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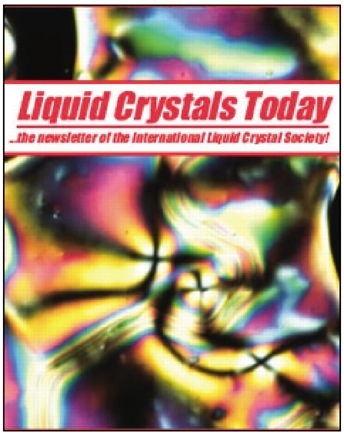

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Structural forces in liquid crystals

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Structural forces in liquid crystals

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This article is a short review of our work on forces in a liquid crystalline medium that has been carried out in recent years. Using an atomic force microscope (AFM), the force between the glass substrate and $\approx 10\,\mu$m glass sphere has been measured. In all experiments, the glass surfaces have been treated for a homeotropic alignment to achieve controlled orientation of the liquid crystal, confined between the surfaces. Force measurements with different liquid crystals have been done in their isotropic phase, but close to the phase transition to an ordered liquid crystal phase. We have found two different mechanisms that influence the force between objects immersed in a liquid crystal. The first is due to a pretransitional partial ordering of the liquid crystal close to the phase transition. Forces of this type are relatively weak and their range is limited by the correlation length of the liquid crystalline order. The second mechanism is a phase transition in the gap between the ordering surfaces. In this case, the force appears suddenly at certain distance and is strongly temperature dependent. The force in this case is stronger, but limited to a narrow temperature range, just above the phase transition.

1. Introduction

Liquid crystals (LCs) have been studied for several decades not only because of their technological importance, but also because of their extraordinary physical properties such as optical anisotropy, flow properties, response to external fields or ability to transmit static torques. Numerous phase transitions between many different liquid crystalline states have also attracted a lot of research interest. It has already been found in the early days of liquid crystal research that different solid surfaces in contact with the liquid crystal determine the spatial orientation of the anisotropic liquid crystalline states [1, 2] and therefore affect the liquid crystalline order. In the beginning, the orienting action of the surfaces was studied in connection with previously investigated properties and, in particular, the exploitation of the orienting effect in thin liquid crystal cells has been considered for display applications. It has been found that forces between the anisotropic LC molecules in the first monolayer and the confining surface are responsible for the orientation. The surface-induced order propagates from the oriented monolayer deeper into the LC sample due to the elastic behaviour of the LC order.

For quite some time it was not recognized that the close proximity of two order-inducing surfaces in a liquid crystal generates forces between the confining surfaces. This is due to the spatial overlapping of the surface-induced LC order emanating from both surfaces. As a consequence of overlapping, the free energy of the system depends on the separation between the surfaces and this results in the structural interaction between the surfaces, as presented in figure 1. Poniewierski and Sluckin were the first to study theoretically the effect of the LC order induced at the confining surfaces on the force between them in 1987 [3]. They determined the interaction between two parallel plates, confining the nematic liquid crystal close to the nematic–isotropic phase transition. After this, several articles, considering the effect of liquid crystal order on the forces between surfaces were published. De Gennes investigated the force between surfaces in a presmectic fluid [4] due to a static surface-induced smectic order in the isotropic phase. The influence of dynamics of the LC order fluctuations on the force was first considered by Ajdari [5], who predicted the pseudo-Casimir effect in liquid crystals. This resembles the Casimir interaction, which occurs as a result of the changed spectrum of fluctuations of a confined electromagnetic field. Later, the effect was thoroughly studied by Ziherl [6, 7]. Stark and Borštnik [8–10] carried out much additional work in considering

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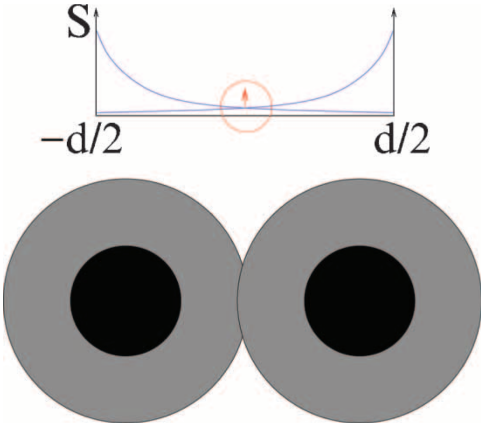

Figure 1. When two surfaces that change the liquid crystal order in their vicinity are brought close together, the regions of LC order perturbation (grey) start to overlap and the interaction (i.e. force) between the surfaces appears. The degree of LC order is described by the order parameter amplitude, which is presented as a red line in the upper part of this figure.

the forces between colloidal particles immersed in a nematic liquid crystal (nematic colloids).

The pioneering experimental work on forces between objects immersed in a liquid crystal was done in 1981 by Horn *et al.* [11]. They used surface force apparatus (SFA) to measure the forces between curved mica sheets immersed in 4′-*n*-*pentyl*-4-*cyanobiphenyl* (5CB) and found different liquid crystal-specific structural forces. Later, SFA experiments were performed on a higher LC homologue 4′-*n*-*octyl*-4-*cyanobiphenyl* (8CB) by Ruths *et al.* [12]. They studied more systematically the effect of an adsorbed surfactant on the liquid crystal anchoring and, in addition, they investigated the influence of shear on the ordering of the smectic-A and nematic phases. Much experimental work on structural forces in the lyotropic liquid crystalline medium was accomplished by the group of Kekicheff by Moreau, Richetti and Antelmi, who made the measurements of the presmectic interaction [13, 14] and the first direct observation of confinement-induced condensation of a lamellar lyotropic phase [15, 16]. Poulin *et al.* carried out fascinating experiments on nematic colloids [17] and related results with LC specific forces.

Our group has decided to use an atomic force microscope (AFM) (see figure 2 for more detail) to measure the force on a micrometre glass sphere, totally immersed in a liquid crystal, and in the vicinity of a flat surface. AFM provides the excellent force sensitivity, which enables use of smaller surface areas, needed for measurements. In addition, only small amounts of LC samples are required and therefore a large number of experiments can be performed. The small amount of sample also allows accurate control of the LC temperature. One important limitation of AFM force measurements in liquid crystals is that the standard optical detection of the cantilever bending, which measures the force, is only possible in the optically transparent isotropic phase. We have systematically studied forces in liquid crystals of the cyanobiphenyl series between glass spheres and glass plates, prepared for homeotropic LC alignment, and found a very rich variety of LC specific structural interactions. More information about our experimental setup is included in the caption to figure 2 This contribution is divided into two sections. In §2 we discuss pretransitional forces that arise owing to overlap of partially ordered LC regions close to the surface as shown in figure 1. Section 3 is about forces that are associated with a phase transition, induced by the narrowness of the gap between the surfaces that confine the liquid crystal.

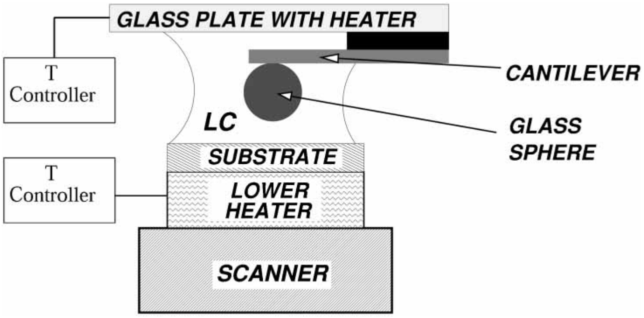

Figure 2. Schematic representation of the most important parts of the AFM for our force experiments. The liquid crystal droplet is trapped between the substrate and the transparent upper glass plate with an integrated heater. There is another heater under the substrate and both heaters with temperature sensors and temperature controllers permit precise temperature control of the LC sample with an accuracy of 0.01–0.02 K. The elastic cantilever with a mounted glass sphere of diameter ≈20 μm is totally immersed in an isotropic liquid crystal, so that air–LC interface does not affect the measurement. The separation between the sphere and the substrate is controlled by an AFM piezo tube with subnanometre precision. The force on the sphere is measured with a precision of approximately 10^{-11} N by optically measuring the deflection of the cantilever. In all our experiments, the glass surfaces were treated with silane [*N*,*N*-dimethyl-*N*-octadecyl-3-aminopropyltrimethoxysilyl chloride (DMOAP)] to assure controllable and strong homeotropic alignment of the liquid crystal at the surfaces.

2. Forces due to the pretransitional ordering of the liquid crystal

It is known that the presence of surfaces influences the order of the liquid crystal. Even if the liquid crystal is in an isotropic phase, the molecules in direct contact with the surface are ordered to some extent because of the interactions between the surface and the molecules, which includes breaking of the translational symmetry at the interface. Numerous experimental studies have shown an ordered layer of molecular thickness adsorbed to the solid surface, even at temperatures where the bulk of the liquid crystal is in an isotropic phase [18–20]. This layer has also been studied by our group [21–23] and we have found that it is well decoupled from the rest of the liquid crystal sample. In addition, we were able to determine the elastic properties of the layer and its thickness, which imparts some information about its structure. We have also found that this layer does not cover the silanated glass surface homogeneously and that the homogeneity of the layer is connected with the surface anchoring strength, i.e. the strength with which the surface forces the orientation of the liquid crystal. Even in the isotropic phase, some of the order is transferred to neighbouring liquid crystal molecules via anisotropic interactions. As a consequence, the LC order decays exponentially from the surface within a correlation length of the liquid crystal order.

What happens if two such surfaces are brought close together in an isotropic liquid crystal? Obviously, there is nothing to observe if the separation between the surfaces is large compared to the correlation length. But when the separation becomes comparable to the correlation length, the surfaces begin to 'feel' each other (see figure 1). The existence of the liquid crystal order in the interfacial region costs free energy at temperatures above the bulk phase transition temperature. In the overlapping region, the free energy expense changes because of the cooperation of both surfaces. In this case, the total free energy of the system changes with the separation between the surfaces and this is observed as a force between two surfaces. Typically, this happens at a separation of a few nanometres in the isotropic liquid crystal and this is exactly the separation at which AFM is really powerful.

We have observed surface-induced pretransitional forces of nematic and smectic origin.

In our experimental set-up the nematic becomes a simple one-dimensional system (due to the homeotropic LC ordering on both surfaces and negligible curvature of the sphere). Due to the overlap of the ordered regions, the total free energy of the system is lowered and an attractive force can be expected. We have observed this attractive force as a result of the nematic ordering just above the isotropic–nematic phase transition temperature (T_{NI}) of 5CB, as shown in figure 3. The expected magnitude of the pre-nematic force is quite small and comparable to the van der Waals force between the surfaces. However, as the van der Waals force is nearly temperature-independent, the pre-nematic force can be resolved as an additional contribution to the total force, which increases in its range and magnitude, as the temperature approches T_{NI}. The experiment and the fit to the model, based on the Landau–de Gennes model are shown in figure 3. These AFM experiments, together with ellipsometric analysis of the isotropic nematic liquid crystal interface with silanated glass, enabled us to determine some of the parameters of the Landau–de Gennes theory (LdG) [23]. A very detailed analysis showed that LdG is a very efficient approach to describe the observed structural phenomena even at a surface separation of few nanometres, where our force measurements took place.

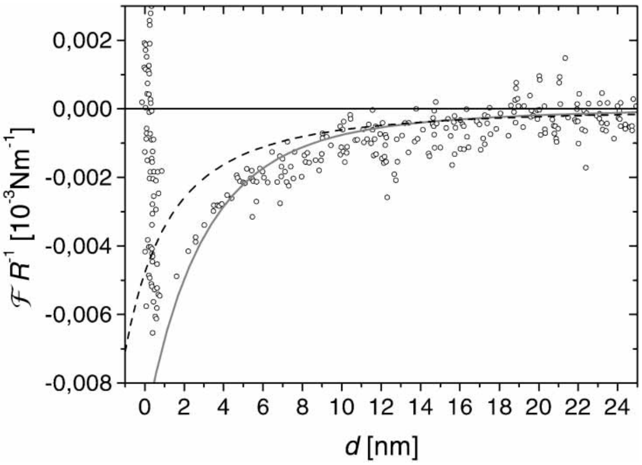

Figure 3. The normalized force $\mathcal{F}/\mathcal{R}$ between the silanated glass sphere with radius R and glass substrate in 5CB at temperature 0.1 K above T_{NI}. The dashed line shows the calculated and temperature-independent van der Waals contribution to the total force. The full line is a sum of the van der Waals force and prenematic interaction, calculated in the framework of the Landau–de Gennes theory [23]. The parameters of the theory are the same as those used to fit the related ellipsometry experiment (not shown here).

If the liquid crystal between both solid surfaces has smectic properties and the surfaces promote smectic ordering with layers parallel to them, a different surface–surface interaction can be observed. The smectic order parameter is two dimensional, where one component measures the amplitude of the smectic density wave and the other component is the phase and measures the thickness deviations of the smectic layer's thickness from its equilibrium. The phase plays an important part when two surfaces are brought together in the presmectic region. When the surface-perturbed regions overlap, the interaction can be attractive if the separation between the surfaces nearly matches the integer number of smectic layers or can be repulsive if the separation does not match the thickness preferred by the smectic ordered liquid crystal. In this case, the amount of smectic order must fall in the middle of the gap in order to accommodate phase mismatch (for more detail see references [4, 24]). With changing separation between the surfaces, the observed force is oscillatory.

This is exactly what we have observed in 8CB, just above the nematic–isotropic phase transition [22]. Here the increase of the presmectic order above T_{NI} is due to the coupling between the nematic and smectic order, which increases the amount of smectic order on the surface [22]. The observed interaction is shown in figure 4.

3. Forces due to the confinement-induced phase transition

An even more dramatic force effect is observed when a spatial confinement induces a phase transition of the liquid crystal in the gap between two objects. The phenomenon of confinement-induced phase transition was theoretically predicted in 1976 by Sheng [25].

This phenomenon is very similar to the well-known capillary condensation of water in tiny cracks and pores. In this case, the unsaturated water vapour condenses into water if the two hydrophilic surfaces are close enough. The size of the pore in which condensation occurs depends on the relative partial pressure of the water vapour. Lord Kelvin described this dependence back in 1871 [26] with thermodynamic arguments. He predicted a linear relationship between the phase transition temperature and the inverse width of the pore. The condensation occurs as a result of the hydrophilicity of the surfaces that prefer condensed water over vapour (and therefore the condensation lowers the free energy) and confined geometry, which reduces the unfavourable energy expense of the condensed phase at unsaturated vapour pressure. If the water condenses between two nonparallel surfaces, like that shown in figure 5, a water bridge is formed between the two surfaces. Because of the Laplace pressure over the curved water–vapour interface the two surfaces are pulled together.

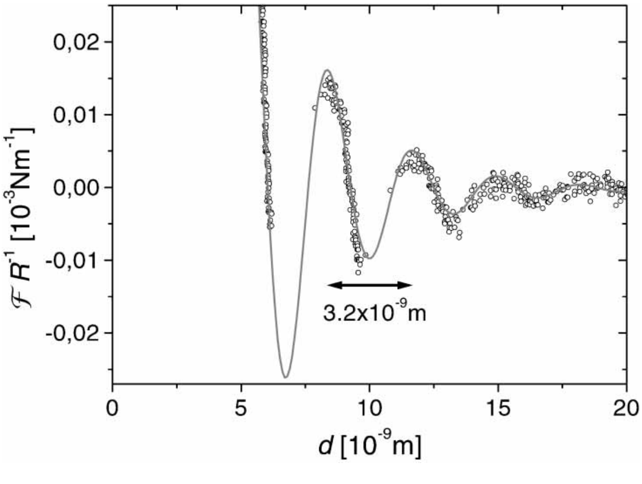

Figure 4. A normalized force $\mathcal{F}/\mathcal{R}$ between the silanated glass sphere of radius R and silanated glass surface 0.15 K above T_{NI}. The solid line is a fit to the combination of the monotonous attractive van der Waals and the prenematic interaction and the oscillatory presmectic interaction [22, 24].

In liquid crystals, capillary phase condensation has not been observed because of severe experimental limitations. Namely, the ordinary experimental techniques used to investigate liquid crystals are much more sensitive to the bulk properties and an interfacial layer only a few nanometres thick cannot be resolved from the bulk. Moreover, the separation between the surfaces has to be controlled with nanometre precision and this has posed additional problems for the detection of confinement-induced phase transitions. To study confinement effects on the liquid crystal ordering, porous materials with a huge fraction of surface with respect to volume have been used to increase surface sensitivity. In all these materials, the distribution of the pores is quite wide and the dramatic sharpness of the phase transition is smeared out. In 1987 Poniewierski and Sluckin pointed out that just as in the case of water capillary condensation, the measurement of the force between two approaching surfaces can lead to direct observation of the confinement-induced phase transition [3]. Unfortunately, SFA experiments lacked sufficiently precise temperature control to allow this phenomenon to be observed in thermotropic liquid crystals.

AFM in force spectroscopy mode, equipped with additional heaters, seems to be the perfect choice for the direct observation of capillary condensation phenomena. In the AFM experiment, the sphere and the

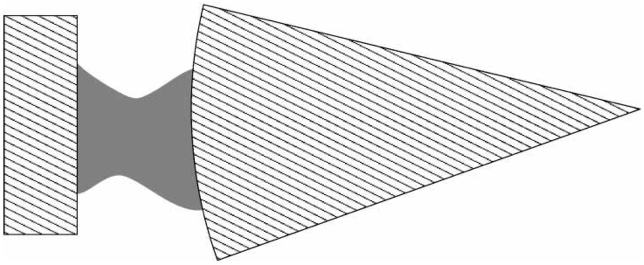

Figure 5. A schematic representation of a condensed liquid crystal (or water) bridge between a sphere and the substrate. The bridge is embedded in the isotropic bath (or water vapour) and there is an interface between both phases.

flat substrate are approached at a small constant speed (tens of $\mathrm{nm\,s^{-1}}$) in an isotropic liquid crystal at a temperature just slightly above the phase transition to some liquid crystalline state (nematic or smectic). The liquid crystal between the surface and the sphere is partially ordered close to the surfaces and the order decays toward the centre of the gap. This is the usual prenematic or presmectic phase-discussed in the previous section. Since the isotropic–nematic or isotropic–smectic phase transitions are of first order, the ordered liquid crystalline phase is metastable at temperatures just slightly above the phase transition temperature. If the surfaces impose sufficient order, which has to be quite strong in order to induce capillary condensation, they stabilize the developed liquid crystalline phase against the spatially distorted prenematic or presmectic phase and a capillary bridge of liquid crystalline phase forms between both surfaces.

The capillary condensation of the nematic phase has been found in 5CB and 8CB with surfaces prepared for very strong anchoring [27, 28]. If the anchoring is lower, pretransitional forces, described in previous section, can be observed. Figure 6 shows a typical experiment in which nematic capillary condensation was observed. At temperatures very close to T_{NI} (less than 0.5 K above the T_{NI}), a sudden attractive force can be observed at a certain separation between the sphere and the substrate. If the temperature is lowered a little bit, the distance at which the force is observed is larger and can reach more than 1 μm. It turns out that the Kelvin equation describes the temperature dependence of the gap thickness at which nematic or smectic condensation occurs very easily. Fitting the data to this equation enables extraction of the interfacial tension between the nematic and isotropic phase [28], which is very hard to measure with other experimental techniques. The interfacial tensions of the nematic–isotropic interface for 5CB and 8CB are collected in table 1.

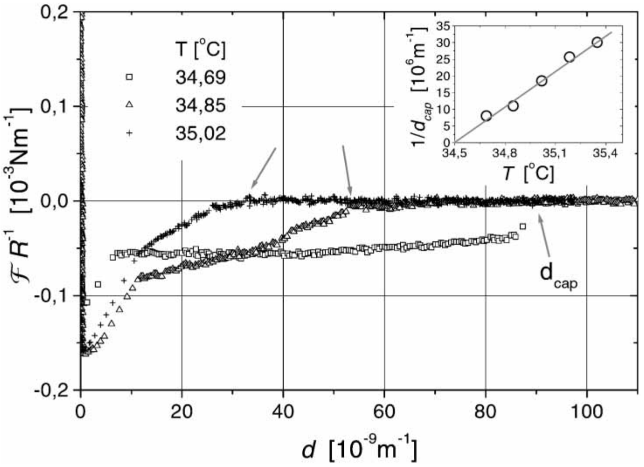

Figure 6. The force between the silanated 10 μm glass sphere and silanated glass substrate at different temperatures in 5CB. Arrows indicate the distances at which capillary condensation occurs at different temperatures (d_{cap}). The inset shows the temperature dependence of the inverse gap thickness, d_{cap}^{-1}, and the fit to the Kelvin equation.

Table 1. Interfacial tensions of the nematic–isotropic interface for 5CB and 8CB as obtained by fitting of the observed phase transition temperatures against d_{cap} to the Kelvin equation.

Liquid crystal	$\gamma_{\mathrm{NI}}/\mathrm{J\,m^{-2}}$
5CB	1.0×10^{-5} (1 ± 0.1)
8CB	1.8×10^{-5} (1 ± 0.15)

When 4′-*n*-dodecyl-4-cyanobiphenyl (12CB) with a direct isotropic–smectic A phase transition is used, capillary condensation of the smectic phase can be observed [21]. As in the presmectic interaction, the two-dimensional order parameter entirely changes the shape of the force between the sphere and the substrate. The initial condensation is associated with an attractive force, but very soon, further approach of the surfaces is stopped by the compression of the developed smectic layers in the condensed bridge. Only when a sufficiently strong force is applied do the smectic layers give up and the separation between the surfaces gradually reduces in steps with the thickness of a single smectic layer. The resulting force measurement, as well as the fit of the temperature dependence of the inverse condensation

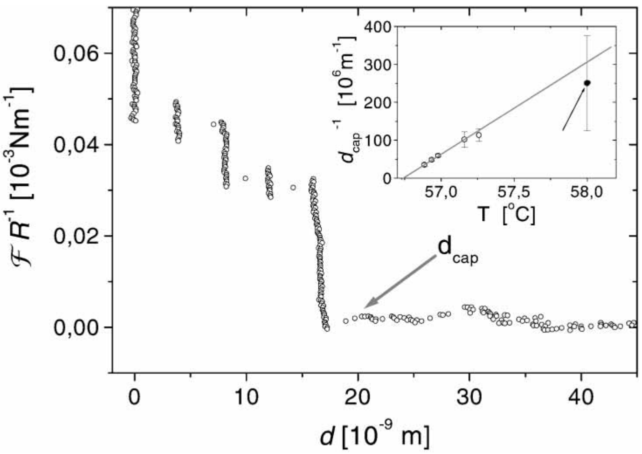

Figure 7. The force between the silanated 10 μm glass sphere and silanated glass substrate in 12 CB at temperature 57.0 K, 0.3 K above the bulk isotropic–smectic phase transition. The inset shows the temperature dependence of the inverse gap thickness, d_{cap}^{-1}, and the fit to the Kelvin equation.

thickness d_{cap}^{-1} to the Kelvin equation are shown in figure 7.

4. Conclusion

Forces between objects immersed in a liquid crystal differ from forces in normal isotropic liquids. Even in an isotropic phase of liquid crystals, some liquid crystalline order is present close to the surfaces. When two such surfaces are close enough that the partially ordered regions of liquid crystal overlap, interaction between the surfaces takes place. The nature of the interaction reflects the structural properties of the underlying liquid crystalline order. The interaction in nematic liquid crystals is monotonous and in smectic liquid crystals it is oscillatory. Forces due to the liquid crystalline ordering in an isotropic phase depend strongly on temperature and are most evident close to the phase transition. When the order imposed by the surfaces is moderately strong, the amplitude of the force increases monotonously when the surfaces approach and are due to the pretransitional ordering of the liquid crystal. In the case where the surfaces induce a strong ordering of the liquid crystal and the temperature is very close to the phase transition, the localized phase transition from the isotropic into the liquid crystalline state occurs in the gap between the surfaces. In this case, the magnitude of the force increases suddenly at the separation at which condensation occurs.

The variability of the interactions in liquid crystals and possibility to influence their strength, range and even direction with external parameters like temperature or electric field promise the use of liquid crystals in colloid dispersions. The control of interactions between colloidal particles could lead to controlled self-assembly of colloidal structures, which would be of great importance in emerging small-scale technologies.

Atomic force microscopy is a tool very well suited to studying directly forces in complex liquids like liquid crystals. In particular, the possibility of precisely controlling the temperature of the sample enables the precise study of forces close to the phase transition. New ways of detecting the bending of the cantilever, like piezo-resistive cantilevers promise to make possible the direct study of interactions in the ordered liquid crystalline phases.

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