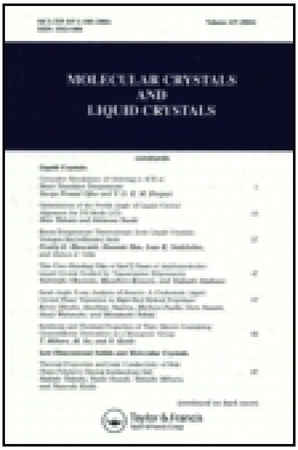

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Simulating Phase Transitions in Binary Liquid Crystal Films

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Liquid crystals (LC) are often subject to external orienting forces, arising either from applied fields or from surface anchoring. The molecular simulation of such systems is an important step towards the prediction of real LC behavior. Recently some progress has been made regarding the simulation of LC models, both in confined spaces (slabs, films) and under the influence of aligning torques. We present Monte Carlo (MC) simulations of Gay-Berne (ellipsoidal) model particles. The present article deals with a binary system of such molecules confined between two walls. Simulations were performed in 3 dimensions. The results are presented as structure visualizations and in the plot of the order parameter.

Keywords: liquid crystal film; Gay-Berne potential; binary equimolar mixture

INTRODUCTION

Continuum theoretical approaches to the study of liquid crystals are limited to macro- and mesoscopic scales – down to several molecular

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lengths. Many phenomena can be explained only on a microscopic level, and a description on the molecular scale is necessary. While the first such investigations concentrated on hard model potentials (ellipsoids, spherocylinders), the soft Gay-Berne (GB) potential [1] has recently become the standard model for simulating anisotropic molecules. It has been studied extensively by Luckhurst et al. [2,3] and de Miguel et al. [4,5].

Recently, progress is being made in the way of applications. LC films based on the Gay-Berne model and related problems are often studied. Stelzer observed a surface-induced smectic A phase [6] and a smectic C phase near a rough surface [7]. Wall employed a non-separable anisotropic molecule-substrate interaction potential in his simulations of confined LC films [8]. On the other hand, Mills reported about an unconfined LC film in equilibrium with its own saturated vapor [9]. Gruhn and Schoen have done extensive investigations of confined films and related problems (substrate-induced order, solvation forces, different anchoring angles etc.) [10]. In his recent work Miyazaki studied the formation of LC order near different types of wall [11].

In their application LC are often used as confined mixtures between two parallel plates at short distances. Therefore, in addition to one-component systems, mixtures of two components have been studied in simulations on the molecular level. Bemrose investigated bi-disperse LC mixtures with lengths (i.e. length-to-width ratios) 3.5 and 3.0 [13]. He used for the interaction between two particles of different lengths a generalised Gay-Berne potential [13]. We have done MC and molecular dynamics simulations of bulk mixtures of particles with lengths 3 and 1.5 [14,15,16] at different concentrations of shorter particles: 25%, 50% and 75%. We found that in most cases the longer particles undergo a transition from isotropic into smectic phase when the system is compressed or cooled. Between the layers of the longer particles are the shorter particles, but even at high density and low temperature they remain in the isotropic phase.

POTENTIAL AND METHOD

We used the Gay-Berne potential [1] for simulating the interaction between two liquid crystal molecules:

$$U(\hat{\vec{u}}_1, \hat{\vec{u}}_2, \hat{\vec{r}}) = 4\varepsilon(\hat{\vec{u}}_1, \hat{\vec{u}}_2, \hat{\vec{r}}) \left[\left\{ \frac{\sigma_0}{r - \sigma(\hat{\vec{u}}_1, \hat{\vec{u}}_2, \hat{\vec{r}}) + \sigma_0} \right\}^{12} - \left\{ \frac{\sigma_0}{r - \sigma(\hat{\vec{u}}_1, \hat{\vec{u}}_2, \hat{\vec{r}}) + \sigma_0} \right\}^{6} \right].$$

We applied the standard GB parametrisation: $\mu = 2$, $\nu = 1$, $\varepsilon_e/\varepsilon_s = 1/5$, $\sigma_e/\sigma_s = 3$, as in our previous studies of the mixtures [14,15]. In modeling a mixture of molecules of lengths of 3 and 1.5, we used the Lorentz-Berthelot rules and modified the elongation of the second (shorter) particles: σ_e/σ_s =1.5. In the literature various methods have been suggested to simulate LC films. We represented the influence of the walls by introducing imaged particles at bottom and top in z-direction, oriented in x-direction as used by Miyazaki [11]. These image particles interact via a GB potential with the molecules in the bulk.

We performed NVT Monte Carlo simulation with N=512 molecules in a cubic box using periodic boundary conditions and the nearest image convention in the x and y directions. Our mixture was equimolar (256 molecules each of lengths 3.0 and 1.5, respectively). We take a system from our previous simulations at reduced temperature T=1.25 and reduced density ρ=0.41, which was well mixed and in the isotropic phase. We then placed both walls (imaged particles) at a large distance (2.5 σ) above and below the original box boundaries and gradually lowered that distance. This system was then very well thermalized before production runs.

Starting from this thermodynamic state, the isochore ρ=0.41 was explored for $0.3 < T < 1.25$ (ΔT=0.0001 with 500 intervening MC steps), and the isotherm T=1.25 for $0.34 < \rho < 0.47$ ($\Delta\rho = 0.0001$, again with 500 intervening MC steps). To check for metastable states, longer thermalization periods were inserted when going along the isotherm (at densities 0.34, 0.35 etc.); only statistical fluctuations were observed.

The order parameter P_2 was calculated from the Q tensor as the largest eigenvalue and the director $\vec{n}$ as the corresponding eigenvector. We calculated P_2 for the longer (reference) particles $P_2(1)$ and for the shorter particles $P_2(2)$.

RESULTS

At cooling the system at the density ρ=0.41, the reference molecules tend to build layers with shorter molecules between the smectic layers (see Figure 1), as we observed in our bulk simulations [14,15]. The influence of the top and bottom walls upon the liquid structure is negligible.

For instance, at T=0.40 the director assumes an orientation of 60^o with respect to the wall normal. This is probably not due to any influence of the walls, but rather a compromise with respect to the packing of complete layers within the periodic (x,y) boundaries. The order parameter for the reference particles $P_2(1)$, averaged over the total system volume, increases upon cooling from $\approx$ 0.3 to 0.9, with two steeper regions around T=0.9 and T=0.65 (see Figure 2). $P_2(2)$ showed no significant value, indicating an isotropic state for the shorter particles, although they are in layers.

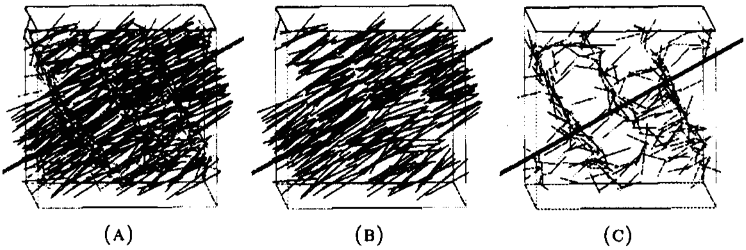
(A) (B) (C)

FIGURE 1: **Snapshot showing A) all particles, B) reference** particles, and C) shorter particles at $T = 0.40$, $\rho = 0.41$.

The influence of the walls is pronounced at higher densities, as is evident from the snapshot at ρ=0.47 (see Figure 3). We separated the particles in five layers of same thickness along the z axis (see Figure 4). Adjacent to the walls a layer is formed that contains mainly longer molecules (69 particles in the top layer, 70 particles in the bottom layer) and only 2 shorter molecules in each layer. The

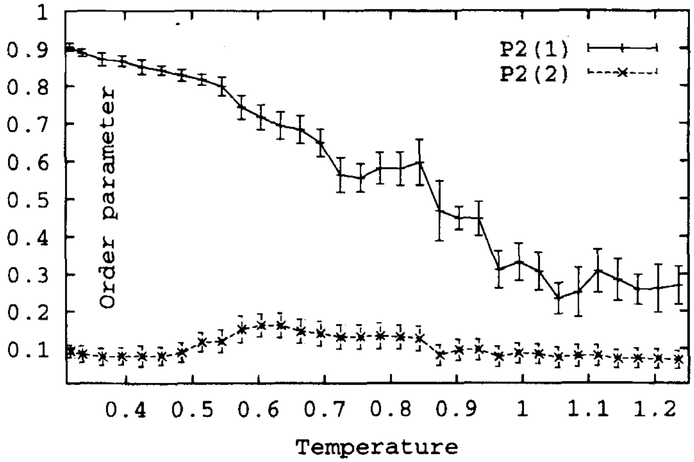

FIGURE 2: Order parameter for reference particles $P_2(1)$ and for shorter particles $P_2(2)$ as function of temperature T at density $\rho = 0.41$.

particles are tilted at an anchoring angle of nearly $\pi/4$. Surprisingly, the "wall particles" at top and bottom are oriented differently. The "inner particles" (reference and shorter), i.e. the three layers in the middle situated far from the walls, are weakly correlated. Their director is oriented almost parallel to the wall. In every "inner layer" we have approx. 70% shorter particles.

Along the compression up to density 0.43 the order parameter for the reference particle rises (see Figure 5). But even at high density $P_2(1)$ is under 0.4. A different orientation on top and bottom causes a low order parameter throughout the system for both particle species. This is evident from a plot of the local order parameter along the z direction for the 5 layers. We have a high order at both walls with $P_2(1) \geq 0.95$ and low in the 'inner' layers $P_2(1) \leq 0.45$ (see Figure 6). The origin of this structure will be investigated in further studies [17].

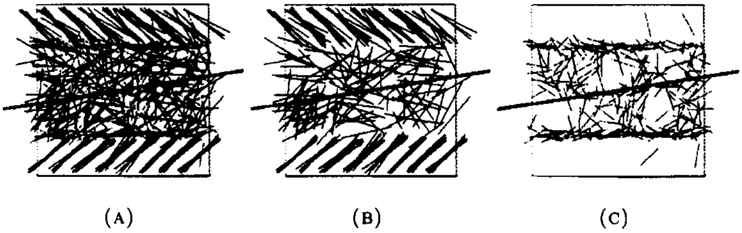

FIGURE 3: Snapshot showing A) all particles, B) reference particles, and C) shorter particles at $T = 1.25$, $\rho = 0.47$.

FIGURE 4: Snapshot showing the particles in five layers along z axis at T = 1.25, $\rho = 0.47$.

CONCLUSIONS

At lower density we find a 'sandwich' structure. The influence of the walls upon the liquid structure is negligible. Upon cooling the reference particles build up layers with the shorter molecules between the smectic layers. At higher density the longer molecules tend to anchoring at both walls. A structure composed of anchored, orientationally correlated reference particles and a more or less isotropic central region is observed.

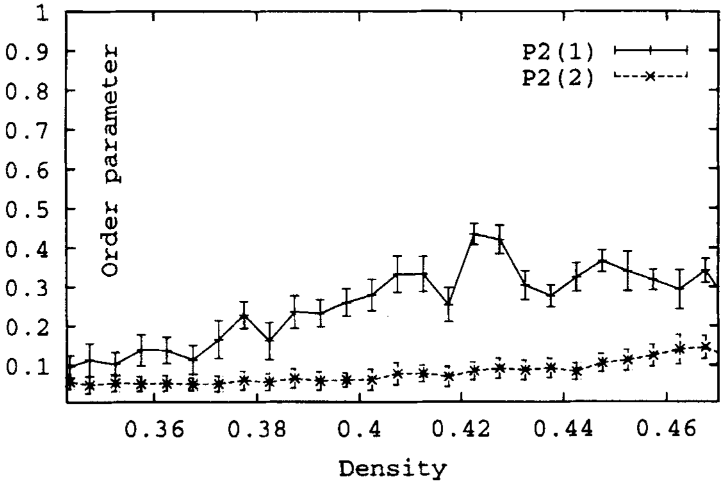

FIGURE 5: Order parameter for reference particles $P_2(1)$ and for shorter particles $P_2(2)$ as function of density ρ at $T = 1.25$.

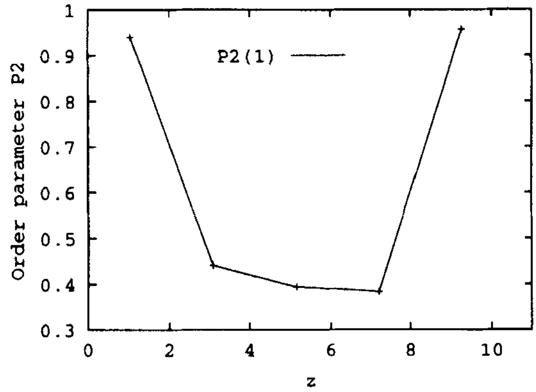

FIGURE 6: Order parameter for reference particles $P_2(1)$ for five layers along z axis at $T = 1.25$, $\rho = 0.47$.

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