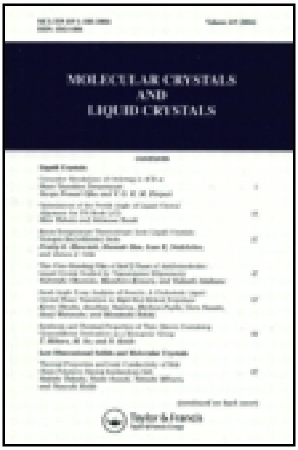

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Simulation of Liquid Crystal Anchoring at an Amorphous Polymer Surface from Various Initial Configurations

T. P. Doerr [a] & P. L. Taylor [a]

[a] Physics Department, Case Western Reserve University, Cleveland, Ohio, 44106-7079, U.S.A.

Version of record first published: 24 Sep 2006

To cite this article: T. P. Doerr & P. L. Taylor (1999): Simulation of Liquid Crystal Anchoring at an Amorphous Polymer Surface from Various Initial Configurations, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 330:1, 491-501

To link to this article: http://dx.doi.org/10.1080/10587259908025626

Mol. Cryst. Liq. Cryst., 1999, Vol. 330, pp. 491-501
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Simulation of Liquid Crystal Anchoring at an Amorphous Polymer Surface from Various Initial Configurations

T.P. DOERR and P.L. TAYLOR

Physics Department, Case Western Reserve University, Cleveland, Ohio 44106–7079, U.S.A.

We have used atomistic molecular dynamics simulations to investigate the anchoring of a liquid crystal at the surface of an amorphous polymer. The system studied consisted of the nematogen 5CB at the surface of amorphous polyethylene. The simulations indicate a clear tendency to nearly homeotropic anchoring. The fact that two starting configurations, one planar and one homeotropic, lead to similar final configurations indicates that the observed final configurations represent the equilibrium state for the system under consideration.

Keywords: anchoring; liquid crystal; amorphous polymer

The interaction of a liquid crystal with the surface of its container is essential to most applications of these materials. A bulk liquid crystal is an ordered fluid whose ground state has both translational and rotational symmetry. The presence of a surface serves to reduce the symmetry of a liquid crystal system because the interaction between the surface and the liquid crystal molecules near it eliminates the translational and rotational degeneracy of the ground state, and thereby determines, in the absence of competing forces such as applied electric fields, the orientation of the liquid crystal molecules in the bulk.[1],[2] This paper reports the results of atomistic molecular dynamics simulations used to study this process in a simple system.

A variety of microscopic mechanisms are thought to contribute to anchoring.[3] Among these mechanisms are van der Waals forces, the interaction of permanent dipoles in the molecules involved, and structure added to the surface by mechanical procedures such as rubbing. Atomistic molecular dynamics simulations have the potential to include these mechanisms and to study their relative importance, as well as to ascertain the anchoring behavior for specific materials and geometries. On the other hand, because atomistic molecular dynamics simulations include the detailed structure of the molecules, considerable demands are made on computing resources. A simple molecule of 5CB (4-n-pentyl-4′-cianobiphenyl), for example, consists of thirty-eight atoms, and so the number of intramolecular interactions that must be taken into account is large, even before intermolecular interactions are considered. It is perhaps for this reason that there seems to have been very little work done on atomistic simulations of anchoring and other surface behavior at nematic interfaces, although a greater number of atomistic simulations of bulk liquid crystals have been performed.[4]–[8]

The method of atomic-level molecular modeling are used in the present work to study the anchoring behavior of nematic liquid crystals. In particular, we study the anchoring of 5CB at an amorphous polyethylene surface. The molecule 5CB is a commonly used liquid crystal, and atomistic molecular modeling simulations on 5CB in the bulk have been performed previously.[4]–[8] Amorphous polyethylene is the simplest of polymers, and has, on average, no favored directions in the surface plane. This will simplify our task, which then reduces to an examination of the tilt angle θ that this system favors.

We describe here simulations at constant number of atoms, constant volume, and constant temperature (constant NVT) of 5CB near an amorphous polyethylene substrate, in which we made use of the commercial software package Cerius^2.[9] The thickness of the substrate was about 2.0 nm, which should be sufficient for representing a surface in an atomistic molecular dynamics simulation.[10] The simulations involved 8, 16, 24, or 32 5CB molecules at 300 K, which is in the nematic range of 5CB.[11] Newton's equations for the system were numerically integrated for time periods ranging from 10 ps to 100 ps with an integration time step of $\Delta t = 1$ fs. The positions of the atoms were recorded every 0.1 ps for later analysis. The temperature was kept constant by scaling the velocities at each time step during the simulation.

Two initial configurations were used for the simulations described here. One initial configuration was formed by positioning an array of 5CB molecules in a homeotropic orientation at the surface of the amorphous polyethylene (Figure 1). The 5CB molecules, which are colored purple, lie along the z-axis, the y-axis lies in the plane of the surface and the page, and the x-axis points out of the page. The area of the substrate varied depending on the number of 5CB molecules used. Periodic boundary conditions in all three directions were applied at the faces of the cell shown by the dashed blue lines. The other initial configuration was formed by positioning an array of 5CB molecules in a planar orientation at the surface of the amorphous polyethylene (Figure 2). The 5CB molecules in this case lie along the y-axis.

The Dreiding force field[12] was used. The main features of this force field are the energies characterized as follows:

$$E = E_{\text{bonded}} + E_{\text{non-bonded}} \tag{1}$$

$$E_{\text{bonded}} = E_{\text{bond}} + E_{\text{angle}} + E_{\text{torsion}} \tag{2}$$

$$E_{\text{non-bonded}} = E_{\text{van der Waals}} + E_{\text{Coulomb}} \tag{3}$$

where E_{bonded} includes the effects of covalent bonding, $E_{\text{non-bonded}}$ includes effects, some of them long range, not directly related to covalent bonding, E_{bond} is the energy for stretching of bonds, E_{angle} is the energy for bending the angles formed by each pair of consecutive bond directions, E_{torsion} is the energy for rotation about the bond directions, $E_{\text{van der Waals}}$ is the van der Waals interactions, and E_{Coulomb} is the electrostatic interaction between partial charges. The Coulomb interaction plays an important role in our simulation because the 5CB molecule has a permanent dipole. The charges

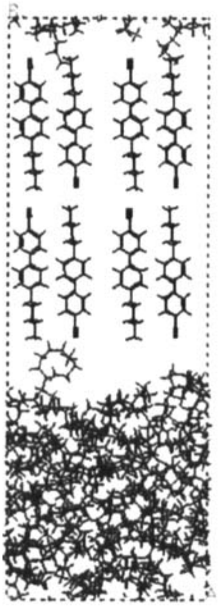

FIGURE 1. The homeotropic initial configuration. An array of 5CB molecules is positioned in a homeotropic orientation at the surface of the amorphous polyethylene.

(See Color Plate XVIII at the back of this issue)

used were taken from the work of Wilson and Allen[6] on simulations of the bulk properties of 5CB.

In order to compute the order parameter of the 5CB molecules, it is necessary to define a molecular axis direction, $\hat{u}$, for each molecule. In models that represent the molecules as elongated rigid objects with rotational symmetry about the elongated direction, there is no problem in identifying the axis of a molecule; it is simply the direction of elongation. In fully atomistic molecular dynamics simulations such as those done here, the molecules are not rigid and so there is ambiguity in specifiying the direction of each

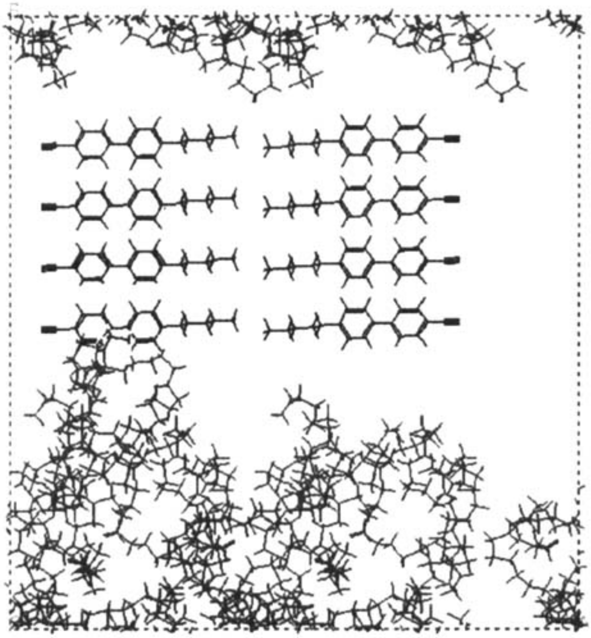

FIGURE 2. The planar initial configuration. An array of 5CB molecules is positioned in a planar orientation at the surface of the amorphous polyethylene.
(See Color Plate XIX at the back of this issue)

molecule. The method chosen was simply to use as the direction of the molecule the bond direction of the bond connecting the two benzene rings in 5CB.

The definition[11] of the tensor order parameter S is

$$S_{ij} = \frac{1}{2}\langle 3(\hat{r}\cdot\hat{e}_i)(\hat{r}\cdot\hat{e}_j) - \delta_{ij}\rangle \tag{4}$$

where $\hat{r}$ is a unit vector along the axis of a molecule, and $\hat{e}_i$ and $\hat{e}_j$ are unit vectors along the space fixed axes, where $i, j = x, y, z$. The order parameter matrix S is diagonalizable. Its largest eigenvalue is also referred

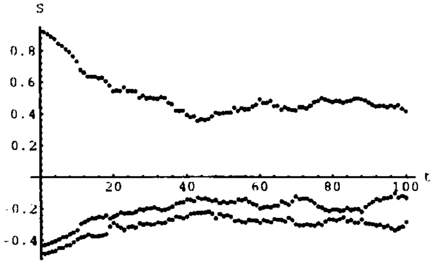

FIGURE 3. The three eigenvalues of the order parameter matrix as a function of time for a simulation starting from the homeotropic configuration. The unit of time is 0.1 ps.

to as the order parameter, and the eigenvector corresponding to the largest eigenvalue is the director. The brackets $\langle \ldots \rangle$ denote an average over a probability density for $\hat{r}$. For our purposes the ensemble average is more suitable since the probability density for $\hat{r}$ is not known *a priori*, and so we make the approximation

$$S_{ij}(N) = \frac{1}{N} \sum_{n=1}^{N} \frac{1}{2} [3(\hat{r}_n \cdot \hat{e}_i)(\hat{r}_n \cdot \hat{e}_j) - \delta_{ij}]. \tag{5}$$

The accuracy of this expression is limited by the modest size of the greatest number of molecules N that can feasibly be modeled. It has been found that no significance can be attributed to values of $S_{ij}(N)$ that are less than $\sqrt{2/3N}$.

Simulations were initiated from the two configurations shown in Figures 1 and 2. Quantitative information about the simulations is obtained by computing the eigenvalues and eigenvectors of the tensor order parameter as a function of time. The three eigenvalues of the order parameter matrix computed for one of the simulations of 24 5CB molecules started from the homeotropic configuration in Figure 1 are shown in Figure 3. The largest eigenvalue decreases from unity to about 0.45, a value more nearly that of

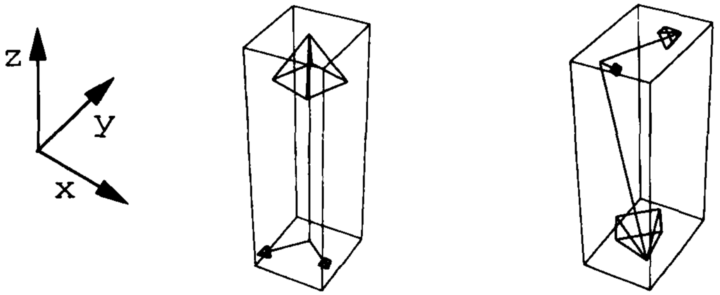

FIGURE 4. The three eigenvectors of the order parameter matrix scaled according to Equation 6 for a simulation starting from the homeotropic configuration. On the left are the eigenvectors near the beginning of the simulation. On the right are the eigenvectors near the end of the simulation. The director remains along the z-axis.

the bulk liquid crystal. The eigenvectors of the order parameter matrix for the simulations starting from the homeotropic state of Figure 1 indicate that the liquid crystal remained in the homeotropic state. Figure 4 shows the eigenvectors of the order parameter matrix at the beginning and end of this simulation. The eigenvectors have been scaled so that the eigenvector corresponding to the largest eigenvalue is longest. In particular the eigenvectors were scaled according to the relation

$$\vec{n}_i \rightarrow (S_i + 0.5)\vec{n}_i \qquad (6)$$

where $\{S_i, \vec{n}_i\}$ are an eigenvalue-eigenvector pair. Furthermore, the eigenvectors have arbitrary sign: if $\vec{n}_i$ is an eigenvector then $-\vec{n}_i$ is a linearly dependent eigenvector. If this inversion symmetry is taken into account, it is clear that the director (the eigenvector corresponding to the largest eigenvalue) has remained essenially constant during the simulation. This tends to indicate that the homeotropic orientation is stable.

However, while it is necessary for simulations starting in a homeotropic state to remain in such a state in order for the conclusion to be drawn that the anchoring for this pair of materials is homeotropic, it is not sufficient grounds for drawing that conclusion. Firstly, in the absence of any influence from the polymer surface we expect the order parameter S to drop from unity to a value closer to the equilibrium value at 300 K. We further expect that the director $\hat{n}$ will remain approximately constant in the absence of any externally applied torque. Thus it could be argued that the result of this simulation is logically consistent with the assertion that the polymer surface had no significant effect. Secondly, it might be unjustified to draw a conclusion from the lack of a rotation of the director in simulations as short as those described here. It is possible that a transition could have occurred if the equations of motion had been integrated for a sufficient amount of time.

In order to eliminate these possible explanations, simulations were also performed from the planar initial configuration shown in Figure 2. The final configuration for such a simulation of 16 5CB molecules is shown in Figure 5. The liquid crystal molecules have coalesced into a bridge between the two polymer surfaces, and have changed orientation. The eigenvalues of the order parameter matrix as a function of time are shown in Figure 6 for a simulation started from the planar configuration of Figure 2. The scalar order parameter falls from an initial value of unity to approximately 0.3, a value more nearly that of the bulk liquid crystal. Figure 7 shows the scaled eigenvectors of the order parameter matrix at the beginning and end of this simulation. The result here confirms that the homeotropic orientation is preferred. The director, initially parallel to the y-axis, has rotated to a nearly homeotropic orientation, nearly parallel to the z-axis.

From this work we conclude that the anchoring of 5CB molecules at an amorphous polyethylene surface at 300 K is predicted to be nearly homeotropic. The conclusion is unhampered by the possibility that integration of the equations of motion for insufficient time resulted in the system being trapped in a metastable state, since simulations were started from both the homeotropic and planar orientations. Both initial configurations led to the same homeotropic final configuration. However, because the sample sizes used were comparatively small, it was not possible to obtain quantitative information about the strength of the anchoring. Another

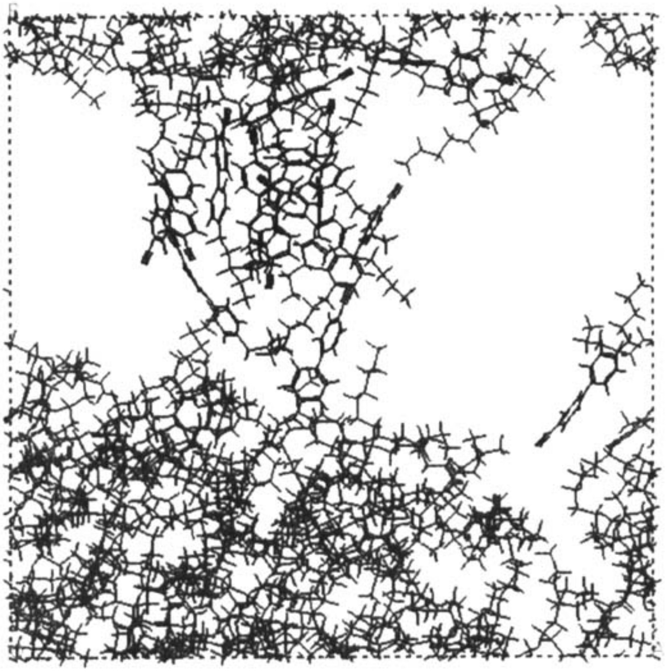

FIGURE 5. Final state of a simulation during which the 5CB molecules have switched from planar to nearly homeotropic orientation. (See Color Plate XX at the back of this issue)

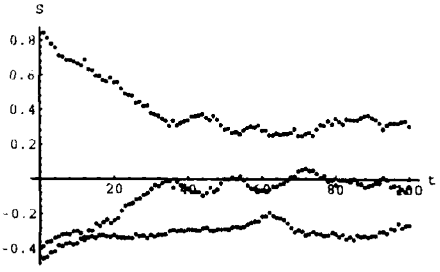

FIGURE 6. The three eigenvalues of the order parameter matrix as a function of time for a simulation starting from the planar configuration. The unit of time is 0.1 ps.

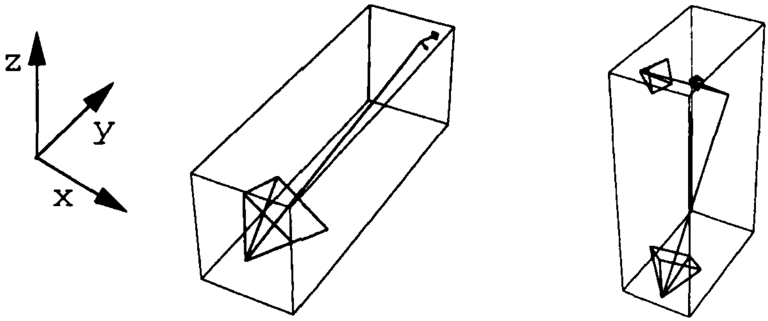

FIGURE 7. The three eigenvectors of the order parameter matrix scaled according to Equation 6 for a simulation starting from the planar configuration. On the left are the eigenvectors near the beginning of the simulation. On the right are the eigenvectors near the end of the simulation. Initially, the director is along the y-axis but by the end of the simulation the director is along the z-axis, indicating a change to the homeotropic orientation.

factor limiting the significance of these results is the fact that they were performed at fixed volume, which resulted in a liquid crystal-vacuum interface area which may have had some influence on the director orientation. For these reasons, it would be desirable to repeat the computations in larger systems and in constant-pressure conditions.

Acknowledgments

This work was supported by the NSF ALCOM Science and Technology Center under Grant DMR89-20147.

References

[1] B. Jerome, *Rep. Prog. Phys.*, **54,** 391 (1991).
[2] C.E. Paraskevaidis, P.L. Taylor, B.M. Mulder and C. Papatriantafillou, *Physica A*, **250,** 517 (1998).
[3] T.J. Sluckin, *Physica A*, **213,** 105 (1995).
[4] A.V. Komolkin, Yu.V. Molchanov and P.P. Yakutseni, *Liquid Crystals*, **6,** 39 (1989).
[5] S.J. Picken, W.F. van Gunsteren, P.Th. van Duijnen and W.H. de Jeu, *Liquid Crystals*, **6,** 357 (1989).
[6] M.R. Wilson and M.P. Allen, *Mol. Cryst. Liq. Cryst.*, **198,** 465 (1991).
[7] M.R. Wilson and M.P. Allen, *Liquid Crystals*, **12,** 157 (1992).
[8] A.V. Komolkin A. Laaksonen and A. Maliniak, *J. Chem. Phys.*, **101,** 4103 (1994).
[9] *Cerius^2 Simulation Tools User's Reference* (Molecular Simulations Incorporated, Cambridge, 1994).
[10] D. He, D.H. Reneker and W.L. Mattice, *Comp. and Theor. Polymer Science*, **7,** 19 (1997).
[11] S. Chandrasekhar, *Liquid Crystals* (Cambridge University Press, Cambridge, 1992).
[12] S.L. Mayo, B.D. Olafson and W.A. Goddard III, *J. Phys. Chem.*, **94,** 8897 (1990).