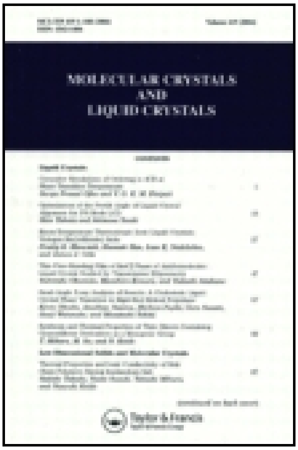

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Computer Simulation of Fractionation in Bidisperse Liquid Crystals

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We present evidence of fractionation at the isotropic-nematic transition in a bidisperse liquid crystal system, using the Gibbs ensemble Monte Carlo technique[1] and the generalised Gay-Berne potential[2]. Using a 50:50 mixture of prolate molecules with identical breadths but different length to breadth ratios, fractionation was observed which shows qualitative agreement with the coexistence behaviour predicted by mean field theory[3]

Keywords: computer simulation; phase transitions; mixtures

INTRODUCTION

The use of liquid crystal mixtures allows access to a number of technologically important effects not displayed by pure systems. It is not surprising, therefore, that experimental and theoretical studies of these mixtures have been performed extensively, in order to open up new possible applications.

One area of interest is the behaviour of rod-like mixtures at the isotropic-nematic (I-N) transition. The coexistence region found at this phase transition is well documented, and a number of theoretical treatments[3] have indicated that, for coexisting bidisperse mixtures containing molecules of differing lengths, there will be a significantly higher mole fraction of the longer rods in the anisotropic phase than in the isotropic. An improved understanding of this fractionation effect would be an important step towards modelling real materials, providing a useful insight into the driving forces behind ordering in bulk mixtures, and also helping to test the validity of mean field approximations for these systems. To date, simulations of this effect have been restricted to lattice models[4]. A simple generic diagram[5] for a bidisperse system is shown below (Figure 1).

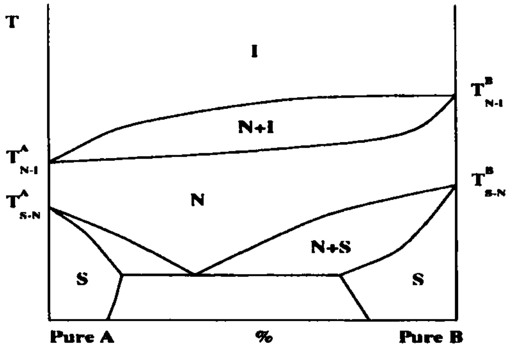

Figure 1 Generic phase diagram

We present here results from a computer simulation of fractionation using soft particles, interacting through a recently developed generalisation[2] of the well established Gay-Berne (GB) potential[6].

THE MODEL

Generalised Gay-Berne Potential

The GB potential has been shown to display a number of liquid crystalline phases[7]. Recently, a generalisation of this potential has been proposed, which gives the interaction between two non-identical anisotropic phase behaviour of a simple bidisperse system has been looked at using molecular dynamics (MD)[8], and shown to display the trends found experimentally and theoretically, such as increased nematic range[5].

The Gibbs Ensemble

The Gibbs ensemble Monte Carlo (GEMC) technique[1] was developed relatively recently specifically for the direct simulation of fluid phase equilibria. Instead of using one simulation box surrounded by its periodic images as in traditional Monte Carlo (MC) methods, two such boxes are simulated simultaneously, with appropriate MC moves that ensure both boxes are in equilibrium with each other. In practice, a Gibbs system in a coexistence region will evolve so that each box contains one of the coexisting phases. The underlying driving force for this is that the system will seek to avoid the energetic cost of an interface, and since the boxes are not in direct physical contact, it can do this by containing a separate phase in each.

SIMULATION DETAILS

Method

Previously published work on GGB systems[8] has concentrated on particles with length to breadth ratios of 3:1 and 3.5:1. However due to this relatively small degree of bidispersity, it was decided that the I-N coexistence region might be too narrow and difficult to pinpoint using the Gibbs technique. Instead, on the basis of some unpublished results obtained using the same MD technique, a more bidisperse system of 3:1 and 4.2:1 molecules was chosen, with the intention of promoting a more easily simulated coexistence. The I-N transition temperature for this system was found to be $T^* \approx 2.9$ at reduced number density $\rho^* = 0.20$.

As is usual in computer simulation[9], we have employed a number of reduced variables and observables to define the system and its behaviour. The reduced temperature is given by $T^* = k_BT/\epsilon_{BB}$, where k_B is the Boltzmann constant, and the reduced number density is simply $\rho^* = N/V$, the volume being in units of σ_0^3. Most of the parameters used are explicitly defined in the GGB potential[2], except a few which require fitting to Lennard-Jones jellium lines. Details of the fitting[8] are omitted here, for completeness the values obtained were $\epsilon_{AA}/\epsilon_{BB} = 1.1752$, $\alpha'_{AB} = 1.0188$, $\chi'_{AB} = 0.6657$.

The simulations were started from an isotropic configuration in both boxes, these having been previously melted at a high temperature ($T^* = 4.0$) from a regular lattice. The system was then cooled down and the Gibbs moves switched on at $T^* = 2.92$. Due to the relatively high density and degree of anisotropy, the particle exchange moves[1] were almost always rejected and it was doubtful as to whether the simulations were viable. However, by modifying the technique to only attempting direct exchanges for the shorter (3:1) molecule and incorporating an inter-box identity swap move[10], reasonably satisfactory results were obtained.

As the system was cooled through the I-N transition, the mole fraction of longer rods, X_A, the nematic order parameter, P_2, and the reduced potential energy, $V^* = V/\epsilon_{BB}$, in each box were monitored to gain an indication of the system progress. The nematic order parameter is given by

$$P_2 = \frac{1}{N}\sum_{i=1}^{N}\left[\frac{3}{2}(\hat{\mathbf{u}}_i\cdot\hat{\mathbf{d}})^2 - \frac{1}{2}\right]$$

where $\hat{\mathbf{d}}$ is the system director (defined as the orientation that maximises the right hand side of the equation). In practice, P_2, varies between $1/N^{\frac{1}{2}}$ for systems in the isotropic phase, up to $0.4 - 0.8$ for nematics.

Typical evolutions of the order parameter and mole fraction values in each box at a coexistence temperature are shown in Figures 2 and 3. These show a clear correlation between the degree of order in each box and the mole the values observed in each box are not stable but switch over long periods of simulation time. An analysis technique based on the use of histograms was therefore required to clarify the results. To obtain reasonable statistics, run lengths of over a million MC sweeps were required.

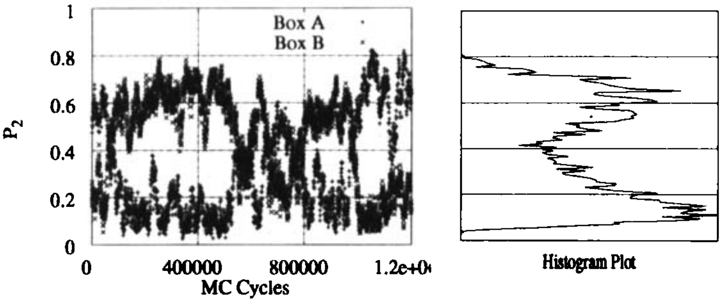

Figure 2 Order parameter evolution ($T^* = 2.74$)

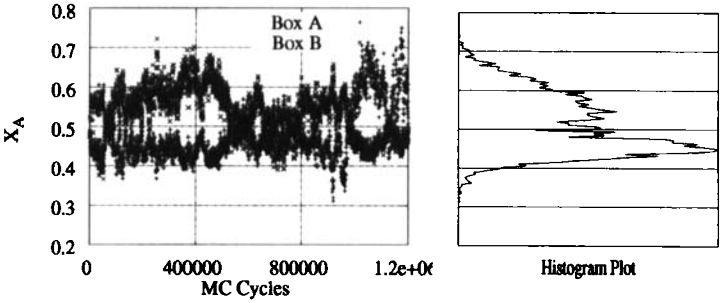

Figure 3 Mole fraction evolution ($T^* = 2.74$)

Analysis

The histograms obtained for the mole fraction, X_A, order parameter, P_2, and potential energy, V^*, distributions were analysed by fitting to a double Gaussian form, corresponding to the distribution of the observables in the two coexisting phases. Good fits were obtained for both X_A and V^*; an example is shown in Figure 4. Less satisfactory fits were obtained for the order parameter distributions, which was attributed to the fact that P_2 is constrained between 0 and 1, and the isotropic box has a value close to this bound. The dependency of P_2 upon the number of particles present as well as the degree of orientational order was also a factor. Attempts to arrive at a more accurate functional form were unsuccessful, and fitting to the P_2 distributions was abandoned.

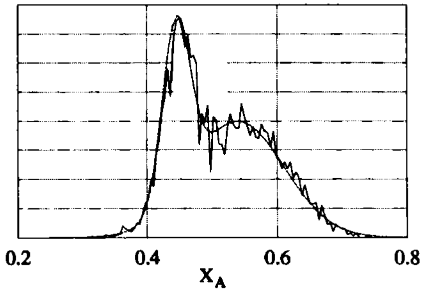

Figure 4 Histogram and fit for X_A ($T^* = 2.74$)

The mean values for the various state points simulated at are shown in Table 1. The errors were calculated using a block averaging technique[9], the blocks consisting of 200,000 sweeps each, giving at least five per state point.

Table 1 Observables at coexisting temperatures.

T^*	$X_A(1)$	$X_A(2)$	$V^*(1)$	$V^*(2)$
3.20	0.500(12)	0.500(14)	-2.871(075)	-2.871(075)
2.86	0.487(24)	0.584(21)	-2.952(102)	-4.230(342)
2.80	0.456(17)	0.553(31)	-2.911(092)	-4 021(322)
2.74	0.448(06)	0.563(31)	-2.930(152)	-4.138(316)
2.68	0.430(05)	0.531(12)	-2.813(112)	-3.913(293)

As can be seen from Table 1, the mole fractions obey the expected trend with temperature, and the values can be used to map out the I-N coexistence envelope for this system (Figure 5). This agrees well with the generic phase diagram shown earlier (Figure 1). Upon further cooling to the temperature

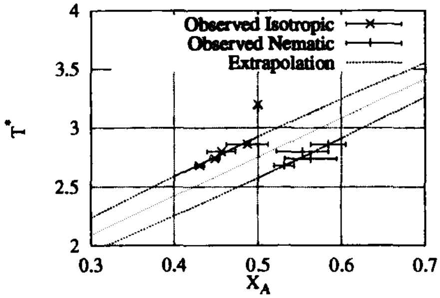

Figure 5 Phase diagram for a mixture of Gay-Berne rods

$T^* = 2.62$, it was found that the dense simulation box began to sample layered configurations, indicating the onset of smectic/crystal order. The series of simulations was ended at this point since the Gibbs method, already pushed to its limit here simulating I-N coexistence, fails at the particularly high densities typical of smectics, due to low acceptance rates of the particle insertion MC move[1].

CONCLUSIONS

The work presented here shows clear evidence of fractionation at the I-N transition using a proven molecular simulation technique, agreeing with theoretical predictions made using mean field theories. As a first attempt at using the Gibbs method in this area, these results are encouraging, although a complete mapping out of the phase diagram for this particular system still appears to be beyond the reach of present computational power, due to the long run times needed at the required densities.

The use of a more appropriate system which still shows the required nematic ordering would, it is believed, show more easily the extent of this effect, and also hopefully enable the complete coexistence envelope to be located. At present we are conducting simulations of such a system, and intend to publish the results of these in the near future.

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