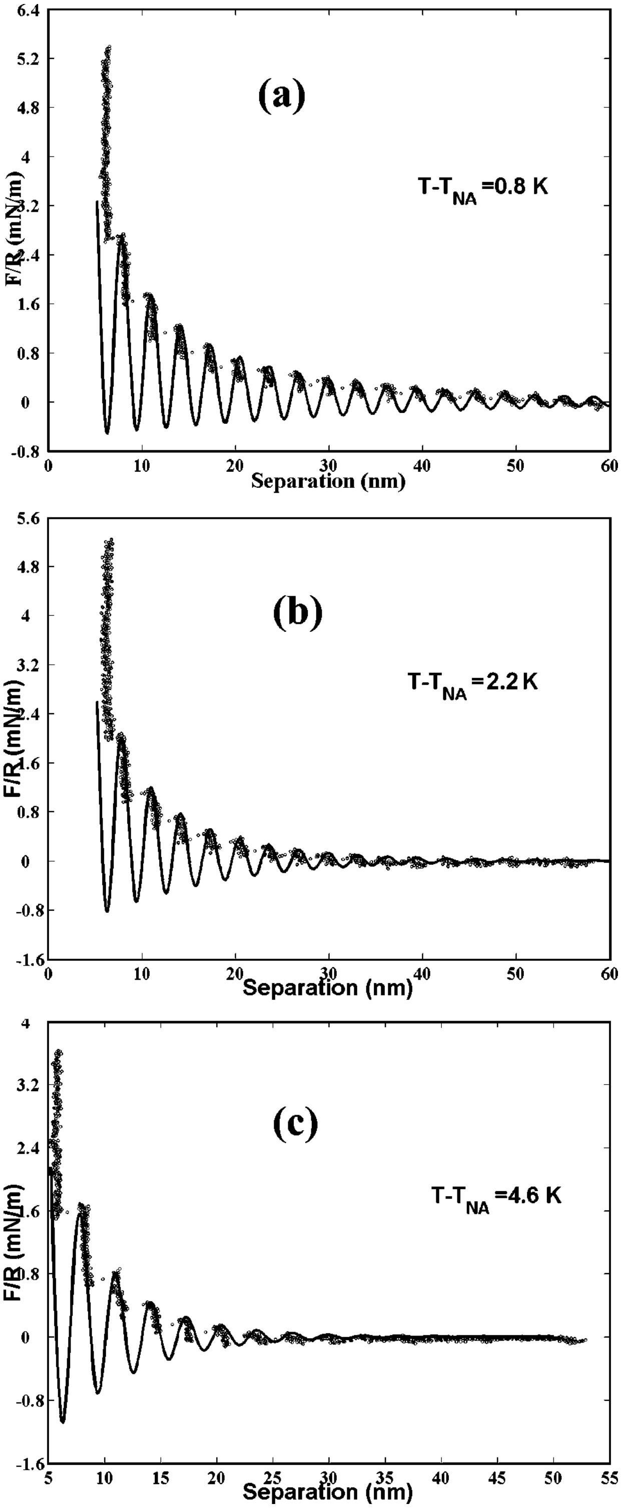

FIG. 3. The normalized force F/R between a DMOAP-covered glass sphere of radius $R = 10\ \mu$m, and a DMOAP-covered glass plate inside a nematic sample of 8CB. The solid line is the fit of the experimental data, by using the expression for the presmectic force, Eq. (1). (a) $T - T_{NA} = 0.8$ K, $\xi = (22 \pm 1)$ nm, $\psi_S^2 = (0.402 \pm 0.008)$ and $a_0 = (3.19 \pm 0.04)$ nm, $d_0 = (6.1 \pm 0.4)$ nm. (b) $T - T_{NA} = 2.2$ K, $\xi = (10 \pm 1)$ nm, $\psi_S^2 = (0.382 \pm 0.004)$ and $a_0 = (3.18 \pm 0.04)$ nm, $d_0 = (6.4 \pm 0.42)$ nm. (c) $T - T_{NA} = 4.6$ K, $\xi = (6 \pm 1)$ nm, $\psi_S^2 = (0.414 \pm 0.004)$ and $a_0 = (3.20 \pm 0.04)$ nm, $d_0 = (5.9 \pm 0.4)$ nm.

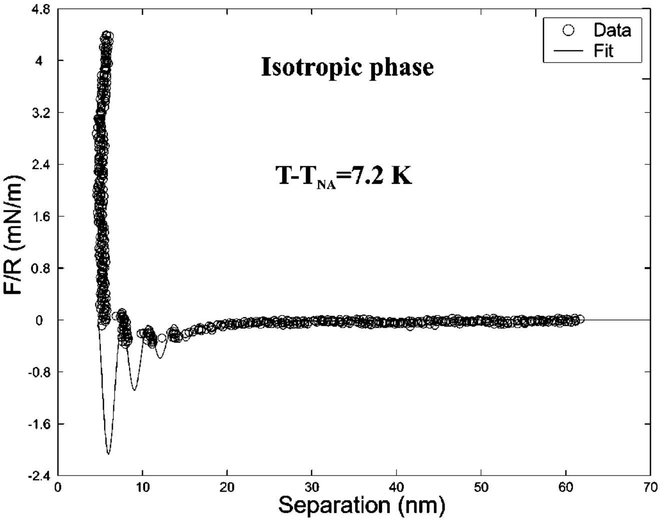

FIG. 4. The normalized force F/R between a DMOAP-covered glass sphere, with radius $R=10$ μm, and a DMOAP-covered glass plate immersed in an isotropic sample of 8 CB at $T-T_0=7.2$ K. The solid line is the pre-smectic fit to the experimental data, using the force of Eq. (1). The parameters of the fit are $w_1=1.4\times10^{-4}$ J/m^2 and $w_2=1.1\times10^{-4}$ J/m^2, $\xi_N=(6\pm1)$ nm, $\xi=(4.6\pm0.6)$ nm, $\psi_S^2=(0.264\pm0.004)$, and $a_0=(3.18\pm0.06)$ nm.

The first term of the equation is the pre-smectic contribution of Eq. (1). The second one is the mean field contribution of the prenematic origin. The parameters w_1 and w_2 are the two surface coupling parameters, generating the surface-induced nematic order and disorder, respectively. ξ_N is the nematic correlation length and L_N is the nematic elastic constant. Similar to Eq. (1), d_0 is the residual gap at the hard contact.

Figure 4 shows the force measurement performed in the isotropic phase at $T=T_0+7.2$ K. The good agreement of the experimental data (circle) with the modelling function of Eq. (2) (solid line) allows us to obtain the following values of the fitting parameters: $\xi=(6\pm1)$ nm, $\xi_N=(6\pm1)$ nm, $a_0=(3.18\pm0.06)$ nm, $d_0=(5.9\pm0.4)$ nm, $\psi_S^2=(0.264\pm0.04)$.

As we have performed a very large number of force measurements at different temperatures in several independent experimental runs, we could determine some very important interfacial parameters. For example, Fig. 5 shows the temperature dependence of the smectic density ψ_S^2 of the nematic phase of 8CB at the DMOAP silanated glass surface. As one can see, the surface smectic density ψ_S^2 is almost constant away from the transitions. Only when the sample approaches the *N-I* phase transition, the surface smectic order ψ_s strongly decreases. This is due to the coupling between the nematic and the smectic order, as suggested before [7]. We should note here that the smectic order at the surface, determined from the AFM force data, is quite sensitive to the quality and shape of the interacting surfaces. The smectic density at the surface is determined primarily from the magnitude of the observed oscillatory force [see Eq. (1)]. As it depends on the local curvature of the sphere, attached on the AFM cantilever, any unknown irregularity in the shape of the contacting surfaces causes changes in the observed magnitude of the force and therefore also calculated smectic density. We have noted this in repeating the experiments and making SEM images of the spheres after the experiments were finished.

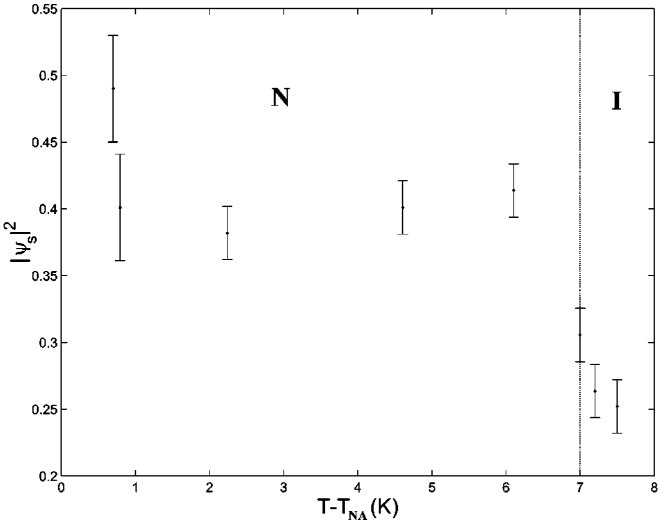

FIG. 5. The temperature dependence of the surface smectic density $|\psi_s|^2$ of 8CB on DMOAP-covered glass, obtained from the AFM force measurements. The plot shows that $|\psi_S|^2$ does not change appreciably in the nematic range $2K>T-T_{NA}>7$ K. The smectic density decreases only at the nematic to isotropic phase transition, because of the coupling between the smectic and the nematic order [7].

Figure 6 shows the temperature dependence of the smectic correlation length ξ in the nematic and isotropic phases. In contrast to the surface smectic order, which exhibits a drop at the nematic-isotropic phase transition, no discontinuity is observed in the temperature dependence of the smectic

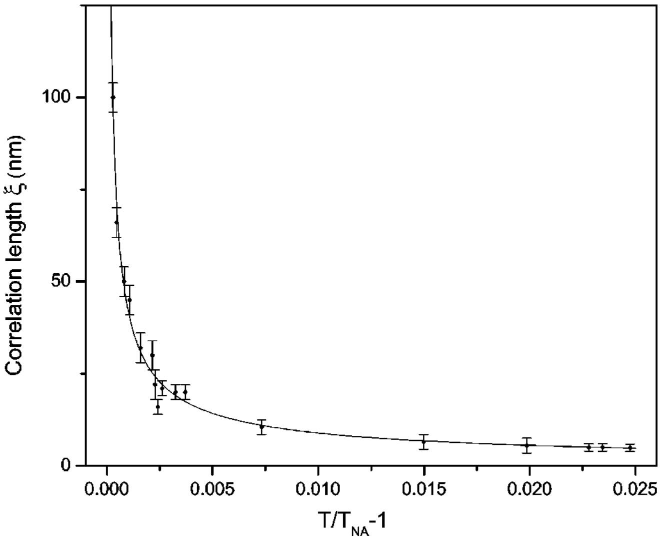

FIG. 6. The temperature dependence of the smectic correlation length $\xi(T)$ in the nematic and isotropic phases of 8CB, as obtained by fitting the AFM force measurements at different temperatures. The solid line is the best power law fit according to Eq. (3). The bare correlation length is $\xi_0=(0.39\pm0.08)$ nm, and the exponent of the correlation length is $\nu=(0.67\pm0.03)$.

correlation length, indicating it is an intrinsic, bulk phenomena. The measured temperature dependence of the smectic correlation length ξ can be fitted very well to the power law (see the solid line of Fig. 6):

$$\xi = \xi_0 \left(\frac{T}{T_{NA}} - 1 \right)^{-\nu}. \tag{3}$$

Here $T_{NA} = 313.65$ K is the SmA-N transition temperature. The best fit yields bare smectic correlation length of $\xi_0 = (0.39 \pm 0.08)$ nm and the critical exponent of $\nu = (0.67 \pm 0.03)$. Both are in extremely good agreement with the values, reported in the literature. For example, Ocko *et al.* have reported a comprehensive x-ray scattering study on alkylbenzoates and thiosulphate LC materials [17]. In 8CB they have measured the smectic bare correlation length of $\xi_0 = 0.37$ nm and $\nu_{\parallel} = 0.67$ (extracted note from Table 1 in Ref. [17]). This is also in agreement with light scattering data of Sprunt *et al.* [22].

IV. CONCLUSIONS

Using a modified AFM head based on the piezoresistive cantilevers, we have measured the temperature dependence of the presmectic force in the nematic phase of 8CB liquid crystal, confined to several nanometer thick homeotropic layer. The AFM data strongly suggest the presence of a first molecular layer adsorbed on each confining surface, which is similar to the results, previously observed in the isotropic phase by K.Kočevar *et al.* Further, the AFM data clearly show that there is a substantial smectic order in the thin confined nematic phase of 8CB, which is temperature independent throughout the nematic phase. Finally, and perhaps most importantly, we have determined the temperature dependence of the smectic correlation length from our AFM force data. The bare smectic correlation length is $\xi_0 = (0.39 \pm 0.08)$ nm and the critical exponential for the smectic correlation length parallel to the director is $\nu = (0.67 \pm 0.09)$. Both values are in very good agreement with the x-ray measurements performed by Ocko *et al.* [17] and light scattering data of Sprunt *et al.* [22]. This is a clear proof that the AFM force experiments open new and exciting possibilities of studying critical phenomena in complex fluids.

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