Capillary Forces between Planar Anchoring Surfaces in the Isotropic Phase of a Nematic Liquid Crystal

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(Received June 10, 2005; CL-050751)

The interaction forces between the planar anchoring surfaces of a carbon microsphere and a graphite plate immersed in 8CB liquid crystal have been measured at different temperatures above the nematic–isotropic transition point, using an atomic force microscopy. The attractive force was observed between the surfaces when they came closer. The magnitude and the range of the attractive force increased with decreasing temperature. This attractive force is attributable to the confinement-induced phase separation of 8CB.

A confinement between surfaces often induces a phase transition of an intervening fluid, which leads to the formation of a lens of a second phase between the surfaces immersed in a bulk medium of another phase. This phenomenon is called a capillary-induced phase separation. Once a fluid confined between surfaces undergoes a phase separation, it gives rise to a strong attractive force between the surfaces. A typical example is water condensation between two hydrophilic surfaces in moist air, which leads to the attractive water-bridge force between them. The capillary condensation and the accompanying attractive force have been observed for several systems, as summarized elsewhere.[1]

Several theories have predicted that similar capillary condensation phenomena can be also observed in a nematogen thin film of elongated molecules confined between two walls including a homeotropic anchoring[2–4] or a planar anchoring,[3–5] which induces the alignment of the molecules perpendicular or parallel to the surfaces. Recently, using an atomic force microscopy (AFM), the Slovenian group led by Muševič has successfully detected the capillary force between the homeotropic anchoring surfaces of a microsphere and a flat plate immersed in the isotropic phase of a nematic liquid crystal; this is a strong evidence for the capillary condensation of the nematic phase.[6] However, a confinement between planar anchoring surfaces still remains to be explored by AFM.

In the present study, we report the AFM measurements of the interaction forces between the planar anchoring surfaces in a nematic liquid crystal at different temperatures above the nematic–isotropic phase transition point.

Using a commercial AFM (PicoSPM, Molecular Imaging), we have measured the interaction force between a highly ordered pyrolytic graphite (HOPG) plate and an Si_3N_4 tip or a carbon microsphere immersed in a nematic liquid crystal of 4′-*n*-octyl-4-cyanobiphenyl (8CB) molecules at temperatures where the bulk liquid crystal is in the isotropic phase. The temperature of the graphite/8CB/carbon (or tip) system was set above the nematic–isotropic phase transition point of $T_{NI} = 40.5\,^\circ\mathrm{C}$ and controlled with a precision of less than $\pm 0.1\,^\circ\mathrm{C}$, which was realized by placing the AFM scanhead with a liquid cell on a hot sample stage in an incubator (MIR-153, Sanyo). 8CB (Wako Pure Chemical Industries) was used as received. HOPG plates (Grade-ZYH, Veeco Instruments) were cleaved in air immediately prior to use. An AFM probe (Model NP, Veeco Instruments), which has a cantilever with a spring constant of about 0.12 N/m and with an Si_3N_4 pyramidal tip of 20–60-nm radius of curvature on the top, was used. The colloidal carbon microsphere (ICB-1020, Nippon Carbon), which had a smooth surface and a typically 10-µm diameter, was attached to the top of the cantilever with epoxy adhesive (Vantico). All the forces F shown below were measured as a function of the surface distance D at scan speed of 20 nm/s, which was slow enough to eliminate the hydrodynamic effects.

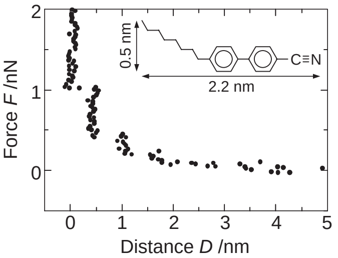

Figure 1. Force curve between an AFM tip and a graphite plate approaching in 8CB liquid crystal at $T = 44.0\,^\circ\mathrm{C}$ ($>T_{NI}$).

The layers of molecules absorbed on a substrate can be observed by the force measurement with a sharp AFM tip. Figure 1 shows a typical force curve between an AFM tip and a graphite plate in the isotropic phase of 8CB liquid crystal at $T = 44.0\,^\circ\mathrm{C}$. The force curves are temperature independent in the range of $T = 41.0$–$48.0\,^\circ\mathrm{C}$. As illustrated in the inset of Figure 1, the 8CB molecule is a rod-like object with ca. 2.2-nm length and ca. 0.5-nm diameter. At large separations there is no detectable force, whereas at a separation of $D = 1.5$–3 nm, a weak repulsive force appears. Then, at $D < 1.2$ nm, the tip touches two relatively firm layers, which are ruptured by increasing the force load. These adsorbed layers have ca. 0.5-nm thickness, which corresponds to the width of the 8CB molecule.[7] This is indicative of the planar alignment of the 8CB molecules at the graphite surface in the bulk isotropic phase. Likewise, the smooth surface of the carbon microsphere employed is expected to give a planar alignment of 8CB thereon. According to the images obtained by AFM[9] and a scanning tunneling microscopy (STM),[10] the 8CB on the graphite substrate forms a two-dimensional double-row structure of antiparallel ordered molecules. In this sense, the surface anchoring by graphite is classified into a uniform planar anchoring other than a random planar anchoring; the former is characterized by a preferred azimuthal direction of

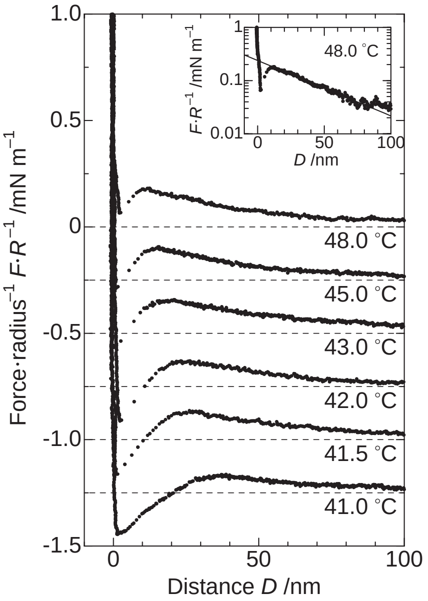

Figure 2. Force curves between a carbon sphere of $R = 5.5\,\mu$m radius and a graphite plate approaching in 8CB liquid crystal at different temperatures: $T = 48.0$, 45.0, 43.0, 42.0, 41.5, and 41.0 °C ($>T_{\rm NI}$). The inset shows the semilogarithmic plot for $T = 48.0\,°$C, where the solid line is a fit to eq 1 with $|\psi_0| = 100$ mV and $\kappa^{-1} = 41.7$ nm.

anchoring in the plane of substrate, whereas the latter has the arbitrary azimuthal direction. Whether the planar anchoring at the carbon microsphere surface is uniform or random remains open for future AFM or STM imaging.

Figure 2 displays the force–distance profiles between a carbon microsphere and a graphite plate in the isotropic phase of 8CB liquid crystal at different temperatures. At large separations, every profile exhibits the repulsive force, which decays exponentially with increasing distance. The exponentially decaying repulsive force shows no temperature dependence in the range of $T = 41.0$–$48.0\,°$C ($>T_{\rm NI}$) and can then be attributable to the electrostatic interaction between likely charged surfaces across a liquid crystal containing ionic impurities. A similar behavior has been found for the silanated glass surfaces inducing a homeotropic anchoring.[6] As shown in the inset of Figure 2, this long-range repulsion is appropriately represented by the electrostatic interaction force between a sphere of radius R and a flat plate with surface potential ψ_0 each:[11]

$$F/R = 4\pi\varepsilon\varepsilon_0\kappa{\psi_0}^2\exp(-\kappa D), \qquad (1)$$

where κ^{-1} is the Debye length, ε_0 is the permittivity of vacuum, and $\varepsilon = 9$ is the dielectric constant of the isotropic phase of 8CB.[12] After fitting eq 1 to the measured distance dependence of force, we obtained similar results of $|\psi_0| \approx 100$ mV and $\kappa^{-1} \approx 45$ nm for every temperature.

At smaller separations of $D < 10$–40 nm, the attractive forces appear, as can be seen in Figure 2. The magnitude and the range of the attractive force increase with decreasing the temperature down to $T_{\rm NI}$.[13] This is a clear indication that the attractive force is a result of capillary-induced phase transition, where the partially ordered isotropic liquid crystal in the gap between the planar anchoring surfaces of a carbon microsphere and a graphite plate changes into the developed nematic phase, as illustrated in Figure 3.[14] A similar behavior has been observed for the homeotropic anchoring surfaces.[6] It is very interesting to note that the direction of this capillary-induced attractive force is the same as that of the molecular alignment of 8CB for the homeotropic anchoring surfaces,[6] whereas they are perpendicular to each other for the planar anchoring surfaces employed here.

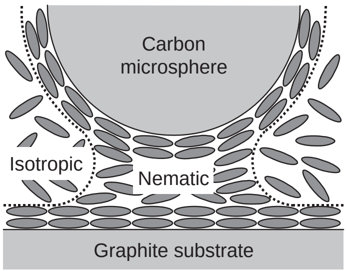

Figure 3. Schematic of the isotropic–nematic phase separation of 8CB liquid crystal confined in the gap between the carbon microsphere and graphite substrate. The bulk liquid crystal is in the isotropic phase.

This work reported the direct measurements of the capillary-induced attractive force between the planar anchoring surfaces in the isotropic phase of a nematic liquid crystal. The detailed results including the interactions between homeotropic anchoring surfaces and between hybrid homeotropic/planar anchoring surfaces will be discussed elsewhere.

We thank Dr. Hideya Kawasaki for the gift of the carbon microspheres. This work was partly supported by the Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology.

References and Notes

1 H. Wennerström, K. Thuresson, P. Linse, and E. Freyssingeas, *Langmuir*, **14**, 5664 (1998).

2 a) P. Sheng, *Phys. Rev. Lett.*, **37**, 1059 (1976). b) P. Sheng, *Phys. Rev. A*, **26**, 1610 (1982).

3 H. Schrönder, *J. Chem. Phys.*, **67**, 16 (1977).

4 A. Poniewierski and T. J. Sluckin, *Liq. Cryst.*, **2**, 281 (1987).

5 M. M. Telo da Gama and P. Tarazona, *Phys. Rev. A*, **41**, 1149 (1990).

6 a) K. Kočevar, A. Borštnik, I. Musevič, and S. Žumer, *Phys. Rev. Lett.*, **86**, 5914 (2001). b) A. Borštnik-Bračič, K. Kočevar, I. Musevič, and S. Žumer, *Phys. Rev. E*, **68**, 011708 (2003). c) I. Musevič, K. Kočevar, U. Kržič, and G. Carbone, *Rev. Sci. Instrum.*, **76**, 043701 (2005).

7 In the nematic and the smectic phases, where the 8CB molecules form dimers with ca. 3.2-nm long and ca. 0.9-nm wide easier than in the isotropic phase, the force between the planar anchoring surfaces of bare mica oscillates with ca. 1-nm periodicity.[8]

8 M. Ruths, S. Steinberg, and J. N. Israelachvili, *Langmuir*, **12**, 6637 (1996).

9 H. Yamada, S. Akamine, and C. F. Quate, *Ultramicroscopy*, **42–44**, 1044 (1992).

10 a) J. S. Foster and J. E. Frommer, *Nature*, **333**, 542 (1988). b) J. S. Foster, J. E. Frommer, and J. K. Spong, *Proc. SPIE*, **1080**, 200 (1989). c) D. P. E. Smith, H. Hörber, Ch. Gerber, and G. Binning, *Science*, **245**, 43 (1989). d) D. P. E. Smith, J. K. H. Hörber, G. Binning, and H. Nejoh, *Nature*, **344**, 641 (1990).

11 J. N. Israelachvili, "Intermolecular and Surface Forces," 2nd ed., Academic Press, New York (1991).

12 J. Thoen and G. Menu, *Mol. Cryst. Liq. Cryst.*, **97**, 163 (1983).

13 The capillary-induced attraction will disappear at $T < T_{\rm NI}$, which should be confirmed by AFM with piezoresistive cantilevers.[6c]

14 It remains to be scrutinized why the structural force across a capillary-induced nematic phase of 8CB at short distances hardly increased with decreasing T, as can be seen in Figure 2.