Capillary Condensation of a Nematic Liquid Crystal Observed by Force Spectroscopy

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(Received 26 January 2001)

We have observed capillary condensation in nanometer-thin films of nematic liquid crystals using force spectroscopy. The liquid crystal was confined to a submicron gap between a flat substrate and a microsphere, attached to the cantilever of an atomic force microscope. A long-ranged and strongly attractive force due to capillary condensation of a nematic phase was observed at temperatures close to the bulk isotropic-nematic phase transition. The critical point, terminating the first-order confined isotropic-nematic transition line, was determined for the first time.

DOI: 10.1103/PhysRevLett.86.5914 PACS numbers: 61.30.Hn, 61.30.Pq, 68.08.–p

Many years ago, Sheng [1,2] and later Poniewierski and Sluckin [3] predicted that a phenomenon, similar to the capillary condensation of water in cracks and pores, could be observed in the isotropic phase of a very thin layer of a nematic liquid crystal, confined between two walls. The phenomenon is interesting not only from the fundamental point of view, but it addresses a more general question of rheological and wetting properties of a nanometer-thin layer of a complex fluid. Similar to the capillary force of water, which is responsible for mechanical and adhesive properties of many substances, the capillary condensation of a complex fluid around microscopic objects could be used for a simple temperature control of forces, responsible for the structure and stability of liquid crystal emulsions and dispersions with remarkable optical properties [4–7].

Whereas water condensation in pores occurs because water wets a solid surface, capillary condensation of a nematic is due to the aligning action of the confining surface on an otherwise isotropic fluid. The liquid crystal-wall interaction creates a weak nematic ordering close to the surfaces, which decays into the isotropic bulk. If two similar surfaces are brought in close proximity, characterized by the separation d between them, and if the temperature is close to the isotropic-nematic phase transition T_{NI}, an orientationally ordered confined nematic phase may spontaneously condense instead of a disordered isotropic phase. The phase transition is of first order, and it was predicted that the line of the capillary phase transition ends in a critical point (d_K, T_K) in a (d, T) phase diagram [1–3]. In spite of great and obvious technological importance of surface and interfacial properties of liquid crystals, the surface-induced spontaneous capillary condensation in thermotropic nematics was never observed directly, in the sense that one would induce the phase transition by continuously decreasing the surface separation at constant temperature. On the other hand, confinement induced condensation from the sponge (L_3) to the lamellar (L_α) phase in lyotropics was observed by Antelmi *et al.* using surface force apparatus [8,9]. Several attempts to determine the line of the nematic capillary phase transition using ellipsometry, light scattering, and NMR [10–16] failed for the obvious reason that the shift of the temperature of spontaneous capillary condensation with decreasing thickness of the sample is very small, i.e., 10^{-2} K for a film of 1 μm thickness and becomes significant for surface separations smaller than 100 nm.

Here we show that capillary condensation of a nematic liquid crystal can be observed and analyzed with unprecedented accuracy using an atomic force microscope (AFM). What is important and new in our experiment is that we can drive nematic capillary condensation by accurately controlling the separation between the two surfaces using atomic force microscope in the force spectroscopy mode. The onset of and nature of the condensation are clearly observed by monitoring the force on a confining surface. We detect strong capillary attractive force over extraordinary large surface separations of several hundreds of nanometers, when the liquid crystal is close to the nematic phase. The transition is of the first order and we follow the line of capillary phase transition down to the thickness of several nanometers, where we locate the critical point. We can describe our experimental results within the Landau–de Gennes (LdG) mean-field formalism and we can directly determine the surface coupling parameters.

Let us first discuss the predictions of the mean-field, LdG theory [1] of the interfacial properties of the nematic liquid crystal, confined between two plan-parallel surfaces located at $z = \pm d/2$ which enforce homeotropic (perpendicular) alignment. In this case the free energy density

$$f(z) = \frac{1}{2}\,a(T)S^2 + \frac{1}{3}\,bS^3 + \frac{1}{4}\,cS^4 + \frac{1}{2}\,L\left(\frac{dS}{dz}\right)^2 + f_{\text{surf}} \qquad (1)$$

depends only on S, the scalar nematic order parameter, and its gradients. $a(T) = \alpha(T - T^*)$ is driving the isotropic nematic phase transition, which is weakly first order. Quartic (c term) stabilizes the free energy density and the gradient term damps out spatial inhomogeneities of the order parameter. The surface free-energy density [6,7] is, in contrast to original Sheng [1] form, a more general two parameter expression covering ordering and disordering effects of the surface, $f_{\text{surf}} = g(S_0 - S)^2\delta(\pm d/2)$. Here g is the surface coupling energy and S_0 is the value of the nematic order parameter, preferred by the surface [1]. After integration of the free energy density, Euler-Lagrange minimization leads to a pair of nonlinear differential equations for the bulk and the surface [6,7], describing the order parameter profile $S(z)$ across the nematic film, which can be solved only numerically. By following the evolution of the order parameter profile as a function of temperature, Sheng predicted a generic form of the (d, T) phase diagram, presented in the inset in Fig. 2. The critical point (d_K, T_K) is that point on the first-order phase transition line between a disordered isotropic phase (gas) and an ordered nematic phase (liquid), where the transition vanishes and the evolution of the order is smooth. The critical thickness was estimated to $d_K \approx (15 - 30)\xi_0$, which for a typical bare correlation length of $\xi_0 \approx 0.3$ nm is of the order of 5–10 nm, whereas T_K is approximately 0.5 K above the bulk isotropic-nematic phase transition temperature T_{NI} [1].

In our experiment, we have measured the force between a glass microsphere and a flat glass or sapphire surface, immersed in a nematic liquid crystal. The temperature of the crystal was kept above the clearing point and controlled with millikelvin precision [17]. The surfaces were carefully cleaned in detergent and oxygen plasma and a monolayer of DMOAP (N,N-dimethyl-N-octadecyl-3-aminopropyltrimethoxysilyl chloride) was deposited, as described elsewhere. This gave an excellent homeotropic alignment of liquid crystals 5CB (4-cyano-4′-*n*-pentylbiphenyl) and 8CB (4-cyano-4′-*n*-octylbiphenyl) in the nematic and smectic phases. The microsphere was attached (glued) to the AFM cantilever, and the force was measured as a function of a separation between the sphere and the flat surface. As the free energy $F = \int f\,\mathrm{d}V$ of a confined nematic layer depends on the nematic order parameter profile $S(z)$, and correspondingly on the layer thickness, any change of the surface separation causes a change in the order parameter profile and results in a structural force, exerted by the nematic on the confining surfaces. This structural force $\mathcal{F}$ is proportional to the negative derivative of the free energy F with respect to surface separation, $\mathcal{F} = -\frac{\mathrm{d}F}{\mathrm{d}d}$ and was calculated numerically, as described elsewhere [6,7].

The results of the force spectroscopy at different temperatures in the isotropic phase of 8CB on sapphire are shown in Fig. 1 and we obtain similar results for 5CB on glass and sapphire surfaces. Far above the phase transition temperature, the force plots show a weak, exponentially decaying repulsive force that does not change with temperature (see the inset in Fig. 1). This weak repulsive force can be attributed to an electrostatic repulsion [18] between equally charged confining surfaces due to ionic impurities in a liquid crystal. It has been subtracted for the whole set of force curves, shown in Fig. 1. In addition, we observe for small separations a very small oscillatory force (see Fig. 1, force plot at 40.11 °C) arising from a weak presmectic modulation. This presmectic force is much more clearly resolved for a different surface preparation with lower anchoring energy and no capillary condensation [19]. A similar presmectic force was observed by Moreau, Richetti, and Barois [20,21] in lyotropic liquid crystals.

By decreasing the temperature towards the isotropic-nematic phase transition, we observe the onset of a weak attractive force approximately 0.6 K above the bulk isotropic-nematic phase transition, as shown in Fig. 1. By slightly lowering the temperature, we observe that at a separation of several tens of nanometers, the sphere is strongly attracted towards the surface. We observe that the critical separation for this instability increases dramatically by further decreasing the temperature and becomes

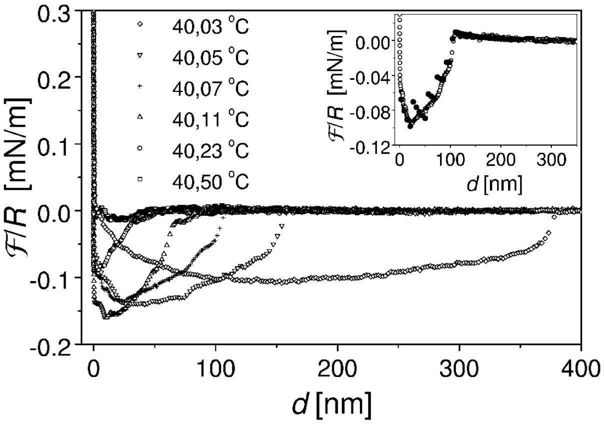

FIG. 1. A set of force plots $\mathcal{F}(d)$, measured at different temperatures near the isotropic-nematic transition in 8CB confined between a flat, silanated sapphire surface and a $R = 11\ \mu$m silanated glass sphere, attached to the AFM cantilever. The inset shows an example of the original force plot (empty circles) together with the theoretical fit (filled circles). The experimental curve was fitted to a sum of an exponentially repulsive electrostatic force with an amplitude of 0.4 nN and a Debye length of 50 nm and a capillary force, calculated within the model, presented in [6,7] with $a = 0.11 \times 10^6$ J/m^3 K, $b = -2.43 \times 10^6$ J/m^3, $c = 5.2 \times 10^6$ J/m^3, $L = 3 \times 10^{-12}$ N, $T^* = 310.9$ K, $g = 10^{-3}$ J/m^2, and $S_0 = 0.3$.

of the order of *several hundreds of nanometers* very close to T_{NI}. The observed phenomenon is evidently related to the phase transition and there are several structural forces that are strongly temperature dependent in the vicinity of T_{NI}: (i) mean-field force due to a symmetric order parameter profile between similar surfaces [6,7], (ii) fluctuation Casimir force due to a characteristic spectrum of order parameter excitations in confined geometry [22,23], and (iii) mean-field capillary force due to the condensation of an ordered phase from the isotropic fluid [3,6,7]. The first possibility is ruled out, as the range of the mean-field force is always of the order of a correlation length, which is nearly 2 orders of magnitude smaller than the observed critical separation. The same argument rules out the Casimir force. We therefore conclude that the observed phenomenon is due to capillary condensation of a nematic order and the instability in the separation between the two surfaces actually represents a discontinuous, first-order transition between the confined isotropic and the confined nematic phase. We perform a numerical analysis of the strength of this interaction, as described elsewhere [6,7], and we also consider the effect of the slight curvature of one of the two surfaces, which "rounds" the discontinuity of the force versus separation plots. The results for 8CB on a sapphire substrate are shown in the inset in Fig. 1 and we find perfect quantitative agreement between the theory and the experiment. Note that in this analysis, the curved surface of the sphere was approximated by a discrete set of concentric rings, which gives rise to a steplike force profile, shown in the inset.

Figure 2 shows the experimentally determined (d, T) phase diagram for 8CB together with the result of the LdG theory, indicated by the solid line. At a given temperature, the phase boundary was determined by measuring the critical distance, where a strong capillary attractive force between the two surfaces was detected with AFM. As we have already mentioned, in the early Letter Sheng [1,2] predicted that the line of the first-order capillary transition would end at a critical point, as indicated in the inset in Fig. 2. This critical point (d_K, T_K) is expected to appear relatively far from T_{NI} and at extremely small separations, i.e., of the order of 10 nm. In order to determine the position of the critical point, we carefully analyze the set of force plots, shown in Fig. 1. We note that at very high temperatures there is practically no attractive force. By slightly lowering the temperature, we clearly observe that the amplitude and the range of the capillary force strongly increase, eventually leading to the onset of discontinuity in the force plot, which becomes more and more pronounced as we are approaching T_{NI}.

We have performed fitting of this sequence of force plots at each temperature and we have determined the discontinuity of the order parameter ΔS at the point of capillary condensation for each temperature, as shown in Fig. 3. After that, we perform a numerical calculation of the expected jump in the order parameter at the point of capillary condensation within LdG. The experimental and theoretical results are shown in Fig. 3, and one can clearly see extremely good agreement. The solid line represents the best fit, which intersects the abscissa at $T_K - T_{NI} = 0.52(1 \pm 0.1)$ K, where the discontinuity of the order parameter vanishes. This happens at a critical distance of $d_K = 17(1 \pm 0.15)$ nm and the transition is continuous for higher temperatures. We have therefore located the position of the critical point in the (d, T) phase diagram for the silanated sapphire-8CB-silanated glass system, which is $0.52(1 \pm 0.1)$ K above the bulk phase transition temperature for a critical wall separation of $17(1 \pm 0.15)$ nm. This

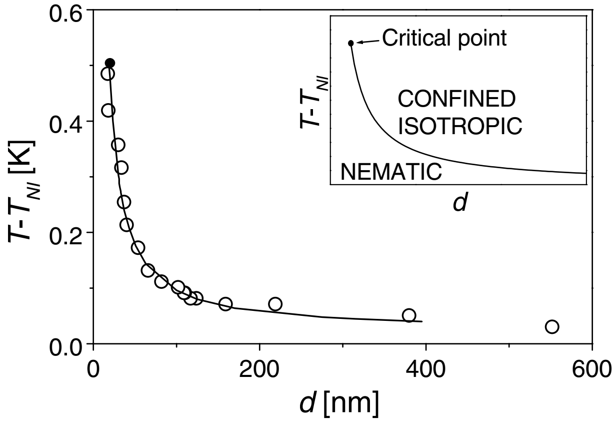

FIG. 2. The (d, T) phase diagram of 8CB, confined to a nanometer-sized gap between a flat, silanated sapphire surface and a $R = 11$ μm silanated glass sphere, attached to the AFM cantilever. The solid line is the fit to the LdG theory with the same set of parameters, used in the analysis of force plots. Note the position of the critical point (shown by a filled circle), where the capillary condensation becomes continuous. The inset shows a generic form of a (d, T) phase diagram [1,2] near the isotropic-nematic phase transition line.

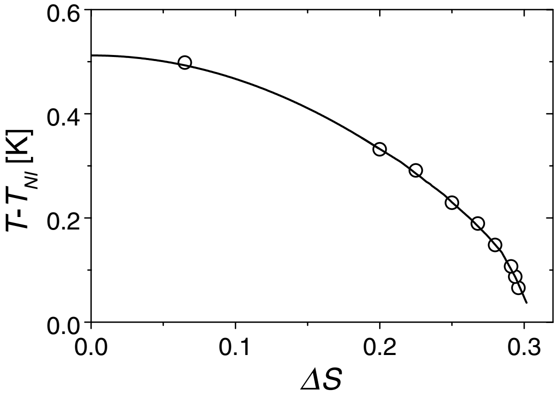

FIG. 3. The magnitude of the jump of the order parameter in the middle of the liquid crystalline layer versus the temperature, obtained from the set of force plots, shown in Fig. 1. The solid line is a LdG fit with the same set of parameters as in Figs. 1 and 2.

is in remarkable agreement with the predictions of the LdG description first theoretically analyzed by Sheng [1,2]. We have also performed several experiments on other systems, including glass-5CB-glass and the overall results are nearly identical to those described above. Finally, we stress an equally important aspect of this experiment—we are able to directly determine the liquid crystal-surface coupling parameters by simply measuring the critical distance, where the nematic capillary condensation appears.

In conclusion, we have determined for the first time the critical point in the (d, T) phase diagram of a nematic liquid crystal, confined to nanometer-sized layers. We have shown that an AFM in the force spectroscopy mode can successfully be applied to the study of critical phenomena near phase transitions in confined complex fluids. Structural forces and their critical behavior, which inevitably appear in confined systems, can be used for the precise determination of many technologically important interfacial parameters of complex fluids, as, for example, surface coupling energy, correlation length, etc. This experiment clearly shows the power and unprecedented sensitivity of the force spectroscopy technique in nanometer-sized systems. We believe it can successfully be applied to the study of interfacial properties of many other either simple or complex confined systems, where standard macroscopic scattering and linear response techniques fail for the reason of vanishing measuring signals.

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