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COMPUTER SIMULATION OF BI-DISPERSE LIQUID CRYSTALS: THE EFFECT OF CONCENTRATION ON PHASE BEHAVIOUR AND STRUCTURAL PROPERTIES

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Abstract We present results from constant-NPT molecular dynamics simulations of bi-disperse liquid crystal mixtures at a range of concentrations. These simulations are performed using the generalised Gay-Berne interaction potential. We observe that the transition temperature between ordered and disordered phases varies linearly with mole fraction. Also, the layer spacing in the smectic-B phase varies approximately linearly with mole fraction. We find that the region of nematic phase stability is very narrow in the NPT ensemble, but establish it for a single-component system. The difficulty in determining this region is related to the sensitivity of the nematic phase to density fluctuations.

INTRODUCTION

Liquid crystal mixtures play an important role in the development of device specifications unattainable using single component systems. For example, an extended nematic phase can be obtained by varying the mole fraction of non-dipolar mesogens. Furthermore, mixtures of highly dipolar mesogens reveal rich phase diagrams containing features such as re-entrant nematics and nematic-nematic transitions.[1]

Whilst simulations of liquid crystal mixtures of hard parallel aligned spherocylinders and hard parallel aligned cylinders[2] have produced qualitative agreement with the theoretical predictions of Lekkerkerker and co-workers[3], they impose some unrealistic constraints. Until recently, simulations with attractive potentials and allowing full freedom of rotation have been limited to mixtures of Gay-Berne (GB) particle and Lennard-Jones sites[4,5], and lattice models.[6] More recently, Lukač and Vesely have reported a brief investigation of a two-component mixture of GB particles[7] based on Lorentz-Berthelot mixing rules. We note, however, that the symmetries of the potential used in Ref. 7 fail to differentiate between all of the T-configurations available to this system. A recent paper by the current authors reports results for a mixture of GB rods obtained using an interaction potential which does differentiate between these configurations.[8] In this latter work, a generalised Gay-Berne potential[9] was used to simulate a binary mixture of rod-like mesogens with axial ratios, l/d, of 3.5 to 1 (molecules A) and 3 to 1 (molecules B).

In this current paper, we present preliminary results from several molecular dynamics (MD) simulations of liquid crystal mixtures at a range of relative concentrations. These are performed using the generalised Gay-Berne potential within the isothermal-isobaric, constant-NPT, ensemble.

MODEL AND SIMULATION DETAILS

When considering a binary system consisting of two molecular species, A and B, with different anisotropic energy and/or shape terms, it is important to use an interaction potential with the correct symmetries. Specifically, the intermolecular potential must be able to distinguish between the four possible interaction types (AA, AB, BA and BB) for non-parallel molecules. Cleaver *et al*[9] have developed such a potential for the interaction between two non-identical, anisotropic particles: the generalised Gay-Berne (GGB) intermolecular potential is expressed in the standard Gay-Berne form

$$\begin{aligned} U(\hat{\mathbf{u}}_A, \hat{\mathbf{u}}_B, \hat{\mathbf{r}}_{AB}) &= 4\epsilon(\hat{\mathbf{u}}_A, \hat{\mathbf{u}}_B, \hat{\mathbf{r}}_{AB}) \left[\left(\frac{\sigma_0}{r_{AB} - \sigma(\hat{\mathbf{u}}_A, \hat{\mathbf{u}}_B, \hat{\mathbf{r}}_{AB}) + \sigma_0} \right)^{12} \right. \\ &\quad \left. - \left(\frac{\sigma_0}{r_{AB} - \sigma(\hat{\mathbf{u}}_A, \hat{\mathbf{u}}_B, \hat{\mathbf{r}}_{AB}) + \sigma_0} \right)^{6} \right] \end{aligned} \tag{1}$$

but with modified anisotropic range parameter, $\sigma(\hat{\mathbf{u}}_A, \hat{\mathbf{u}}_B, \hat{\mathbf{r}}_{AB})$, and well depth parameter, $\epsilon(\hat{\mathbf{u}}_A, \hat{\mathbf{u}}_B, \hat{\mathbf{r}}_{AB})$.

The modified range parameter is of the form

$$\begin{aligned} \sigma(\hat{\mathbf{u}}_A, \hat{\mathbf{u}}_B, \hat{\mathbf{r}}_{AB}) &= \sigma_0 \left[1 - \frac{1}{2}\chi \left\{ \frac{(\alpha\hat{\mathbf{r}}_{AB} \cdot \hat{\mathbf{u}}_A + \alpha^{-1}\hat{\mathbf{r}}_{AB} \cdot \hat{\mathbf{u}}_B)^2}{1 + \chi(\hat{\mathbf{u}}_A \cdot \hat{\mathbf{u}}_B)} \right. \right. \\ &\quad \left. \left. + \frac{(\alpha\hat{\mathbf{r}}_{AB} \cdot \hat{\mathbf{u}}_A - \alpha^{-1}\hat{\mathbf{r}}_{AB} \cdot \hat{\mathbf{u}}_B)^2}{1 - \chi(\hat{\mathbf{u}}_A \cdot \hat{\mathbf{u}}_B)} \right\} \right]^{-1/2} \end{aligned} \tag{2}$$

where the new scalar quantity, α, is defined in terms of the lengths, l, and breadths, d, of the two interacting molecular species A and B. The anisotropic energy term takes a similar form but with the inclusion of a new parameter, α'. Refer to Ref. 9 for a full explanation of the GGB potential. In addition, the parameterisation route used for this potential can be found in Bemrose *et al*[8].

In our previous paper[8] we presented results for a 50:50 mixture of 3.5:1 and 3:1 molecules within the microconical, constant-NVE, ensemble. In this current work we consider the effect of varying concentration on the phase behaviour of a liquid crystal mixture. To achieve this, it is necessary to undertake simulations within the isothermal-isobaric, constant-NPT, ensemble; this enables direct comparison of simulations performed at different concentrations. Constant volume simulations are inappropriate for this purpose, since the effective volume of a GB particle is ambiguous, leading to difficulties in defining a meaningful density for a GB mixture.

We follow the method of Anderson[10], and construct the NPT ensemble from a combination of isobaric and isothermal constraints. To take account of the anisotropic shapes of the molecules, temperature is conserved by constraining the angular velocities according to the method of Fincham *et al.*[11]

We report here molecular dynamics (MD) constant-NPT results from simulations of binary systems containing $N = 500$ GGB rod-like molecules with length to breadth ratios of 3.5:1 (molecules A) and 3:1 (molecules B) for molecule A mole fractions, $\chi_A = 0\%, 12.5\%, 25\%, \ldots, 100\%$. For both species, the mass, m, was set to unity, and the reduced moment of inertia, $I^* = I/\sigma_0^2 = 4.0$, whilst the Gay-Berne energy exponents were $\mu = 1$ and $\nu = 2$. The remaining parameters are given in Table I. Those marked **FIT** were obtained via the parameterisation described elsewhere[9] and have values : $\alpha' = 1.011$, $\chi' = 0.6662$, $\epsilon_0^{A\text{-}A}/\epsilon_0^{B\text{-}B} = 1.103$.

TABLE I Generalised Gay-Berne parameter values used for this investigation. Parameters marked **FIT** were obtained via a parameterisation.[9]

	$A-A$	$B-B$	$A-B$	$B-A$
	3.5:1	3.0:1	mixed	
$\sigma_0 = \sqrt{2}d$	1.0	1.0	1.0	1.0
χ	0.849	0.800	0.824	0.824
χ'	0.666^r	0.666^r	**FIT**	$\chi'^{A\text{-}B}$
ϵ_0	**FIT**	1.0	$\sqrt{\epsilon_0^{A\text{-}A}\epsilon_0^{B\text{-}B}}$	$\epsilon_0^{A\text{-}B}$
α'	1.0	1.0	**FIT**	$1/\alpha'^{A\text{-}B}$

The potential cut-off was $r_c^* = r_c/\sigma_0 = 4.5$ and a neighbourhood list, of radius $r_{nlist}^* = 5.1$, was used to save computational time. The integration time-step was $\delta t^* = (\epsilon_0^{B\text{-}B}/\sigma_0^2)^{1/2}t = 0.003$. The external mass of the piston[10], $M = 0.0019$. For each state point in the isotropic states, the system underwent equilibration and production periods of 40,000 and 50,000 time-steps. Unless otherwise stated, near transitions to higher ordered states these periods were extended to 80,000 and 100,000 respectively. An average reduced pressure of $\langle P^* \rangle = P\sigma_0^3/\epsilon_0^{B\text{-}B} = 3.0$ was used for all simulations in order to promote liquid crystalline phases.

RESULTS AND DISCUSSION

The series of simulations performed at each concentration commenced from an f.c.c lattice at a reduced density of $\langle\rho^*\rangle = 0.17$ and a reduced temperature of $T^* = 3.0$. The nematic order parameter, $\langle P_2\rangle$, was observed to decrease to a limiting value of $\langle P_2\rangle \simeq 0.1$ at each concentration. Extended equilibrium periods, typically of 100,000 time-steps, were required to allow each system to attain a stable density under the influence of constant-NPT. During this period, the nematic order parameter remained constant at each concentration. Furthermore, no significant density waves were observed in pair distribution functions resolved in all directions, $g(r^*)$ and parallel to the director, $g_{\|}(r^*)$ thereby establishing isotropic phases for each concentration. Upon cooling each state point by $\Delta T^* = 0.1$ with respect to the previous reduced temperature, all concentrations remained in the isotropic phase, the density of each being observed to increase linearly with decreasing temperature.

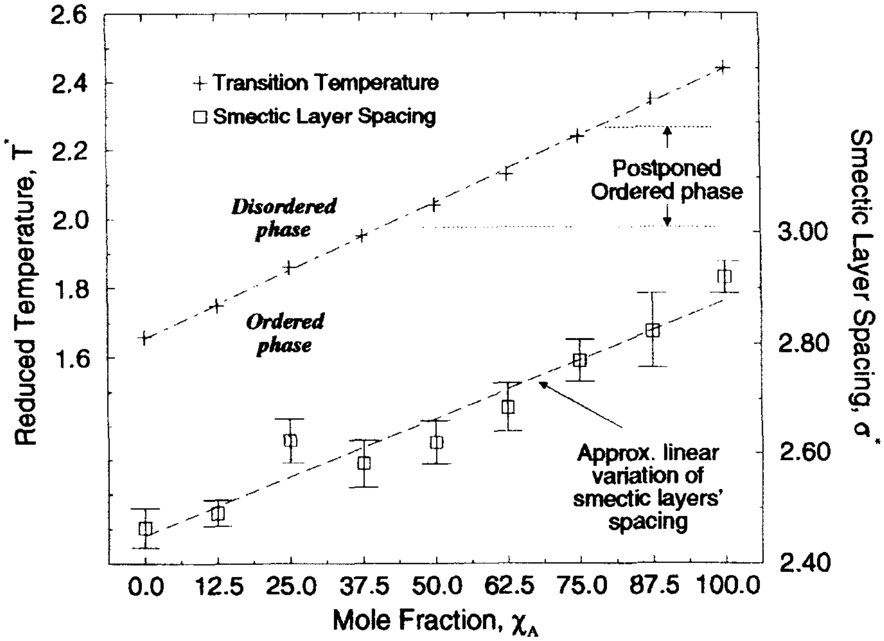

FIGURE I Effect of mole fraction, χ_A, on the order-disorder transition temperature and the smectic layer spacing resolved parallel to the director.

Near transitions from disordered to ordered phases, reductions in temperature were reduced to $\Delta T^* = 0.02$ and run times were increased due to observation of sizable precursor fluctuations in $\langle P_2\rangle$ and $\langle\rho^*\rangle$. At concentration-dependent temperatures, the order parameter and density of each the systems spontaneously increased with the onset of an orientationally ordered phase, typically with $\langle P_2 \rangle \simeq 0.85$. From three-dimensional visualisation, and analysis of $g_{\parallel}(r^*)$ and $g_{\perp}(r^*)$, these ordered phases were identified as smectic-B. Preliminary results (see Figure I) indicate an approximately linear variation of these transition temperatures with change in χ_A. We also note an approximately linear variation of the smectic layers thickness, which arises from competition between the two molecular species of differing lengths. This linearity implies that there is no evidence of demixing.

We note, from Figure I, a non-linear behaviour in the smectic layer thickness over the region $12.5\% \leq \chi_A \leq 37.5$ where we postulate the existence of an extended nematic region. The search for this region is the subject of current work. To this end, we have determined that a single-component system of 3:1 molecules exhibits a nematic phase over a narrow reduced density range $0.300 \leq \langle \rho^* \rangle \leq 0.302$ and reduced temperature range $1.67 \leq T^* \leq 1.68$ (see Table II). We believe that these results represent the first observation of the nematic phase within the constant-NPT ensemble. Verification of the nematic stability at $T^* = 1.68$ and $T^* = 1.67$ has been achieved by extended production periods of 720,000 time-steps. The lower of these temperatures was determined to be the more stable, having a gaussian distribution of $\langle P_2 \rangle$ and $\langle \rho^* \rangle$ albeit with fluctuations in $\langle P_2 \rangle$ which are considerably greater than those within the microconical, constant-NVE, ensemble.

TABLE II Molecular dynamics constant-NPT simulations results from a single-component system of $N = 500$ GGB molecules of axial ratio 3:1 (molecules B). A nematic phase is found to exist over a narrow reduced density range $0.300 \leq \langle \rho^* \rangle \leq 0.302$ and reduced temperature range $1.67 \leq T^* \leq 1.68$.

T^*	$\langle P_2 \rangle$	$\langle \rho^* \rangle$	$\langle PE^* \rangle$	Phase
2.30	0.07 ± 0.03	0.281 ± 0.002	-3.63 ± 0.07	*I*
2.20	0.08 ± 0.03	0.283 ± 0.002	-3.68 ± 0.08	*I*
2.10	0.08 ± 0.03	0.285 ± 0.002	-3.72 ± 0.07	*I*
2.00	0.09 ± 0.03	0.286 ± 0.003	-3.79 ± 0.08	*I*
1.90	0.09 ± 0.03	0.289 ± 0.002	-3.89 ± 0.08	*I*
1.80	0.10 ± 0.03	0.291 ± 0.002	-3.98 ± 0.09	*I*
1.78	0.16 ± 0.08	0.291 ± 0.002	-4.01 ± 0.12	*I*
1.76	0.12 ± 0.05	0.291 ± 0.002	-3.99 ± 0.10	*I*
1.74	0.19 ± 0.07	0.292 ± 0.002	-4.08 ± 0.11	*I*
1.72	0.16 ± 0.07	0.292 ± 0.002	-4.06 ± 0.11	*I*
1.70	0.15 ± 0.08	0.292 ± 0.003	-4.06 ± 0.14	*I*
1.68	0.53 ± 0.08	0.300 ± 0.004	-4.75 ± 0.25	*N*
1.67	0.56 ± 0.08	0.302 ± 0.004	-4.96 ± 0.26	*N*
1.66	0.87 ± 0.01	0.330 ± 0.003	-7.53 ± 0.12	*Sm-B*
1.64	0.88 ± 0.01	0.336 ± 0.003	-8.01 ± 0.15	*Sm-B*
1.62	0.87 ± 0.01	0.337 ± 0.003	-8.10 ± 0.12	*Sm-B*
1.60	0.88 ± 0.01	0.338 ± 0.003	-8.13 ± 0.12	*Sm-B*
1.58	0.88 ± 0.01	0.339 ± 0.003	-8.23 ± 0.12	*Sm-B*

CONCLUSIONS

We have undertaken a series of MD simulations of liquid crystal mixtures in the constant-NPT ensemble. The system used employs the generalised Gay-Berne potential for various concentrations of 3:1 and 3.5:1 rod-like particles. Both the order-disorder transition temperature and the smectic layer spacing are found to vary linearly with concentration. The latter indicates that there is no demixing of the two components, and corresponds to the formation of highly interdigitated, randomly mixed smectic layers. We note some departure from the linear behaviour of the layer spacing for a restricted concentration range. We have determined a narrow range of nematic phase stability for a single-component system. The nematic phase is found to be particularly sensitive to the density fluctuations inherent in the constant-NPT ensemble. Work is in progress to delineate the nematic-smectic phase boundary for bi-disperse systems. We are also investigating the origin of the nonlinearity in the smectic layer spacing.

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