

Simulated anchoring of a nematic liquid crystal at a polymer surface

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(Received 23 January 2007; revised manuscript received 4 January 2008; published 29 February 2008)

Liquid-crystal anchoring at a polymer surface arises from interactions at several different length scales. At the molecular level, a liquid-crystal molecule may tend to align with the substrate polymer chain, while at the nanometer length scale grooves can exist that arise from the periodic repeat structure of a polymer chain or from nanometer-scale undulations due to surface stresses. On a still longer scale there is the secondary effect of grooves or surface inhomogeneities. We have performed a total of more than 900 ns of atomistic molecular dynamics simulations in order to study the relative importance of the molecular-level interaction and the topography of the polymer surface in liquid-crystal anchoring. Substrates were constructed in which grooves were induced along a direction perpendicular to the constituent molecular chains. In the results presented for the case of 32 5CB molecules on a poly(vinyl alcohol) substrate, the liquid-crystal director orientation appeared to be determined principally by the substrate chain orientation. Only for the deepest grooves did the director align along the grooves and perpendicular to the substrate molecular chain direction.

DOI: [10.1103/PhysRevE.77.021707](https://doi.org/10.1103/PhysRevE.77.021707)

PACS number(s): 61.30.Cz, 61.30.Hn

I. INTRODUCTION

It is a property of a nematic liquid crystal (LC) that the average orientation of its constituent molecules is influenced by the nature of the surface of the containing vessel. Industrial applications of LCs in display devices rely on the ability of the manufacturer to prepare a substrate surface that will promote a particular type of alignment. The interaction between substrate and LC molecule is referred to as anchoring, and is said to be planar anchoring if the molecule tends to lie flat on the surface.

Various techniques can be used to induce the LC director to lie in a particular direction within the plane of the substrate surface. The traditional approach is simply to rub the surface of a polymer layer that has been applied to coat the substrate. This in most cases leads the director to lie in the rubbing direction [1]. Alignment can also be achieved by etching a periodic grating on an inorganic surface [2], inducing spontaneously generated grooves through uniform laser illumination [3–6], using a phase mask to laser etch a grating on a polyimide surface [7], and using an atomic-force microscope to inscribe grooves [8].

Although some of the alignment techniques have been in use for decades, the mechanism responsible for LC anchoring is still debated. The earliest suggestion was that rubbing induced grooves in the surface, and that with planar anchoring the topography favored alignment in the direction of rubbing, since in that case no bending elastic energy would be introduced. Berreman [9] made a theoretical study of the interaction of a nematic LC with an undulating surface. He assumed a planar anchoring that was completely isotropic in the local tangent plane to the surface, and calculated the resulting elastic energy as a function of the azimuthal orientation of the LC director in the bulk LC relative to the direction of the undulations. He showed that the anchoring energy introduced by an alignment perpendicular to the grooves was

dependent on the depth and period of the grooves. Newsome and co-workers [7] have used twisted nematic cells to measure the anchoring energy of aligned LC molecules on a polyimide surface. The cells consisted of a nematic LC between two polyimide substrates, one of which had a laser-etched periodic grooved structure and the other of which was rubbed in a perpendicular direction. Their measurements showed good agreement with Berreman's theory, resulting in the conclusion that the alignment was due to the geometrical structure of the surface. In another experiment Hallam and Sambles [10] found good agreement between measurements and the theory for shallow grooves, but with less satisfactory agreement for deeper grooves.

According to another point of view, alignment is primarily due to molecular interaction between LC molecules and polymer chains [11,12], an effect that also usually makes the molecules line up in the rubbing direction. On a macroscopic scale, rubbing a polymer surface creates grooves with a period of fractions of a micrometer, but on a microscopic scale it is also believed to order the polymer chains that lie in the surface by drawing them along the rubbing direction. Even a flat crystalline surface of parallel chains can then be considered as having grooves on a scale of fractions of a nanometer along the chain direction. It is thus tempting to view the debate as to whether grooves or chain orientation is the dominant cause of LC alignment as equivalent to a discussion of whether microgrooves or nanogrooves are more effective agents in aligning LC molecules.

This, however, would be too much of an oversimplification. The surface of a perfectly ordered crystal facet of a polyimide, for example, has a periodicity along the chain direction that gives rise to a periodic potential with a wavelength of the order of a nanometer [13]. There are thus channels on a scale intermediate between that of the distance between parallel chains and that of macroscopic grooves, and in a direction perpendicular to both. A further complication is that some polymers, such as polystyrene, have phenyl groups attached at right angles to their chain backbone. Rubbing these materials has been found to orient 5CB (4-*n*-pentyl-4'-cyanobiphenyl) molecules in a direction perpendicular to

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the rubbing direction [14]. The cause of this appears not to be related to the mutual attraction of phenyl groups in polymers and mesogen, but rather to the formation of submicrometer-scale meandering grooves perpendicular to the rubbing direction [15,16].

The conclusion we draw from the available data is that the root origin of the anchoring energy is the molecular interaction between surface and LC, but that the surface topography can combine with this interaction to yield an effective anchoring that may or may not be aligned with the direction of any grooves. The question of interest then becomes to ask what are the relative strengths of (a) the intrinsic anchoring anisotropy due to molecular interactions and (b) the induced anisotropy due to the effects of surface topography on the isotropic component of the planar surface anchoring.

One way in which to answer this question definitively would be to prepare a surface in which the effects of intrinsic and induced anisotropy are in competition. A step in this direction was taken by Chung *et al.* [17], who prepared a grooved surface of about 1 μm spacing by uniform laser irradiation, and then used polarized light to induce cross-linking at an angle of 45° from the grooves. They varied the depth and periodicity of the grooves by changing the intensity of the laser beam, and measured the resulting orientation of the LC molecules. Their results showed that there were indeed two competing effects trying to align the LC molecules in different directions. Deep laser-induced grooves resulted in alignment close to the groove direction, whereas shallow ones could not significantly affect the direction of the molecules, resulting in alignment parallel to the photoalignment direction. Even this careful experiment, however, did not present a clearcut competition between grooves and chains, as the photoalignment process does not lead to creation of a surface consisting of well-ordered chains. For this reason we have used atomistic molecular modeling to examine the behavior of a nematic liquid crystal in contact with surfaces in which an array of parallel molecular chains are deformed into an undulating structure. In this way the relative strengths of the effects of grooves and chains can be determined.

A number of previous molecular-dynamics simulation studies of LC anchoring exist in the literature. These include the work of Yoneya and Iwakabe [18,19], who studied the alignment of 8CB (4'-*n*-octyl-4-cyanobiphenyl) on a polyimide surface, and of Binger and Hannah [20–22], who simulated the anchoring of 5CB and 8CB molecules in contact with different substrates, including polyvinyl alcohol (PVA). Doerr and Taylor [23,24] investigated the anchoring of 5CB on an amorphous polyethylene surface. However, none of these authors used grooved surfaces in their simulations. In fact, to the best of our knowledge, only van der Vegt *et al.* [13] have simulated grooved substrates. They studied the anchoring of 8CB on poly-3-APM (poly-3-alkanpyromellitimide) and poly-4-APM (poly-4-alkanpyromellitimide) substrates. They noted that the polymer chain itself has a repeat length, and that this introduces the equivalent of shallow grooves of subnanometer depth perpendicular to the chains. They concluded that in single 8CB molecule simulations these nanogrooves dominated, causing the molecules to align perpendicular to the

chains, whereas in monolayer simulations the nanogrooves were less important, both in the case of poly-3-APM and particularly in the case of poly-4-APM, where the nanogrooves are shallower. Their results give a partial answer to the question we have posed about the relative strength of chains and grooves in aligning LC molecules. However, this study was limited to comparing the aligning influence of chains with that of nanogrooves of a single very small wavelength and fixed depth. It thus seems useful to examine a system in which the depth of grooves can be varied.

II. SIMULATIONS

We have studied the relative importance of chains and grooves in LC alignment by performing molecular dynamics (MD) simulations of 5CB molecules in contact with a PVA substrate that has been deformed to introduce grooves. These materials were chosen for a number of reasons. First, the small repeat length of PVA has the consequence that there are no nanogrooves of wavelength larger than a small fraction of a nanometer on the surface of a crystalline facet. Second, because of the comparatively small molecular weight of 5CB it responds rapidly to orienting forces. Finally, there is also the fact that these materials are commonly used in experiments and have been previously studied in computer simulations [20].

Choosing an appropriate force field is probably the most important factor in running successful simulations. Our simulations were performed using a force field recently developed by Cheung *et al.* [25,26], which has been specifically designed to simulate liquid crystals. The energy function of this force field is the same as that of AMBER (Assisted Model Building with Energy Refinement) [27], except that up to twelve terms are kept in the Fourier expansion of the torsional force. In our simulations, however, only the first four terms were kept, as the higher order terms are much smaller. Simulations were performed using the code LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulation) [28].

Nonbond (van der Waals and electrostatic) interactions play an important role in any MD simulation, and it is especially important to take into account efficiently the long-range electrostatic forces. In this study the algorithm particle-particle particle-mesh (PPPM) [29] was used to calculate long-range interactions between atomic charges. The cutoff distance for nonbond interactions was set to be 1 nm.

In our simulations, 32 molecules of 5CB and six PVA chains, each comprising 16 monomers, were enclosed in a cell as shown in Fig. 1. Because the experimentally observed crystal structure of PVA [30] is not greatly dependent on the tacticity of the material, it was convenient to use purely syndiotactic PVA in our model. (Atactic material, in which the hydroxyl groups are randomly placed in left- and right-hand positions, cannot be reasonably represented within the small chain length that we employed.) Following Binger and Hanna [20] the chains were oriented in such a way that the simulated surface corresponds to the (100) plane of PVA, as illustrated in Figs. 2(a) and 2(b). The distance between the chains is 0.55 nm [30]. In its initial flat condition the surface

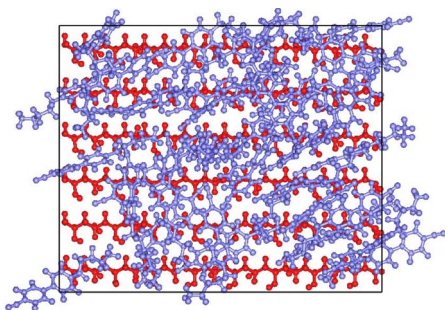


FIG. 1. (Color online) The PVA-5CB system with a flat substrate, when viewed from above. The rectangle shows the boundaries of the cell. In the molecular arrangement shown, the director makes an angle of about 30° with the chain axes.

(with an area of $4.0 \text{ nm} \times 3.3 \text{ nm}$) lies in the x - y plane with the chains parallel to the x axis. Periodic boundary conditions were applied in the x and y directions, but not in the z direction. To make a grooved substrate, the chains were deformed as shown in Fig. 3. The resulting periodic substrate, with grooves in the y direction perpendicular to the chains, is characterized by its period λ , and its amplitude a . Simulations were performed for a flat substrate [substrate (a)] and for four different curved surfaces with $\lambda=3.60, 3.24, 2.93, 2.57 \text{ nm}$ and $a=0.4, 0.5, 0.6, 0.7 \text{ nm}$, respectively [substrates (b), (c), (d), and (e)]. The four systems with curved substrates are shown in Fig. 3. In order

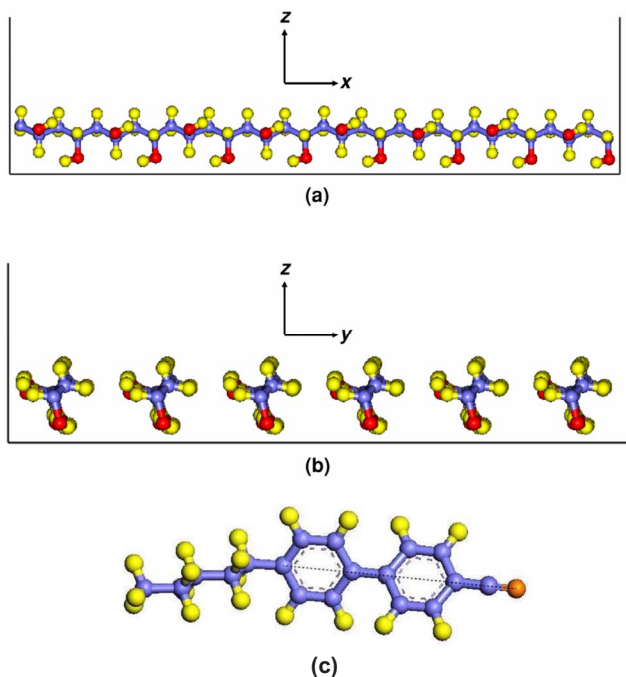


FIG. 2. (Color online) (a) and (b) This figure shows the orientation of the PVA chains and the location of their OH groups. The chains are oriented in such a way that the surface corresponds to the (100) plane in PVA. In the online version of this figure the hydrogen, oxygen, and carbon atoms are colored in yellow, red, and blue, respectively. (c) This figure shows the line characterizing the orientation of a 5CB molecule

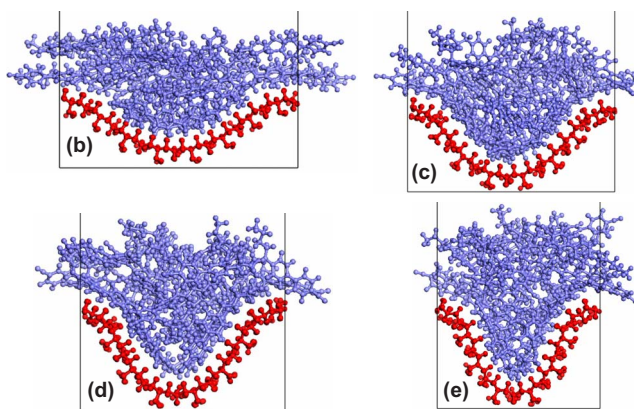


FIG. 3. (Color online) The 5CB-PVA system is shown for a curved substrate having (b) $a=0.4 \text{ nm}$, $\lambda=3.60 \text{ nm}$, (c) $a=0.5 \text{ nm}$, $\lambda=3.24 \text{ nm}$, (d) $a=0.6 \text{ nm}$, $\lambda=2.93 \text{ nm}$, and (e) $a=0.7 \text{ nm}$, $\lambda=2.57 \text{ nm}$. The flat substrate (a) is not shown.

to make sure that the substrate maintained its shape, in all the simulations the positions of the carbon atoms in the polymer chains were held fixed.

Since the 5CB molecules have flexible tails, it is not obvious how their orientation should be specified. The mesogenic core of the molecule consists of two rigidly connected benzene rings, and so we characterize the orientation of each 5CB molecule by a line drawn from the nitrogen atom to the carbon atom connected to the tail, as illustrated in Fig. 2(c). It is convenient to define a unit vector \hat{u} parallel to this line, pointing to the nitrogen atom. The orientation of molecule i then can be specified by the unit vector $\hat{u}^{(i)}$.

Once the orientation of each 5CB molecule is known, one can calculate the order parameter and the director by evaluating the largest eigenvalue S and the corresponding eigenvector of the matrix

$$S_{jk} = \frac{3}{2N} \sum_{i=1}^N u_j^{(i)} u_k^{(i)} - \frac{1}{2} \delta_{jk}, \quad (1)$$

where N is the number of molecules. The orientation of the director is then described by the azimuthal angle ϕ and the declination angle θ ($0^\circ < \theta < 90^\circ$). The angle ϕ is the most important for our purposes, as we are interested in the orientation of the director relative to the chains and grooves.

Molecular dynamics simulations were carried out to determine ϕ and θ as a function of time for systems with different substrates. In each simulation, first the commercial software package MATERIALS STUDIO [31] was used to build an amorphous cell of 32 5CB molecules in the nematic phase. In the case of a flat substrate the 5CB molecules formed a bilayer. This liquid crystalline layer was then placed on top of a previously prepared substrate. The system was then equilibrated using LAMMPS as follows: First a 50 ps NVT simulation was run at $T=50 \text{ K}$, then the system was heated to $T=300 \text{ K}$ over a period of 50 ps. The system was then equilibrated at constant temperature and volume ($T=300 \text{ K}$) for 150 ps. The time step in the equilibration stage was chosen to be 0.5 fs, and the velocity-Verlet inte-

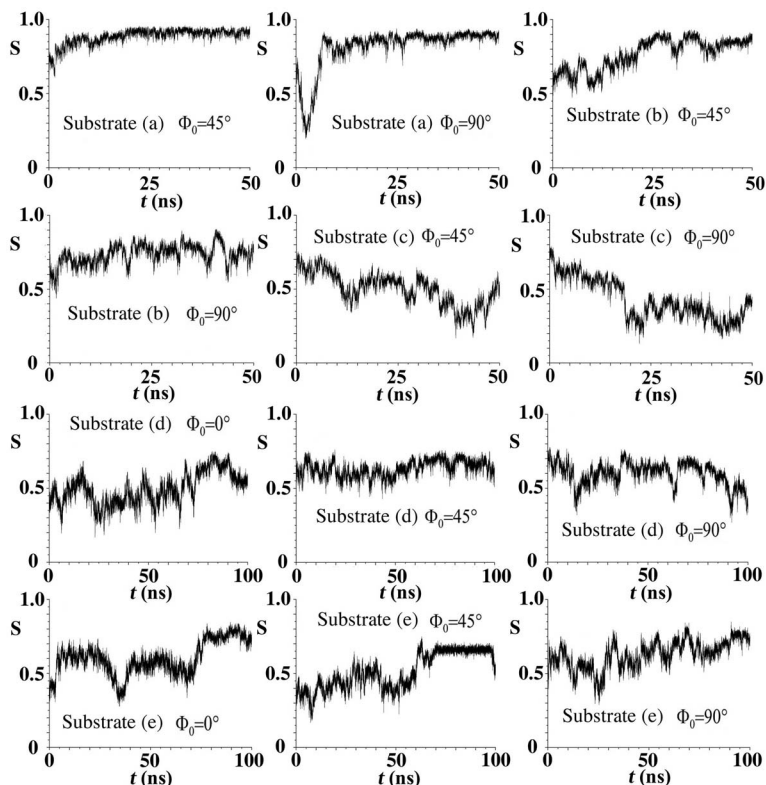


FIG. 4. The order parameter as a function of time for different substrates and initial configurations.

grator was used [32]. After equilibrating each system, an *NVT* simulation (using the Nosé-Hoover method [33,34] for controlling temperature) was run for 50 ns for substrates (a), (b), and (c), and for 100 ns for substrates (d) and (e), and the coordinates of all atoms were recorded every 5 ps.

The rRESPA algorithm (reversible reference system propagator algorithm) [35] was used in the production stage of the simulations, allowing longer time steps to be used for calculating nonbond interactions. This method uses different time steps to calculate different types of interactions. In our simulations, all bond-related interactions were calculated using a 0.5 fs time step. The time step for evaluating nonbond interactions between a pair of particles less than 0.6 nm apart was set to be 1 fs, whereas for pairs with distances between 0.6 and 1.0 nm a 2 fs time step was chosen. A 4 fs time step was used to calculate long-range electrostatic forces.

III. RESULTS

The recorded coordinates of the atoms were used to calculate the order parameter S , and the angles ϕ and θ as functions of time. In all simulations, the LC molecules were initially oriented such that $\theta_0 \sim 90^\circ$ and $S_0 \sim 0.6$. For substrates (a), (b), and (c), two simulations with different initial configurations ($\phi_0 \sim 45^\circ$ and $\phi_0 \sim 90^\circ$) were performed. For each of substrates (d) and (e), which have deeper grooves, an additional simulation was carried out with $\phi_0 \sim 0^\circ$. The results for S , ϕ , and θ are shown in Figs. 4, 5, and 6, respectively.

In the case of the flat surface [substrate (a)] the order parameter, regardless of the initial configuration, reaches a

value close to 0.9, which is higher than the expected order parameter of bulk liquid crystal. This can be explained by the fact that in our simulations the liquid-crystal layer in contact with the surface is very thin, and so all the molecules strongly interact with the substrate, resulting in a highly ordered system. It is interesting to note (Fig. 4) the sharp decrease and then increase in the order parameter when $\phi_0 = 90^\circ$. This may be explained by the fact that the perpendicular orientation is not favored by the LC molecules, and so they reorient to align with the chains. This can be clearly seen from Fig. 5. The molecules rotate in two possible directions (clockwise and counterclockwise), which reduces the order parameter, and also causes very large and fast variations in ϕ . The order parameter, however, increases again as the molecules become more or less parallel to the chains. The angle θ , as expected, remains very close to 90° regardless of the value of ϕ_0 .

As expected, when the substrate is gently curved [substrate (b)], the order parameter is a little lower than for the case of the flat substrate, but the system is still highly ordered. Figure 5 again shows a clear tendency for the molecules to line up with the chains. The angle θ undergoes bigger fluctuations, and at times becomes less than 70° , but remains mostly close to 90° . On the basis of these findings one can safely conclude that gently curved substrates behave in a very similar manner to flat ones.

In the case of substrate (c), large fluctuations are observed in S , ϕ , and θ . The order parameter is much lower and reaches its lowest value in comparison with all other cases. In fact, Fig. 4 shows that increasing the curvature of the substrate over its full range causes first a decrease, and then an increase, in the average order parameter. This behavior

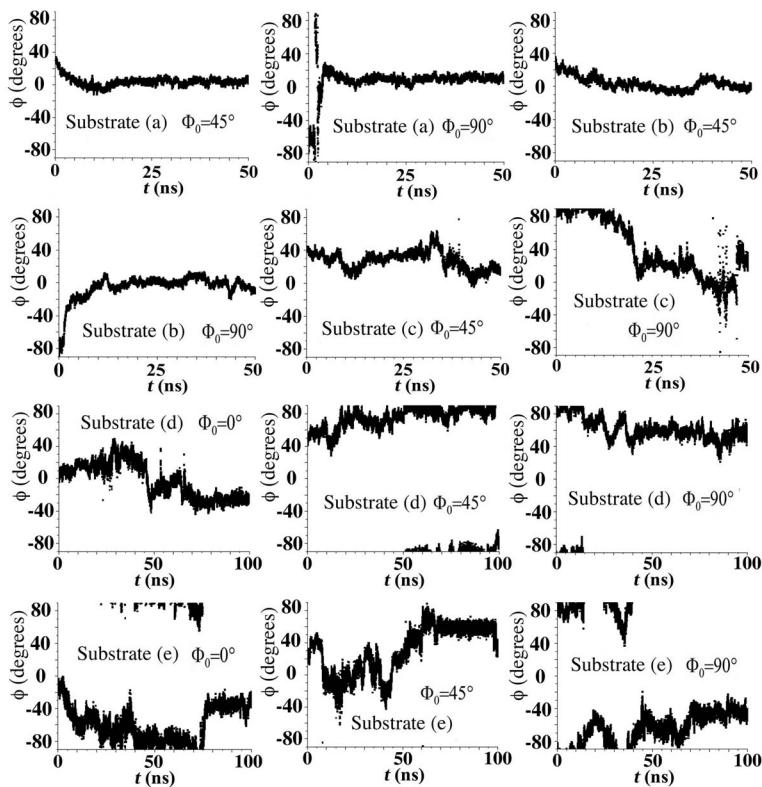


FIG. 5. The angle ϕ as a function of time for different substrates and initial configurations.

can be understood in terms of competition between the two aligning mechanisms mentioned before. A flat or gently curved substrate is expected to align the molecules with the chains ($\phi \sim 0^\circ$), whereas a very deeply grooved surface

tends to orient the molecules in the groove direction ($\phi \sim 90^\circ$). When the substrate is modestly curved the two competing effects are comparable, and so the molecules orient in an intermediate direction, and undergo larger fluctuations re-

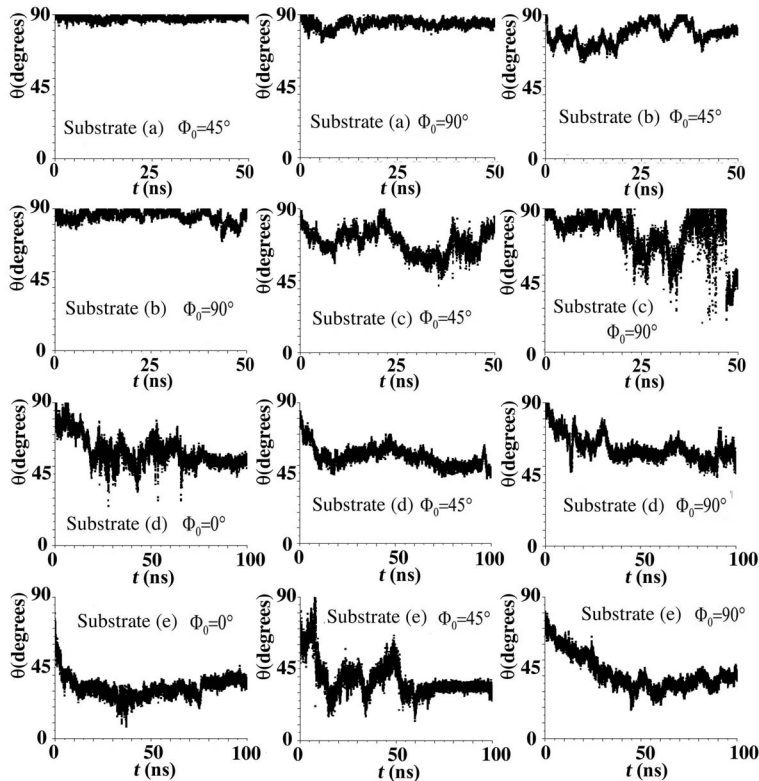


FIG. 6. The angle θ as a function of time for different substrates and initial configurations.

sulting in a less ordered LC. Also the molecules seem to follow the curvature of the surface, resulting in a smaller θ , and so a lower order parameter.

As mentioned before, the order parameters for systems with substrates (d) and (e) are slightly higher than that with substrate (c). The angle θ , however, reaches its lowest value when the groove has the highest curvature [substrate (e)]. For these two systems, simulations were carried out starting from three different initial configurations ($\phi_0=0^\circ$, 45° , and 90°), and were run for 100 ns, which is double the time of the previous runs. As can be seen from Fig. 5, in both cases [substrates (d) and (e)], there is a discrepancy between the results obtained from simulations with different starting configurations. Of the three simulations performed for substrate (d), the one starting from $\phi_0=0^\circ$ indicates that the preferred director orientation is closer to the chain direction than to the groove direction, while the other two starting points lead to a director orientation closer to the groove direction than the direction of the polymer chains. This suggests that the increasing depth of the grooves has introduced a new local minimum in the free energy, leaving the state in which ϕ is close to 0° as a metastable state. This idea is reinforced by the results for substrate (e), which has even deeper grooves. In this case the director has a tendency to wander between the parallel and perpendicular orientations during the course of the simulations. This is consistent with the interpretation that the local minimum for ϕ close to 0° has almost disappeared, leaving the free energy with a broad minimum spanning a range of orientations.

To have a better understanding of the results given in Fig. 5, we plot in Fig. 7 the quantity $\psi = \langle \cos 2\phi \rangle$ as a function of a/λ , which is a measure of the curvature of the substrate. Here the angular brackets $\langle \dots \rangle$ imply a time average. Since it takes several nanoseconds for the angle ϕ to equilibrate, the average is calculated over the last 30 ns of the 50 ns simulations, and over the last 80 ns of the 100 ns simulations. A negative ψ indicates a tendency to align with the grooves, whereas a positive ψ means that the molecules are more inclined to align along the polymer chains. One sees that increasing the depth of the grooves does not lead to a smooth variation in ψ , but rather introduces a bistable region when $a/\lambda \sim 0.2$, followed by a preference for negative ψ when $a/\lambda > 0.25$.

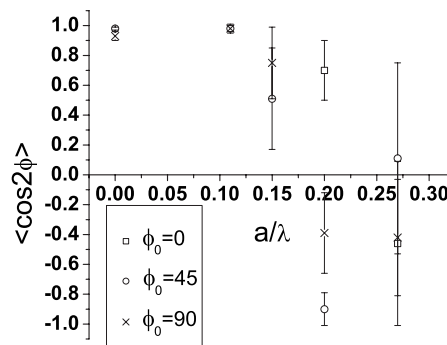


FIG. 7. This figure shows the time average of $\cos 2\phi$ for different substrates and starting points. In each case the average was calculated over the last 30 ns of the simulation. The error bars show the standard deviations.

IV. CONCLUSION

The data from Fig. 7 support the view that there is at least a local minimum in free energy in all five substrates for the configuration where the director lies in the direction of the molecular chains, but that for substrates (d) and (e) a new minimum has appeared corresponding to the director lying perpendicular to the chain direction and parallel to the direction of the grooves. The wide variations in the orientations ϕ found for the deep grooves of substrate (e) are consistent with a very shallow local minimum in the free energy for molecules aligned parallel to the chains. The conclusion that we draw from this work is that the tendency for liquid-crystal molecules to align in the direction of the molecular chains forming the substrate is sufficiently strong that at the nanometer scale it can be overcome by only the deepest of grooves.

ACKNOWLEDGMENTS

This work was supported by the Petroleum Research Fund of the American Chemical Society, and was made possible by use of facilities at the Case ITS High Performance Computing Cluster and the Ohio Supercomputing Center.

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