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A molecular dynamics simulation study of the nematic–isotropic interface of a Gay–Berne liquid crystal

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Abstract

We present a computer simulation study of the nematic–isotropic interface for a system of elongated molecules interacting via the Gay–Berne intermolecular potential. The simulations suggest that the orientational ordering at the interface is planar rather than homeotropic or tilted. © 1997 Elsevier Science B.V.

1. Introduction

As a nematic liquid crystal is heated to form an isotropic liquid, it undergoes a weak first order transition at which the two phases coexist. In a suitably prepared system, a flat interface can exist between the two phases [1]. The nematic director, which can align in an arbitrary direction in the absence of a field, will tend to adopt an orientation with a certain tilt angle with respect to the surface normal. For some liquid crystals (e.g. MBBA [2]) planar anchoring, or a tilt angle near $\pi/2$, has been observed at the nematic–isotropic (NI) interface whilst for others (e.g. the *n*CB series [3,4]) tilt angles closer to $\pi/3$ or $\pi/4$ are more common.

An understanding of the interfacial alignment in this seemingly simple inhomogeneous system presents some fundamental questions about which molecular features, if any, are necessary to produce a certain type of anchoring. From the theoretical point of view, both Landau–de Gennes [5–7] and molecular treatments of the NI interface, based on models with purely steric [8–10] and attractive–repulsive interactions [11–13], have been proposed. However, these theoretical approaches lead to rather different predictions, most probably because of the approximations involved. For example, whilst a $\pi/3$ tilt was predicted for long hard rods by Hołyst and Poniewierski [8], planar anchoring has also been predicted for the same steric model by Moore and McMullen [9] and confirmed using a numerical solution of the Onsager variational approach by Chen and Noolandi [10].

At the molecular level it is clear that a major feature of the interface is to constrain the intermolecular vector $\boldsymbol{r}_{ij}$ of the molecules belonging to the surface. For this constraint to be effective, an essential feature should be that the intermolecular potential is not separable into a distance dependent part and an angular dependent part but rather that the full dependence of the potential is retained, hence excluding the use of simple Lebwohl–Lasher [14] and Luckhurst–Romano [11,15] type models. A systematic approach is that of expanding the intermolecular

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potential in rotational invariants [13,16–18]; here, either planar or homeotropic alignment can be expected according to the sign of the term that couples orientational and positional variables [13] and that tilted alignment can be obtained by a more general combination of terms [17]. The addition of certain contributions of dipolar or quadrupolar symmetry have been shown to modify the interfacial anchoring (see, for example Ref. [19] and the references therein) and the existence of such multipolar interactions is thought to be essential to obtain tilted anchoring at the interface [20]. However, in our view a problem with the systematic approach is the large number of terms involved and the variety of combinations of these terms that could presumably lead to a certain anchoring. From this point of view, computer simulation studies of simple anisotropic potentials can provide reference data for testing the approximations in the various theoretical approaches.

As far as we are aware, there have been no computer simulation studies to investigate the behaviour at the NI interface; this absence is rather surprising, especially when considering the number of bulk phase simulations of liquid crystals. In this area, a particularly simple but successful model is the anisotropic potential proposed by Gay and Berne (GB) [21], which has been shown to exhibit isotropic, nematic, smectic A and smectic B phases [22–24]. The interaction between a pair of uniaxial molecules i and j is defined as

$$U(\hat{\boldsymbol{u}}_i,\hat{\boldsymbol{u}}_j,\boldsymbol{r}_{ij}) = 4\epsilon(\hat{\boldsymbol{u}}_i,\hat{\boldsymbol{u}}_j,\hat{\boldsymbol{r}}_{ij})\left[\left(\frac{\sigma_s}{r_{ij}-\sigma(\hat{\boldsymbol{u}}_i,\hat{\boldsymbol{u}}_j,\hat{\boldsymbol{r}}_{ij})+\sigma_s}\right)^{12} - \left(\frac{\sigma_s}{r_{ij}-\sigma(\hat{\boldsymbol{u}}_i,\hat{\boldsymbol{u}}_j,\hat{\boldsymbol{r}}_{ij})+\sigma_s}\right)^{6}\right], \qquad (1)$$

where $\hat{\boldsymbol{u}}_i$ and $\hat{\boldsymbol{u}}_j$ are unit vectors representing the orientations of the molecules. The functions $\epsilon(\hat{\boldsymbol{u}}_i,\hat{\boldsymbol{u}}_j,\hat{\boldsymbol{r}}_{ij})$ and $\sigma(\hat{\boldsymbol{u}}_i,\hat{\boldsymbol{u}}_j,\hat{\boldsymbol{r}}_{ij})$ represent the strength of the interaction and the contact separation, as defined in Ref. [24]. The simplicity of these interactions, in comparison to an atomistic detail model, allows systems with large numbers of molecules to be studied, which is essential if we are to investigate the NI interface. The nematic–vapour (NV) interface for the GB model has been investigated both theoretically [20] and by computer simulation [25,26].

The lack of simulation studies of the NI interface is probably due to the difficulty of both generating and maintaining an interface in the relatively small size systems presently accessible. Here we introduce a simple method to partially overcome this problem, based on the preparation of a suitable temperature inhomogeneity in the system. This is somewhat similar to the method used experimentally to prepare interfaces in which the opposite edges of a sample are connected to ovens at different temperatures and the system calibrated so that the interface occurs in the observable area [1]. In our simulation the interface is prepared and maintained by thermostating two regions at slightly different temperatures either side of the NI transition. Further details of the simulation experiment are described in Section 2 and our observations of the anchoring at the interface are discussed in Section 3. Our conclusions are presented in Section 4.

2. The model interface and computational details

To study the interface between the nematic and isotropic phases, we introduce a method in which the two halves of the sample are maintained at two slightly different temperatures either side of the NI transition. Thus a nematic phase is simulated at T_N in one half of the box and an isotropic phase is simulated at T_I in the other half of the box; here, T_N and T_I are temperatures just below and just above the transition temperature, respectively. We assume that the interface is flat and normal to the z axis and arbitrarily thermostat the regions $-\frac{1}{2}l_z < z < 0$ and $0 < z < \frac{1}{2}l_z$ at temperatures T_I and T_N, respectively, where l_z is the z dimension of the simulation box. The geometry of the system is shown schematically in Fig. 1. We apply full periodic boundary conditions to the system; thus two interfaces, infinite in the xy plane and separated by a distance of $\frac{1}{2}l_z$, are studied. We note that whilst the molecules are free to cross the interfaces, the thermostats ensure that the positions of the two interfaces do not move during the simulations.

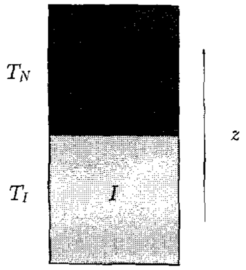

Fig. 1. Schematic illustration of the inhomogeneous system used to study the NI interface. The upper half of the box is thermostated at a temperature T_N, just below T_{NI}, and the lower half of the box at a temperature T_I, just above T_{NI}. The temperature inhomogeneity stabilises a flat interface perpendicular to the z axis.

We have studied the NI interface for a system of molecules interacting via the Gay–Berne potential with length to breadth ratio $\kappa = 3$, well depth anisotropy ratio $\kappa' = 5$ and energy exponents $\mu = 1$ and $\nu = 3$ [24] using molecular dynamics simulations. The temperature of each region was independently maintained to be constant by rescaling the velocities of the appropriate molecules at each timestep [27]. The equations of motion were integrated using the leapfrog Verlet scheme [28] with a time step $\delta t^* = 0.002$, the moment of inertia perpendicular to the molecular long axis was taken to be $I_\perp^* = 1.0$ and a spherical cutoff of $r_c^* = 4.5$ was applied to the potential. The GB parameters σ_s and ϵ_0, as defined in Ref. [24], are used to scale all quantities, which are denoted by the starred variables.

The nematic–isotropic transition temperature for this model at a density ρ^* of 0.3 has previously been determined using canonical Monte Carlo simulations for a system of 1000 molecules as $T_{NI}^* = 3.57$ [24]. To test our two temperature method, preliminary simulations were performed starting from an isotropic configuration at the same density using 6480 molecules in a box of dimensions 30 × 30 × 24 with the nematic temperature set at T_N^* of 3.40, 3.45 and 3.50; the isotropic temperature T_I^* of 3.60 was used in each case. The low temperature region was observed to order in the simulations at T_N^* of 3.40 and 3.45 after approximately 150000 time steps, but not at T_N^* of 3.50, even after a long equilibration run of 400000 time steps. Thus it appears that the transition temperature is slightly lower than that determined in Ref. [24] for the smaller sample. This difference in the transition temperatures occurs because of finite size effects in conjunction with the periodic boundary conditions.

As the preliminary simulations indicated that the two temperature method could be used to study the NI interface, our main simulation was performed using this method with a system of 12960 molecules in a box of dimensions 30 × 30 × 48 at $T_N^* = 3.45$ and $T_I^* = 3.60$. An isotropic configuration equilibrated at $T^* = 3.60$ was used as a starting point for the simulation so as not to bias in any way the direction of the nematic director at the interface. The simulation was run in the normal way, but with the two temperature scaling turned on. An equilibration run of 450000 time steps was found to be necessary for the low temperature region to become orientationally ordered and the nematic director to align and remain constant in its preferred orientation. This equilibration period was followed by a production run of 100000 time steps, during which configurations were dumped every 200 time steps for later analysis of the interfacial properties.

3. Simulation results

To analyse the behaviour in the interfacial region, we have calculated the density profile, $\rho(z^*)$ and two second rank orientational order parameter profiles, $\eta(z^*)$ and $\sigma(z^*)$, defined by the averages

$$\eta(z^*) = \langle P_2(\hat{\boldsymbol{u}}_i \cdot \hat{\boldsymbol{n}}_z) \rangle_{(z^*)}, \tag{2}$$

and

$$\sigma(z^*) = \langle P_2(\hat{\boldsymbol{u}}_i \cdot \hat{\boldsymbol{z}}) \rangle_{(z^*)}, \tag{3}$$

where $\hat{\boldsymbol{n}}_z$ is the local director calculated from the Q-tensor for each histogram bin [26] and $\hat{\boldsymbol{z}}$ is a unit vector along the z axis. These profiles are shown in Figs. 2 and 3, respectively. The density profile is consistent with the form expected for an interface between two liquids. We note that the width of the interface is comparable in magnitude to $\frac{1}{2}l_z$ and so the region of bulk nematic and isotropic phases is small. However, we do not believe that the close proximity of the two interfaces significantly affects

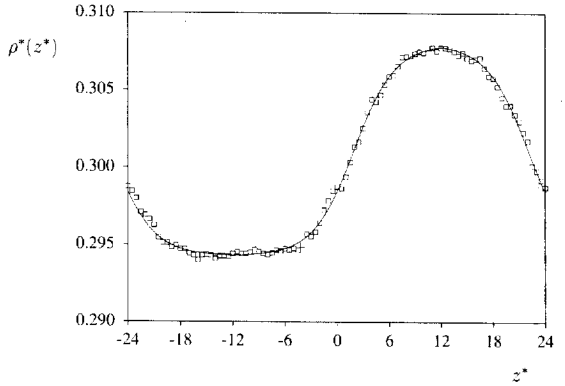

Fig. 2. The density profile (□) $\rho^*(z^*)$ calculated from the molecular dynamics simulation and (—) the corresponding fit to a hyperbolic tangent function (Eq. (4)).

the orientational ordering at the NI interface for this model. We observe that the order parameter $\eta(z^*)$ is essentially zero in the middle of the isotropic region and positive in the nematic ($\eta_N = 0.66$), as we expect for these phases. We also observe that $\sigma(z^*)$ is zero in the isotropic region but negative in the nematic ($\sigma_N = -0.33$). This negative value of $\sigma_N = -\frac{1}{2}\eta_N$ implies that the molecules tend to align, on average, perpendicular to the z direction in the nematic region. Indeed, we observe that $\sigma(z^*) = -\frac{1}{2}\eta(z^*)$ not just in the nematic region but also as the interface is crossed into the disordered isotropic region. We conclude that the molecules tend to align parallel to the interface and, therefore, that this system exhibits planar anchoring. This planar alignment can be confirmed by calculating the director profile $\hat{n}(z^*)$; we find that $\hat{n}(z^*)$ is perpendicular to the z axis throughout the nematic and interfacial regions and that the orientation of the director does not vary in the xy plane. The planar alignment can also be clearly observed in a snapshot taken from the simulation. A typical configuration is shown in Fig. 4, colour coded such that the molecules which align parallel to the director are shaded darker.

Having determined that this model liquid crystal exhibits planar anchoring, we now turn to some physical properties of the NI interface. We have calculated the interfacial width by fitting the hyperbolic tangent

$$\rho^*(z^*) = \tfrac{1}{2}(\rho_N^* + \rho_I^*) + \tfrac{1}{2}(\rho_N^* - \rho_I^*)\tanh\left(\frac{z^* - Z^*}{2\delta^*}\right) \qquad (4)$$

to the simulation density profile, which has been

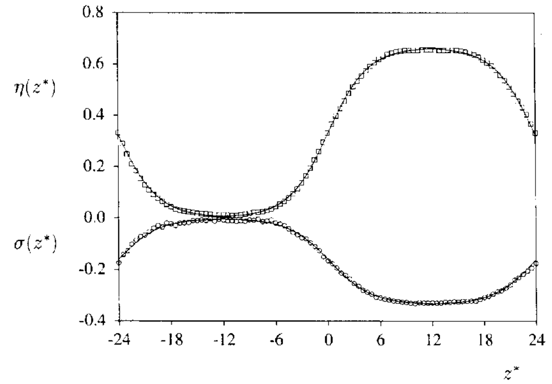

Fig. 3. The second rank orientational order parameter profiles (□) $\eta(z^*)$ and (○) $\sigma(z^*)$ calculated from the molecular dynamics simulation and (—) the corresponding fits to a hyperbolic tangent function.

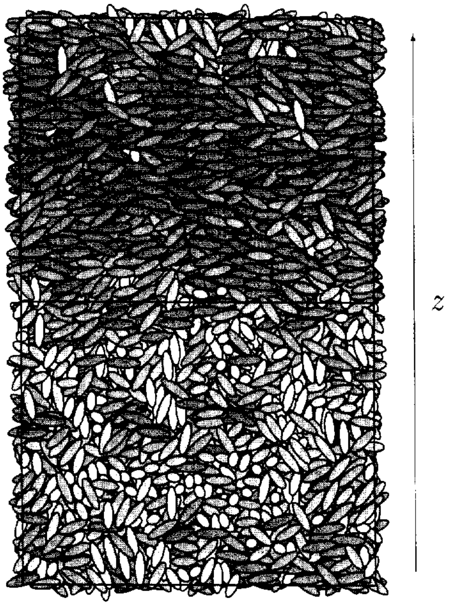

Fig. 4. Snapshot of a configuration from the simulation of the nematic–isotropic interface. The molecules are represented by ellipsoids and are shaded to indicate their orientation with respect to the nematic director.

shown to give a good description of the interfacial density profile at the NV interface [25,26]. The adjustable parameters ρ_N^* and ρ_I^* are the bulk densities of the coexisting nematic and isotropic phases, Z^* is the position of the Gibbs dividing surface and δ^* is the interfacial thickness. The thickness δ^* is related to the 10–90 width Δ^*, calculated by Chen and Noolandi [10], by $\Delta^* = 4.394\delta^*$. We find that a least squares fit of Eq. (4) to the simulation data gives $\delta^* = 2.37$ or $\Delta^* = 3.46L$, where L is the length of the molecule. This value is rather large in comparison to that of approximately $1.5L$ found for the NI interface of long hard rods within the Onsager approach [10]. However, this is expected because the transition between the two phases is weaker for the GB system than for the hard rod system. Thus the change in density across the interface is 4.5% for the GB model but 25% for long hard rods; similarly the values of η_N in the coexisting nematic phase are 0.66 and 0.80, respectively. Indeed, we note that experimental values of the interfacial thickness for the nCB series are even larger, of the order of 400–700Å [3].

We have also fitted a hyperbolic tangent similar to Eq. (4) to the orientational order parameter profiles. We find that the interfacial widths are essentially equal to those calculated for the density profile. However, we find that the positions of the Gibbs dividing surface for $\eta(z^*)$ and $\sigma(z^*)$ are offset from that of $\rho(z^*)$ by a value of $0.6L$; this is similar to the value of $0.5L$ found for long hard rods [10]. This shift of the order parameter profiles towards the isotropic phase can be justified by considering that it takes approximately half a molecular length for the orientational correlation function $\langle P_2(\hat{u}_i \cdot \hat{u}_j) \rangle$ to decay to zero in the orientationally disordered isotropic phase [22].

4. Conclusions

We have performed a computer simulation study of the nematic–isotropic interface for a system of elongated molecules with both translational and rotational freedom. We find that the molecules tend to align, on average, perpendicular to the layer normal. We therefore observe that the orientational anchoring at the interface is planar rather than homeotropic or tilted. The simulation provides novel information for a well defined and relatively simple Gay–Berne system that should prove to be a useful test bed for the various theoretical approaches. We expect that the two temperature method developed here will be a useful tool for studying coexisting phases in a variety of situations.

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