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Observation of an electrostatic force between charged surfaces in liquid crystals

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We report on the atomic force microscope observation of an electrostatic force between glass surfaces immersed in cyanobiphenil liquid crystals. The measured force is repulsive and decays exponentially with increasing surface separation. A mean field description of the electrostatic interaction in liquids has been used to determine the Debye screening length, the concentration of dissolved ions, and the surface electric potential. The effect of the observed interfacial electric field on the liquid crystal orientation at the surface has been discussed. It has been found that the coupling between the liquid crystal order and the surface electric field does not contribute considerably to the surface orienting action.

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When surfaces are immersed in a liquid crystal, they may become charged due to selective surface adsorption or dissociation of certain ionic species [1]. As a result, a surface electric field is developed from the charged surface, that extends over a Debye screening length into the bulk liquid crystal. It has been argued for a long time that this charging of surfaces and consequent development of electric double layer across the liquid crystal-solid interface could have significant influence on the anisotropic anchoring properties of surfaces [2–6]. Recently [7], it has been pointed out that electrostatic interaction could be used for the efficient stabilization of nematic colloidal dispersions with interesting optical properties.

In spite of great technological importance, surface charging and surface electric field have never been observed directly in liquid crystals. Instead, these phenomena were either used to explain indirectly some interesting interfacial phenomena, such as dependence of the surface anchoring energy of a nematic liquid crystal on the cell thickness [8,2], or to propose the onset of surface anchoring transitions in nematics [3,4].

In this paper, we report on the direct observation of spontaneous charging of glass surfaces, immersed in a liquid crystal. We have measured the separation dependence of the force between two glass surfaces, immersed in a liquid crystal, using an atomic force microscope (AFM). We have observed a strong, repulsive electrostatic force, that decays exponentially with increasing surface separation and indicates that glass surfaces are charged in a liquid crystal. We determine the surface potential, surface charge density, and the Debye screening length in different liquid crystals.

Generally, the electrostatic forces between bodies immersed in liquids are quite usual and are a consequence of the charging of the surfaces of the body, immersed in a liquid [1]. Static electrostatic interaction in liquids is quite different than that in the vacuum. The presence of charged ions in the solution screens the electric field, emerging from the surfaces, and on the other hand, gives rise to a repulsive entropic contribution due to the repulsion between charged ions that have to remain in the gap between the bodies, as demanded by the electroneutrality condition [1]. In water colloid dispersion, the electrostatic force is very often used as a stabilizing repulsive force between colloidal particles [9].

The electric effects in liquid crystals are very important in liquid crystal displays [10]. The presence of ions in a liquid crystal, confined between the electrodes, is usually disturbing, as it gives rise to ionic conduction and increased power consumption. The ions also screen the external electric field and higher voltages have to be applied to control the orientation of the liquid crystal, which also increases power consumption. The surface electric field due to the charged surfaces may significantly affect liquid crystal orientation and may give a nonlocal contribution to the surface anchoring. The nonlocality can be observed as a thickness dependence of the anchoring strength [8,2].

The electrostatic force between two glass surfaces, immersed in an isotropic liquid crystal, has been measured with a commercial Nanoscope III AFM (Digital Instruments), equipped with a heating stage to control the temperature of the liquid crystal, as described elsewhere [11]. The AFM was used in a force spectroscopy mode, where a surface of a sample is periodically approached and retracted to the AFM probe at the speed of ≈ 80 nm/s, and simultaneously the force on the AFM probe is monitored. We have used flat plates of either LaSF glass or sapphire, attached to the piezoscanner of the AFM and a small sphere made of BK7 glass, attached to the commercial AFM cantilever with an elastic constant of $k=0.1$ N/m. The radius of the sphere was typically 10 μm. All glass surfaces have been thoroughly cleaned in an ultrasonic detergent bath, carefully rinsed with distilled water and acetone and finally cleaned with a radio-frequency (rf) oxygen plasma. A monolayer of *N*, *N*-dimethyl-*N*-octadecyl-3-aminopropyltrimethoxysilyl chloride (DMOAP) has been deposited from the water solution onto the glass surfaces to assure good homeotropic orienta-

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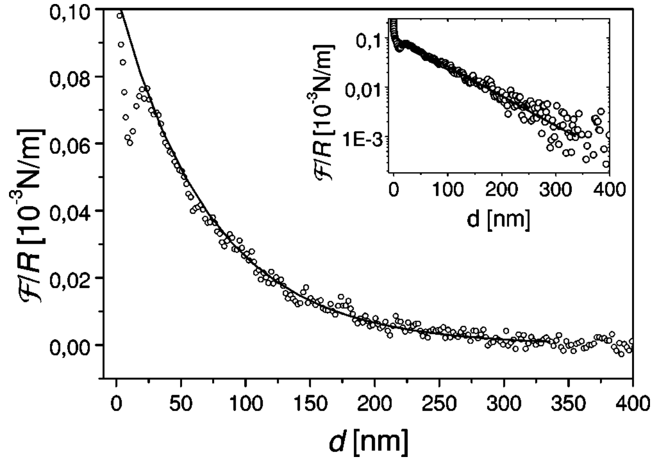

FIG. 1. The distance dependence of the normalized force $\mathcal{F}/R$, between the silanated glass sphere ($R=9$ μm) and silanated sapphire plate in 8CB at $T-T_{NI}=0.5$ K. The solid line is a fit to an electrostatic repulsive force given by Eq. (2). The fit parameters are $\delta=1\times10^{-4}(1\pm0.07)$ A s/m^2, $\lambda_D=73(1\pm0.07)$ nm. The inset shows the same data in a log-lin scale.

tion of the liquid crystal. Nematic liquid crystals 5CB (4-cyano-4′-*n*-pentylbiphenyl) and 4-cyano-4′-*n*-octylbiphenyl (8CB) were used in the experiments.

A typical force measurement that shows the presence of the electrostatic force, is presented in Fig. 1. Here, the force between the silanated 10-μm glass sphere and a flat surface of a silanated sapphire plate was measured in the isotropic phase of 8CB at a temperature 0.5 K above the phase transition temperature (T_{NI}). A very strong repulsive force can be observed. As one can see from the data in the inset, this force decreases exponentially with increasing separation and can be detected even at a separation of 300 nm. At smaller separations of $\approx$20 nm, we have observed an attractive force, which is a result of the capillary condensation of the partially ordered isotropic liquid crystal into the developed nematic phase, as already reported [12]. The exponentially decaying repulsive force showed no temperature dependence in a wide range of temperatures above the nematic to isotropic phase transition temperature.

Similar results were observed in the isotropic phase of 5CB. A typical measurement of the force between a silanated glass sphere and a silanated LaSF glass plate immersed in 5CB, is presented in Fig. 2.

As can be seen in Figs. 1 and 2, the observed repulsive force can be perfectly fitted to the exponentially decaying function, with the decay length of 70–100 nm. The only exponentially decaying force with such a long range and no significant temperature dependence, which can be expected in this case, is the electrostatic force.

Let us now briefly discuss the electrostatic interaction in liquids, which is, in general, difficult to describe theoretically. Different effects due to the solvent-ion and ion-ion interaction should be taken into account to describe the force completely [13]. Since this is a very complicated task, the mean field approximation is usually employed. In this approximation, the liquid and the ionic distribution are considered continuous [1] and the Poison-Boltzmann equation for

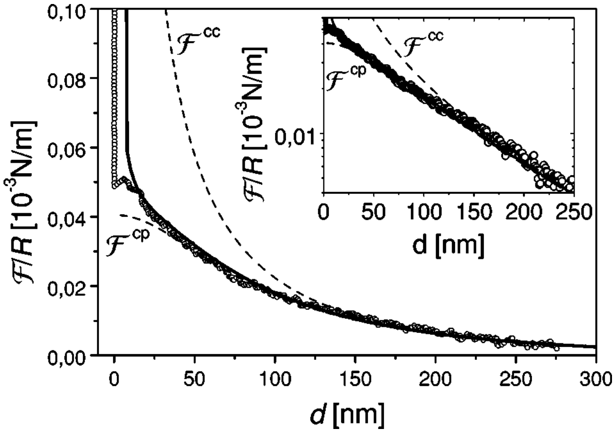

FIG. 2. The distance dependence of the normalized force $\mathcal{F}/R$, between the silanated glass sphere ($R=10$ μm) and silanated LaSF glass plate in 5CB at $T-T_{NI}=11$ K (open circles). The dashed lines represent the numerical solution of the Poisson-Boltzmann equation. The upper dashed curve is calculated for the constant surface charge density $\delta=10^{-4}$ A s ($\mathcal{F}^{cc}$), and the lower dashed curve is calculated for the constant surface potential $\Psi_0=80$ mV ($\mathcal{F}^{cp}$). The full line represents the superposition of both curves $\mathcal{F}=p\mathcal{F}^{cc}+(1-p)\mathcal{F}^{cp}$, with $p=0.04$. The inset shows the same data in a log-lin scale.

the ion distribution ρ and the electric potential profile Ψ is solved. The Poisson-Boltzmann equation is a second-order nonlinear differential equation and cannot be solved analytically, in general. However, the electric potential profile in the liquid can be simplified, if the ion concentration and the surface charge densities are small enough. In this case the potential decays exponentially from the charged surface, located at $z=0$, into the liquid crystal as $\Psi=\Psi_0 e^{-d/\lambda_D}$ [1]. Here Ψ_0 is the value of the electric potential on the surface and the Debye length λ_D is the characteristic decay length of the electric field [1]

$$1/\lambda_D=\sqrt{\sum_i \rho_{\infty i}e^2 z_i^2/\epsilon\epsilon_0 k_B T}. \qquad (1)$$

Here, the sum is over all ionic species in the solution, e is the fundamental charge, z_i is the valence number of an ion i, $\epsilon\epsilon_0$ is the total dielectric permitivity of the liquid crystal, k_B is the Boltzmann constant, and T is the absolute temperature.

The electrostatic contribution to the interaction free energy between two equally charged parallel surfaces is a result of excess osmotic pressure of the ions in the midplane over the bulk pressure [1]. In the limit of large surface separation, a given surface does not feel the screened electric field of the opposite surface, and the electric potential in the middle of the sample, which determines the ionic concentrations in the midplane, is approximated by a sum of potential contributions from both surfaces as if they were isolated. This is justified for separations larger than λ_D [1] and for low surface electric potential, which is expected in our case where both liquid crystal and silane coating are nonpolar.

In this approximation, the force $\mathcal{F}$ between the sphere of radius R and a flat surface is [1].

TABLE I. Surface charge densities δ, surface potentials Ψ_0, Debye lengths λ_D, and ion number densities ρ_∞. Only singly charged ions were considered.

System	$\delta(10^{-5}\ \mathrm{A\,s/m^2})$	$\Psi_0(\mathrm{mV})$	$\lambda_D(\mathrm{nm})$	$\rho_\infty(10^{21}\ \mathrm{m^{-3}})$
Sapphire-8CB-BK7	$10.3(1\pm0.07)$	$80(1\pm0.07)$	$73(1\pm0.07)$	$2.8(1\pm0.14)$
LaSF-8CB-BK7	$9(1\pm0.1)$	$59(1\pm0.1)$	$61(1\pm0.08)$	$4.1(1\pm0.16)$
LaSF-5CB-BK7	$6.3(1\pm0.1)$	$65(1\pm0.1)$	$97(1\pm0.1)$	$1.6(1\pm0.2)$

$$\mathcal{F}\approx\frac{4\pi R\epsilon\epsilon_0\Psi_0^2}{\lambda_D}e^{-d/\lambda_D}. \tag{2}$$

Here, the Derjaguin approximation [1] has been used to connect the force between the flat surface and the sphere with the interaction free energy between two parallel plates. From Eq. (2) it follows that the Debye length λ_D and the surface electric potential Ψ_0 can be determined from the measured separation dependence of the force. At surface potential below about 25 mV, the surface potential is directly connected to the surface charge density δ through the relation [1]

$$\delta\approx\epsilon\epsilon_0\Psi_0/\lambda_D, \tag{3}$$

and the adsorbed surface charge can be simultaneously determined.

The measured electrostatic forces could be in all cases surprisingly well fitted to the Eq. (2). The results of the analysis are presented in Table I. The Debye length is well determined and we have found that it is around 100 nm in commercial cyanobiphenyls. Assuming that only singly charged ions are present, the concentration of the ions in our samples is in the range 1×10^{21}–$5\times10^{21}\ \mathrm{m}^{-3}$, or $(2-7)\ \mu\mathrm{M}$.

The surface charge densities, determined from the approximate relation Eq. (3), are less accurate, but give an important estimate. The typical value of $\delta=1\times10^{-4}\ \mathrm{A\,s/m^2}$, gives a mean separation between singly charged adsorbed ionic impurities of $a=40$ nm, which is relatively large. However, since our surfaces are covered with a hydrophobic DMOAP, it is expected that the surface charge is low.

As stressed above, the Eq. (2) is only valid when the interacting surfaces are more than λ_D apart. At closer distances, the electric potential in the midplane can no longer be approximated by a sum of potential contributions from both planes and the Poisson-Boltzmann equation has to be solved numerically with surface charge density δ, or the surface electric potential Ψ, as the boundary condition. Generally, the electrostatic interaction between surfaces immersed in a liquid is intermediate between the case, where the charge on the surface is constant, and the case, where the surface electric potential is constant [1]. To obtain a better picture of the observed double layer interaction in liquid crystals, we have numerically solved the Poisson-Boltzmann equation for both types of boundary conditions: (i) constant surface potential and (ii) constant surface charge. The theoretical results are shown by dashed lines in Fig. 2, together with the measured separation dependence of the force. The surface potential was set to $\Psi_0=80$ mV in the first case and the surface charge density was set to $\delta=10^{-4}\ \mathrm{A\,s/m^2}$ in the second case. Both curves coincide in the limit of large separations and the force calculated at the constant surface potential $\mathcal{F}^{cp}$ (Fig. 2) fits the measurement much better than the force at the constant surface charge $\mathcal{F}^{cc}$. The best fit is obtained to the model interaction, proposed by Behrens and Borkovec [14]: $\mathcal{F}=p\mathcal{F}^{cc}+(1-p)\mathcal{F}^{cp}$ with $p=0.04$. It indicates, that the surface adsorbed charge reduces considerably at small separations and the net surface charge is extremely sensitive to any variation of the surface potential, either due to desorption of ions from the surface or adsorption of counterions onto the surface.

At this point, we would like to add a comment on the applicability of a mean field model for the electrostatic interaction that we have used. As recently discussed by Nazarenko *et al.* [15] and Kühnau *et al.* [16], the concept of the Debye screening length is only applicable, if the number of ions adsorbed on the surface is very small compared to the total number of ions in the sample. In our case the thickness of the sample is 1 mm, which gives the number of ions per unit area in the bulk sample $\approx2\times10^{18}\ 1/\mathrm{m}^2$. This is considerably higher than the number of surface adsorbed ions $\approx7\times10^{14}\ 1/\mathrm{m}^2$, so that the concept of Debye length is justified.

It is also very important to emphasize that the electrostatic repulsion has not been observed in all experiments. One thing that we are aware of, is that electrostatic force has been observed mainly in the experiments (but not all), where the surfaces have been cleaned in oxygen rf plasma. Probably, the plasma cleaning process has revealed and activated several binding sites for ions on the surface. We should also add that the electrostatic force was measured between two different surfaces. The reported surface electric potentials are then most likely a geometric mean of surface potentials on both surfaces.

At the end we would like to estimate, if the detected surface charge densities and corresponding electric field could contribute significantly to the surface anchoring energy of nematic liquid crystal molecules at the DMOAP interface. There are two different mechanisms that couple the mesoscopic liquid crystalline orientational order to the electric field that emanates from the surface [2,17], direct dielectric coupling, and flexoelectric effect. It has been shown by Barbero *et al.* [17], that the direct dielectric coupling is dominant if $\epsilon_a>2e^2/3\epsilon_0\ K$. Here $\epsilon_a=\epsilon_\parallel-\epsilon_\perp$ is the dielectric anisotropy of a nematic liquid crystal, K is the effective elastic constant in the one constant approximation, and e is the sum of splay and bend flexoelectric coefficients. Taking typical values for cyanobiphenyls, $K=5.5$ pN and $e=6\times10^{-12}$ A s/m, the value of ϵ_a has to be larger than 0.49. Since the dielectric anisotropy in the nematically ordered 5CB is larger, $\epsilon_a\approx10$, we can conclude that the direct dielectric coupling is dominant in this case and only its contribution to the surface coupling energy will be considered.

The anisotropic dielectric free energy density contribution, describing the direct dielectric coupling is $f^{diel}=-\epsilon_a\epsilon_0(\boldsymbol{n}\cdot\boldsymbol{E})^2/2$, where $\boldsymbol{n}$ is the nematic director, f^{diel} is angle dependent, and the electric field $\boldsymbol{E}$ tends to orient liquid crystal in the region close to the surface. The dielectric anisotropy of cyanobiphenyls is positive, therefore, the direct dielectric coupling tends to orient the liquid crystal homeotropically. Its contribution to the linear (ordering) anchoring energy w_1, defined by Poniewierski and Sluckin [18], is approximately $f^{diel}\lambda_D$, if the exponentially decaying electric field $E=E_0e^{-d/\lambda_D}$ is considered. The value of the electric field on the surface in the limit of large separations relevant in ordinary liquid crystal cells is $E_0=\delta/\epsilon\epsilon_0\approx7\times10^5$ V/m and the contribution to the surface free energy in the case, when the orientation is homeotropic is $f^{diel}\lambda_D\approx2\times10^{-6}$ J/m^2. To test this value, we have used the exact profile of the electric field in the semi-infinite sample, confined by a charged plate, as numerically calculated from the Poisson-Boltzmann equation and performed numerical integration $\int_0^\infty f^{diel}dz$. The surface value of the electric potential $\Psi_0=80$ mV has been used as determined from our measurements. In this case, the contribution to the linear anchoring energy is somehow higher and gives 5×10^{-6} J/m^2. Comparing this values to the typical values of the surface anchoring energies on silane covered substrates $w_1\approx1\times10^{-4}$ J/m^2 [11], we can conclude that the electrostatic coupling is weak compared to the coupling between the liquid crystal and alkyl chains of the DMOAP.

In conclusion, we have measured the electrostatic interaction in cyanobiphenyl liquid crystals 5CB and 8CB. We have shown that one can determine the Debye screening length, the concentration of dissociated ions, as well as the values of the surface electric potential and surface charge density from a single force experiment. In addition to that, we have found that the charge regulation processes are very important in the case of silanated glass-liquid crystal interface and that the net surface adsorbed charge reduces considerably in the limit of small separations. The method opens more ways to the study of electric properties of liquid crystals interfaces and we believe that also other AFM-related techniques will be applied in the near future to these interesting systems.

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