Abrupt orientational changes for liquid crystals adsorbed on a graphite surface

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We have determined the alignment of a Gay-Berne model liquid crystal near a graphite surface using Monte Carlo computer simulations. We find in this regime, where adsorption is dominating with respect to the intermolecular interactions, a discontinuous change in anchoring from planar to normal on going from the first to the second adsorbed layer. We also find that the structure of the first two adsorbed layers is not affected by different director orientations induced in the bulk liquid crystal, but is entirely determined by the surface potential. This is a clear example of a breakdown of standard continuum theory in the proximity of a surface. [S1063-651X(98)51003-3]

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The alignment of a liquid crystal (LC) near a solid surface is an extremely important process whose fundamental physics is far from being completely understood [1,2]. A great deal of attention has recently been devoted to this problem, possibly also because of its importance in display technology applications. The classical approach has used continuum theory, often with controversial points of view (see [3–7] and references therein). Microscopic approaches using approximate theories [8–12] and computer simulations [13–15] have also been employed to shed light on the problem. A common intuitive notion is that the ordering in a nematic near a flat solid surface propagates smoothly from the surface into the liquid crystal. One expects the surface to couple to the first layer and influence its ordering and this order to propagate inside the sample, so that if the surface produces a certain alignment this will be transmitted at least for distances up to a correlation length, producing a surface induced bulk alignment [16]. Starting from the other end, the director field in a nematic is normally assumed to vary continuously approaching the surface, in a defect-free region. The orientation of the macroscopic director **n** at a planar surface is expected to be: $\lim_{z\to 0^+}\mathbf{n}(z)=\mathbf{n}_m$, where z is measured from the plane along the surface normal **z**. Since continuum theory should inevitably break down at a molecular length scale, the identification of $\mathbf{n}_m$ with the local microscopic director $\mathbf{n}(0)$ is by no means obvious and, even though very often true, cannot be taken for granted without a knowledge of the molecular interactions between the mesogen and surface molecules. Computer simulations of Gay-Berne fluids near a rough surface with a large pretilt indicate the possibility of strong director distortions [15] while these were not found in models of polymer rubbed surfaces [14], where the bulk pretilt angle was found to be controlled by that at the surface. In this paper we present a case where the behavior of the first layer turns out to be completely different from the rest of the bulk. The model is based upon 4-*n*-octyl-4′-cyanobiphenyl (8CB) on graphite, as detailed later, even if in view of the approximations and the critical balance of forces involved it may not necessarily represent what actually happens in this particular molecular system, but rather present a plausible scenario that can be realized by a selection of suitable molecules on a given surface with strong interactions. We investigate the molecular ordering of a model liquid crystal deposited onto graphite using Monte Carlo simulations. To describe the intermolecular interactions U^{MM} between the mesogenic molecules we use an anisotropic, attractive-repulsive, Gay Berne (GB) potential [17,18]

$$U_{ij}^{MM}(\hat{\mathbf{u}}_i,\hat{\mathbf{u}}_j,\mathbf{r})=4\,\epsilon_s\epsilon(\hat{\mathbf{u}}_i,\hat{\mathbf{u}}_j,\hat{\mathbf{r}})\left[\left\{\frac{\sigma_s}{r-\sigma(\hat{\mathbf{u}}_i,\hat{\mathbf{u}}_j,\hat{\mathbf{r}})+\sigma_s}\right\}^{12}\right.$$
$$\left.-\left\{\frac{\sigma_s}{r-\sigma(\hat{\mathbf{u}}_i,\hat{\mathbf{u}}_j,\hat{\mathbf{r}})+\sigma_s}\right\}^{6}\right] \quad (1)$$

with the unit vectors $\hat{\mathbf{u}}_i,\hat{\mathbf{u}}_j$ along the axes of particles i and j, $\mathbf{r}=\mathbf{r}_j-\mathbf{r}_i\equiv r\hat{\mathbf{r}}$ the intermolecular vector of length r. The anisotropic contact distance $\sigma(\hat{\mathbf{u}}_i,\hat{\mathbf{u}}_j,\hat{\mathbf{r}})$ and strength of interaction $\epsilon(\hat{\mathbf{u}}_i,\hat{\mathbf{u}}_j,\hat{\mathbf{r}})$ are defined as in [17] and we employ the same parametrization used in [18], in particular: length-to-width ratio $\sigma_e/\sigma_s=3$, ratio of the side-side and end-end energy minima $\epsilon_s/\epsilon_e=5$. σ_s and ϵ_s are used as molecular units of length and energy. With this choice of parameters the GB model yields smectic and nematic phases, as well as a temperature dependence of order parameters similar to that of bulk cyanobiphenyls [18]. Here we choose $\sigma_s=0.495$ nm and $\epsilon_s=0.735$ kJ/mol in order to match respectively the van der Waals cross section and the clearing temperature of 8CB.

The total interaction between an anisotropic particle and the graphite substrate U^{MG} is obtained by adding two contributions: a sum of pairwise heteromolecular GB (HGB) interactions between the GB particle and the C atoms (taken as spherical particles) in the first two layers of graphite, so that our surface potential is anisotropically corrugated on the atomic scale, and a standard Fourier series Steele potential [19] which accounts for the interaction between the GB particle and all the other underlying graphite layers [20,21]. In practice, since the anisotropic part of the GB potential is relevant only in proximity of the energy minimum, we can approximate, with an error <2%, this last contribution with the first term of the isotropic Steele potential. The potential constructed in this way is sufficiently simple to allow us to treat a large number of LC molecules and at the same time

suitable to explore the subtleties in the ordering of the molecular adlayer. In practice we adopt the rod-sphere HGB potential U^{MC} consistent with Ref. [22] for the molecule-carbon interaction:

$$U_{ij}^{MC} = 4\,\epsilon(\hat{\mathbf{u}}_\mathbf{i},\hat{\mathbf{r}}) \left[\left(\frac{\sigma_g}{r - \sigma(\hat{\mathbf{u}}_\mathbf{i},\hat{\mathbf{r}}) + \sigma_g} \right)^{12} - \left(\frac{\sigma_g}{r - \sigma(\hat{\mathbf{u}}_\mathbf{i},\hat{\mathbf{r}}) + \sigma_g} \right)^{6} \right] \tag{2}$$

with anisotropic shape and energy terms

$$\sigma(\hat{\mathbf{u}}_\mathbf{i},\hat{\mathbf{r}}_{\mathbf{ij}}) = \sigma_g[1 - (\hat{\mathbf{u}}_\mathbf{i}\cdot\hat{\mathbf{r}}_{\mathbf{ij}})^2 c]^{-1/2}, \tag{3}$$

$$\epsilon(\hat{\mathbf{u}}_\mathbf{i},\hat{\mathbf{r}}_{\mathbf{ij}}) = \epsilon_g[1 - (\hat{\mathbf{u}}_\mathbf{i}\cdot\hat{\mathbf{r}}_{\mathbf{ij}})^2 c']. \tag{4}$$

σ_g, c are parameters related to the width of the molecule and of the carbon atom, while ϵ_g and c' are related to the strength and well depth anisotropy of the molecule-carbon interaction [22]. We have determined these parameters by fitting to a sum of these HGB contributions the total potential energy of a single 8CB molecule, calculated with a detailed atom-atom potential [21,23] at different distances and orientations with respect to the graphite basal plane. This in turn results from the sum of atom-atom Lennard-Jones contributions (a united atom approximation is used for the CH, CH_2, and CH_3 groups) [23] and of the image potential [21] experienced by the partial atomic charges on the molecule, that we obtain from *ab initio* GAUSSIAN92 calculations followed by Mulliken's population analysis [24]. In this system the contribution of the van der Waals interactions is dominant ($>90\%$ for $z < 1$ nm) over the electrostatic one as already found in [21]. The best fit parameters are the following: $\sigma_g = 0.424$ nm, $c = 0.882$, $\epsilon_g = 3.71$ kJ/mol, $c' = 1.161 \times 10^{-2}$. The potential curves for the HGB molecule-surface interaction are shown in Fig. 1 for a GB particle lying flat or normal to the graphite. We find the minimum (adsorption) energy for these two key configurations to be 190 and 50 kJ/mol, at distances between the center of mass and the basal plane of 0.42 and 1.2 nm, respectively. Although this approach neglects conformational effects these values appear to provide sound orders of magnitude not only for 8CB [21], but also for a variety of molecular systems adsorbed on graphite [25].

After specifying the potential in this way, we have run various canonical (constant number of molecules N, volume V, temperature T) MC simulations to obtain equilibrium molecular organizations. We have first studied a low density system with $N = 225$ on a graphite slab filling the $z < 0$ half-space and consisting of 39×45 unit cells (9.6×9.6 nm^2) on the basal xy plane, with periodic boundary conditions (PBCs) in x, y and a potential wall at $z \simeq 5$ nm to preserve the number of particles, giving a bulk density $\rho = 0.488$ molecules/nm^3. A starting configuration with particles positioned normal to graphite at $z = 4\sigma_s$ was heated at $T = 1300$ K and then slowly cooled to 300 K and after an equilibration stage, production runs of 20 kcycles were performed (1 cycle $= N$ molecule updates). We found a striking behavior with the first monolayer adsorbed parallel to the surface and the second normal to it. To check the influence
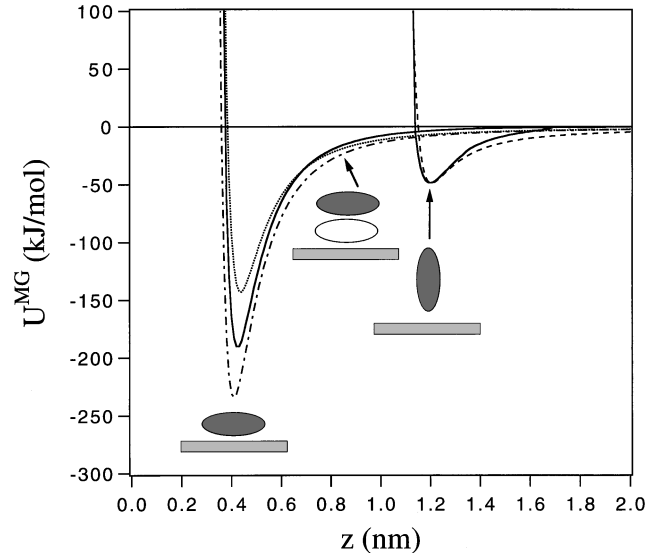

FIG. 1. The potential energy curve U^{MG} between a model 8CB molecule and the graphite surface at distance z. We show the atom-atom potential (see text) for 8CB parallel to the surface with phenyl rings flat (dot-dashed) or normal (dots) to the graphite and for 8CB, cyano-down, perpendicular to the surface (dashed). We also show the GB potential employed (bold continuous). The sketches indicate three relevant configurations.

of density and system size on this result, we have then studied a much larger and more dense system at the same T, with $N = 1810$ and $\rho = 0.3$ molecules/$\sigma^3 = 2.47$ molecules/nm^3. Under such conditions the GB potential with PBC yields a bulk nematic phase [18]. Here we have used a wall of fixed GB particles (a GB ''lid'') to confine the evolving system within the 0–8-nm z range. The lid is a 2.0-nm-high box with 444 particles whose orientations and positions are initially obtained from an equilibrium configuration of a PBC bulk system at the same temperature and kept fixed. To test the effects of the counter surface on the adlayers two different lids with the particles aligned along the z axis (homeotropic) and along one of the graphite lattice directions (planar) have been used (Fig. 2). The sample is pre-equilibrated from an ordered configuration at low density and with the lid very far ($z = 22$ nm) from the surface. The lid is then lowered by 14 nm in 20 kcycles until the desired density is
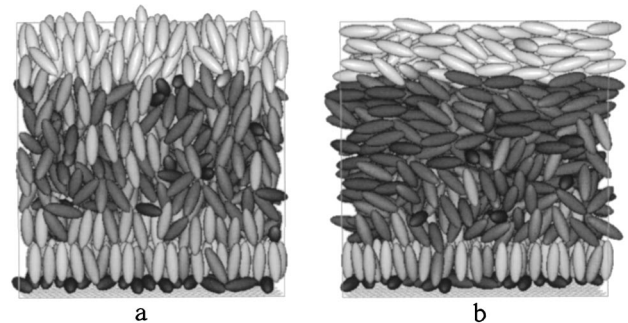

FIG. 2. Configurations at $T = 300$ K, density $\rho = 2.47$ molecules/nm^3 for homeotropic top lid (a) and planar (b) top lid alignment. The molecular orientation with respect to graphite is gray coded (dark corresponds to parallel, light to normal). The fixed lid molecules are coded white.
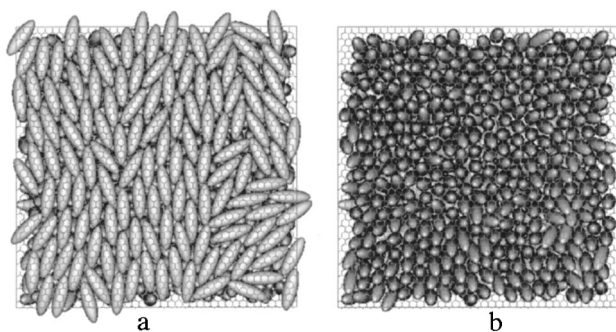
FIG. 3. Molecular ordering with respect to the graphite basal plane in a configuration with normal lid [cf. Fig. 2(a)]: view of first (a) and second (b) adsorbed layers from the bottom with superimposed the honeycomb arrangement of the graphite C atoms. No gray scale is used.

reached at $T = 440$ K. Finally the temperature is decreased to $T = 300$ K in 6.4 kcycles, and the proper equilibration and production runs started. We show in Fig. 2 typical snapshots of the molecular organization for the two cases viewed from the side. We see that both exhibit the change from parallel to normal orientation from the first to the second adsorbed layers. We notice also that the orientation of the top surface propagates to the bulk as usual. Figure 3 shows a view from the graphite side of the first and second adsorbed layers. It is interesting to see that the second layer molecules intrude in the first layer holes to touch the graphite. In Fig. 4(a) the peaks at $z \simeq 0.4$ nm and 1.2 nm show the contraction of the interlayer spacings with respect to the equilibrium distances of the potential (2). There is also a small peak at 2.5 nm, and the structure disappears for distances well above the 2 nm cut-off of the interaction (2). In Fig. 4(b) we monitor the evolution of the local orientational order parameter $\langle P_2 \rangle_z = \langle 3(\mathbf{u}_i \cdot \mathbf{n}_z)^2 - 1 \rangle_{i \in z}/2$, where the average is over the particles i in a bin centered at z, with director $\mathbf{n}_z$. The order parameter in the first two layers is large and there is no evidence of lid effects. The orientation of the second adsorbed layer propagates into the rest of the phase, while the first layer shields the graphite surface and has little effect on the other molecules. In the parallel lid system the contrasting boundary effects going from the second layer towards the bulk reduces the order in a transition region.

Our result can be explained in terms of the much larger adsorption energy with respect to the intermolecular interactions and the competitiveness in terms of energy of having a molecule normal to the graphite rather than flat on top of the first adsorbed one (cf. Fig. 1). This drives the particles above the first monolayer to arrange as close as possible to the substrate, with their ends penetrating the voids within the noncompact first monolayer. We suggest that this kind of self-coating behavior can be obtained in real systems with a suitable selection of molecules on graphite, e.g., choosing substituents to tune the molecular thickness (cf. Fig. 1). An indication of large changes in orientation between the first
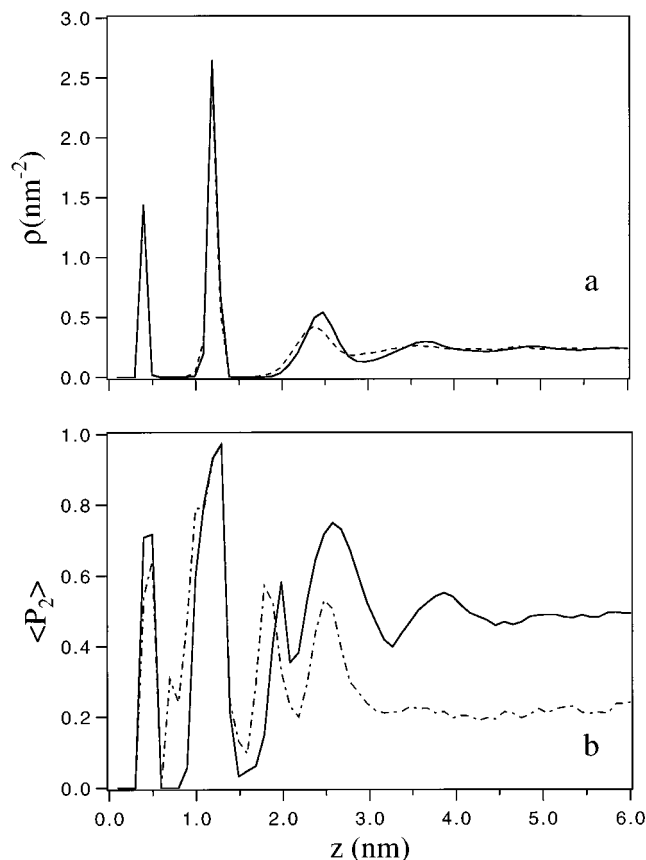

FIG. 4. Surface density (a) and order parameter (b) vs distance from graphite for lid with normal (solid) and parallel (dashed line) orientation.

and the second layer has also been given for simple liquids, such as benzene on graphite [20]. It is worth noting that scanning tunneling microscopy studies of cyanobiphenyls [26] and other liquid crystals [27] on graphite have necessarily concentrated on the first adlayer, which is found to be planar, even if more regular (really a two-dimensional crystalline system) than what we find here. However, other techniques sensitive to the structure of layers above, such as the surface force apparatus [28], ellipsometry [29], and NMR [30] could be used to test our predictions of the $\pi/2$ director switch. We believe that the possibility of such large director jumps near a surface offers challenging problems to continuum approaches based on local Taylor expansions of the free energy, prompting for truly nonlocal generalizations of this type of theories.

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