Nanospheres in a nematic liquid crystal solvent: the influence of particle size

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We use Monte Carlo simulations to investigate a simple lattice model for nematic liquid crystals containing nanospheres. The influence of particle size on the phase behaviour is studied using two different sized particles. The phase diagram is found to be topologically equivalent for both particle sizes, with a large biphasic region corresponding to coexistence between a rod-rich nematic and a rod-poor isotropic phase. For small spheres, the rod-rich nematic phase is stable for relatively large volume fractions of spheres (up to a maximum of about 16%). In contrast, the nematic phase for the system with larger spheres is constrained to a much narrower region of the phase diagram.

1. Introduction

Despite their simplicity, lattice models have played a useful role in the investigation of liquid crystals at the microscopic level [1]. The majority of lattice simulations follow the pioneering study of Lebwohl and Lasher (LL) [2], who introduced a model that was capable of forming nematic (N) and isotropic (I) phases. In their model, uniaxial molecules on neighbouring sites interact via a simple anisotropic potential which depends on the angle between the two molecular symmetry axes. Whilst this model clearly lacks the chemical structure of real molecules, it retains the essential physics necessary to reproduce the nematic–isotropic transition characteristic of many real systems. It has, therefore, become a simple prototype model for testing theories of ordering in nematic phases. Indeed, the temperature dependencies of the orientational order parameters of the LL model at the nematic–isotropic transition are found to be in surprisingly good agreement with those of real nematogens [3, 4]. The Lebwohl–Lasher model has been extended to include a wider range of pair potentials and simulation box geometries, thus allowing the exploration of different kinds of liquid crystal behaviour [1]; Geoffrey Luckhurst has played a leading role in the development of these systems, along with co-workers including Claudio Zannoni and Silvano Romano. Some variations of the model have involved changing the nature of the molecular interactions. These have included, for example, extensions to dimer [5] and V-shaped [6] molecules, biaxial molecules [7, 8], rod–disc

mixtures [9] and rod–disc dimers [10]. In other simulations, the interaction model itself has remained the same but the boundary conditions have been varied. This has led to the study of, for example, thin films [11], polymer dispersed liquid crystals in various geometries [12, 13], free droplets or tactoids [14] and aerogels [15]. If instead the potential is based on the expansion of the anisotropic polarizability, this leads to a slightly more complex but similar potential in which the energy also depends on the orientation of the intermolecular vector [16]. This leads to free surfaces in which either planar or homeotropic anchoring can be observed, depending on the parameterization used [17]. In this paper, we use the basic LL model to investigate systems containing small water drolets or nanospheres.

Recent studies on ternary mixtures have shown that a demixing transition occurs when surfactant stabilized water droplets are dispersed in a thermotropic liquid crystal [18]. The demixing transition leads to the coexistence of a phase rich in rods in which the liquid crystal is in its nematic state, and an isotropic phase with a lower composition of rods. The resulting phase diagram is topologically very similar to that predicted by theory [19–21] and computer simulation [22], as shown in figure 1 (*a*), for a liquid crystal system in which the water droplets are modelled as small inert spheres or, equivalently, holes in the system. The extent of the demixing depends critically on the temperature. At high temperatures above the N–I transition, only an isotropic phase is observed no matter what the sphere concentration is, as we should expect. Below the N–I transition, a rod-rich nematic coexists with an isotropic phase that contains slightly more spheres than the
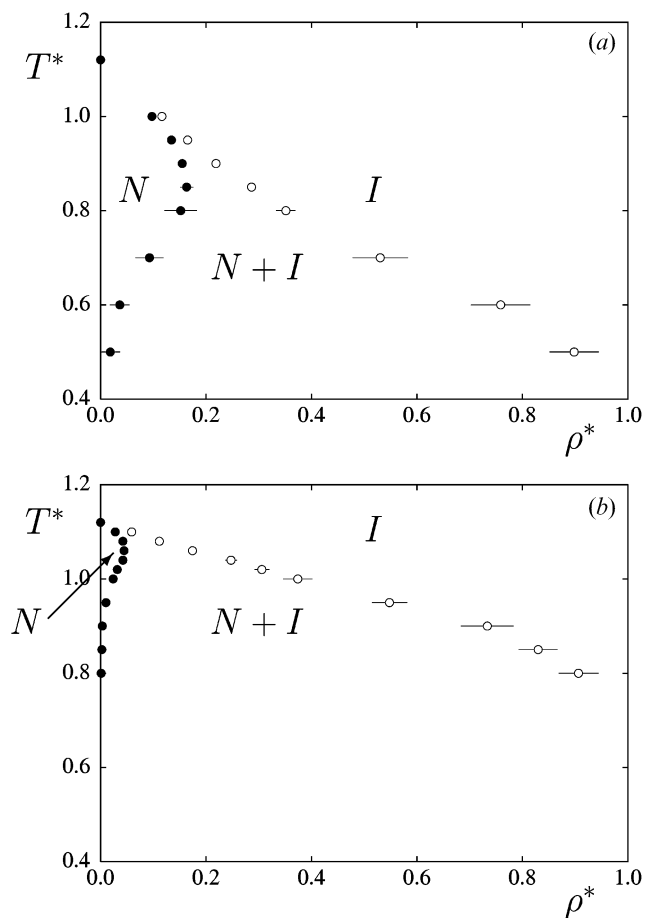

Figure 1.   Temperature–composition phase diagrams for the nanosphere-doped liquid crystal systems. (*a*) Small (*d*=1) spheres, (*b*) large (*d*=2) spheres.

nematic, but is still relatively dense. As the temperature is decreased, the composition of the spheres in both the coexisting phases increases, with the composition gap widening, see figure 1 (*a*). On further cooling, the sphere composition of the coexisting isotropic phase continues to increase. However, the composition of the coexisting nematic begins to decrease; that is, the spheres start to be excluded from the nematic at lower temperature. This means that a maximum is observed in the nanosphere composition in the nematic phase as the system is cooled.

The difference in the sphere composition at coexistence can be understood in terms of an induced interaction between the spheres, arising from their disordering nature [18]. This induced interaction occurs because the spheres will have a disordering effect on the nematic correlations between the liquid crystal molecules, and so the stability of the nematic depends crucially on the concentration of the droplets, as well as the temperature. Long range nematic correlations can

only appear where the sphere concentration is low or, equivalently, long range correlations force the spheres from the nematic phase and into the isotropic phase. Thus the phase diagram has a rod-rich region which is nematic in nature and a rod-poor region in which the concentration of rods is too low to permit long range order and so is isotropic in nature.

Although the predicted phase diagrams are topologically equivalent to those found experimentally, there are two significant differences. Namely, the nematic phase is found to be stable only in experimental systems in which the volume fraction of the droplets is a maximum of about 1.5% [18], whereas the simulation model predicts that the nematic phase is stable for much larger volume fractions for the spheres up to about 16% [22]; mean field theory predicts the critical composition above which a nematic cannot be observed to be even larger [21]. Similarly the temperature range in which the micellar droplets can be dispersed in the nematic is experimentally found to be small. The nematic island in the phase diagram extends over a temperature range of about 15 K [18] and is bounded above by the N–I transition temperature of the pure mesogen at about 300 K. Thus, the scaled temperature range over which the mixing can occur in the nematic phase is about 5%, which compares unfavourably with the value of 55% predicted by simulations using the lattice-gas Lebwohl–Lasher model [22].

One way of overcoming the composition differences between the experimental and predicted results is to use a simple scaling in the model system in which the volume fraction of a lattice cell containing a sphere or water droplet is taken to be smaller than that of the cell containing a rod. However, this is not very satisfactory and there is no similar simple scaling possible to resolve the temperature range differences between the model and experimental systems. We have therefore performed further simulations to investigate how the size of the droplets can influence the phase diagram at both a qualitative and quantitative level.

2.   Model and simulation details

As we have already described, the LL model [2] is a primitive model which retains the basic physics necessary for studying the behaviour of uniaxial nematic liquid crystals, with the detailed short range chemical structure of mesogen stripped away. In the LL model, the interaction between two neighbouring molecules *i* and *j* on a cubic lattice is written as

$$U_{ij} = -\varepsilon P_2\big(\cos\beta_{ij}\big) \qquad (1)$$

$$= -\varepsilon P_2\big(\mathbf{u}_i \cdot \mathbf{u}_j\big) \qquad (2)$$

where ε is an energy parameter, $\mathbf{u}_i$ and $\mathbf{u}_j$ are unit vectors describing the orientation of the uniaxial particles at site i and j, respectively; β_{ij} is the angle between these vectors and $P_2(x) = 3x^2/2 - 1/2$ is the second Legendre function.

This model was recently combined with the lattice-gas model [23–25], which is a simple model for the investigation of condensation phenomena in which the density of occupied lattice sites can vary, to give the lattice-gas Lebwohl–Lasher (LGLL) model [22]. In this model, the potential between two neighbouring sites i and j is given by

$$U_{ij} = -s_i s_j \varepsilon P_2\left(\cos \beta_{ij}\right). \tag{3}$$

Here s_i is the occupation of site i and is equal to one if the site is occupied by a mesogen and zero if empty (or occupied by a sphere). This model is most readily simulated using grand canonical (or semigrand canonical) simulations in which the chemical potential difference between the liquid crystal species and the holes (or spheres) is fixed and the density or composition of the system is allowed to fluctuate until equilibrium is reached. By performing a series of simulations varying the chemical potential, the equation of state for a particular temperature can be determined [22]. From the equation of state, the coexistence densities at either side of the biphasic or coexistence region can be readily obtained. Such simulations were previously performed for a range of temperatures and the temperature–composition phase diagram for the LGLL model constructed, see figure 1 (*a*). We should note that in reality, the model differs from experiments at high water/sphere concentrations since, in the model, the spheres remain intact as individual particles. In contrast, in the experiments the individual droplets are not likely to be stable at high water concentrations, with oil-in-water type microemulsions forming instead. However, this need not concern us since we are primarily interested in the low sphere concentration regime where the nematic is stable. We should also point out that it is possible to introduce surface-anchoring terms between the spheres and the liquid crystal into this simple model in two ways. The first is to add a term which depends on the angle between the vector joining the sphere and rod and the vector describing the orientation of the rod, which is appropriate for micellar systems; simulations using such models indicates that the phase diagram is not greatly affected, at least in the low sphere regime [26]. The second is to use a potential based on the anisotropic expansion of the polarizability, which is appropriate for molecular systems [16]; in this approach, the loss of neighbouring rods (when replaced by spheres) leads to

an orientational dependence of the potential energy of rod at a surface [17]. Simulations of a model using this latter approach give phase diagrams quantitatively very similar to those exhibited by the simple LGLL model for both planar and homeotropic anchoring of the rods at the sphere surface. We should also point out that the analysis of the results by Bellini *et al*. [18] leads to the explanation that the nm-sized micelles can indeed be pictured as holes with essentially free boundaries, or ones in which the anchoring is weak. For this reason, we will use only the simple Lebwohl–Lasher-derived model, equation (3), in which surface anchoring is not included.

As noted in the introduction, although the phase diagram has the correct topology, the model does not predict the quantitative behaviour of the surfactant-stabilized water droplet system. This is not surprising, given the simplicity of the interactions between the different species in the model. However, given that the model does exhibit a similar phase diagram, we can examine how modifications of the model change the phase diagram. In particular, we are interested in how the size of the spheres affect the quantitative nature of the phase diagram. We should point out that, in a simulation using a LL type model, the concept of what the individual lattice sites represent is not well defined. Although they are often described as molecules, they can equally well be defined as a small volume of liquid crystal, and the orientation vector represents an average localized director rather than the orientation of a single molecule. Thus it is impossible formally to assign a definitive length scale to the rods, and hence to the spheres, that we are modelling. What we can do is change the size of the sphere whilst keeping the model for the nematic unchanged to investigate the influence of the size of the sphere. Rather than try to map the experimental system onto the model one, we will perform two independent series of simulations for different sphere sizes to investigate how changing the size of the sphere changes the phase behaviour. The simplest way to change the size of the sphere in the LGLL model [22] is to allow each sphere to occupy more than one cell. For the larger particles, we shall use a model in which each sphere occupies a volume of $2 \times 2 \times 2$ cells. As in the original model, spheres cannot overlap; that is, each of the multiple cells that make up a single sphere blocks this volume from both other spheres and rods. We should, of course, point out that for a model based on a cubic lattice, small inclusions (whether $1 \times 1 \times 1$ or $2 \times 2 \times 2$) are necessarily cubes rather than spheres, but to make contact with experiments we will call them spheres.

It is also worth pointing out that for the simple LGLL model, it does not matter if grand canonical

simulations are performed by inserting (or removing) spheres into (or from) a background fluid of rods, or if rods are inserted and removed from a fluid of spheres. These two methods would be equivalent, since each species occupies one lattice site and the chemical potential actually specified in the grand canonical simulations is not an absolute one, but that of species of interest with respect to that of the background fluid (the second component). Indeed, both methods correspond exactly to a semi-grand canonical ensemble simulation, in which the identity of the species at a particular site can be swapped from sphere to rod or *vice versa* and the chemical potential difference between the two types of particles is imposed. However, for practical reasons when simulating the larger spheres model, it is more convenient to perform semi-grand canonical trials by inserting (or removing) spheres into (or from) the background fluid of rods, and canonical trials in which we translate the spheres rather than the rods. Clearly these trials are equivalent to removing, inserting and moving groups of $2 \times 2 \times 2$ rods and then performing checks to ensure that the remaining empty regions correspond to allowable size distributions for individual or groups of spheres. For book-keeping reasons, the former trials are more practical. Therefore, in the simulations we impose the chemical potential of the spheres (relative to that of the single rods) and trials are performed in which the spheres are inserted, deleted and translated.

In addition to these, extra trials were performed in which a rod selected at random is given a new random orientation, to ensure that the background fluid of rods was able to adopt different orientational states according to the temperature and composition. The equation of state is then obtained by performing a series of simulations at fixed temperature, just as for the small sphere systems. Simulation runs in which the chemical potential of the spheres was both increased and decreased were performed, to identify and locate the coexistence densities or compositions of the transitions [22]. This was repeated for a number of temperatures to map out the phase diagram as a function of temperature ($T^* = kT/\varepsilon$) and composition ($\rho^* = d^3 N_s/N_l$, where d is the 'diameter' of the sphere (1 or 2), N_s is the number of spheres and N_l the number of lattice sites). Note that we define the composition as a volume fraction, so that if the composition of a $d=1$ system is the same as that of a $d=2$ system, then the $d=1$ system contains eight times more spheres.

Initial runs were performed with a small $10 \times 10 \times 10$ lattice to highlight the important regions to study in more depth. These were followed by simulations on a lattice of size $40 \times 40 \times 40$. Typically, 20–50 000 Monte Carlo cycles were used for equilibration and a further 25 000 cycles for calculating averages of the composition and order parameter at each state point, as in our previous study of small spheres [22]. We note that when the volume fraction of spheres was larger than about 80%, the simulations were found to be very slow to equilibrate, since the system often became locked into configurations where the $d=2$ spheres could not be moved, nor new spheres inserted as the chemical potential was increased. Of course, this does not happen for the $d=1$ sphere model, since a single sphere replaces a single rod in this model, so there are no arrangements of spheres from which other spheres are excluded, except for a fully condensed lattice. Fortunately, we are not interested in this high sphere composition region of the phase diagram, so this region can be ignored. This is because, at these compositions in the real system, the liquid crystal is so dilute that it would form an oil-in-water rather than a water-in-oil type microemulsion; that is, the spheres used in the model would no longer keep their individual identities but coalesce to form a background medium in which droplets of liquid crystal would disperse.

3. Phase diagram and discussion

The phase diagram for the system containing the larger spheres of size $d=2$ is shown in figure 1(b). When this is compared with the corresponding phase diagram for $d=1$ spheres, see figure 1(a), it is immediately apparent that the composition range over which the nematic phase is stable is significantly reduced for the system containing the larger spheres; this is reduced from volume fractions of 0.16 for small spheres to 0.04 for the larger spheres. In a macroscopic system in which the composition was fixed at, say, 0.10, the phase behaviour observed on cooling for the smaller spheres would be isotropic, then a narrow nematic plus isotropic biphasic region, followed by a nematic and finally a re-entrant biphasic region. In contrast, for larger spheres, the phase sequence at the same volume fraction would be isotropic followed by a single biphasic region and no pure nematic phase would be observed. The nematic phase is therefore squeezed towards the low sphere concentration side of the phase diagram on increasing the particle size. Similarly, the temperature range over which the nematic island appears in the phase diagram is dramatically reduced from about $T^*=0.5-1.12$ to just $T^*=0.95-1.12$. This corresponds to the relative temperature range over which the nematic island is stable being reduced from about 55% to a value of 15%, closer to the value of 5% as observed in the experiments. Of course, we do not expect to obtain quantitative agreement given the relative simplicity of the model.

However, the simulations do indicate that the size of the sphere dispersed in the nematic liquid crystal does have a large effect on the quantitative nature of the phase diagram. In particular the larger spheres tend to destabilize the nematic more when the concentration is increased and so are expelled into the coexisting isotropic phase. Indeed further simulation [26] using $3 \times 3 \times 3$ spheres, indicate that larger spheres are completely excluded from the nematic phase for this model.

We may wonder why the nematic phase is stable at relatively large compositions for small spheres and only at relatively low compositions for the larger spheres. We first recall the arguments of Bellini *et al.* [18] described earlier. The presence of the dispersed droplets will have a disordering effect on the nematic and so the nematic is unstable above a certain sphere concentration. We may be tempted, therefore, to think that at a fixed concentration the behaviour of the systems with large and small spheres would be the opposite to that observed. At the same concentration, there would be a larger number of disordering sites in the liquid crystal for the small sphere system compared with the large sphere system, and so a nematic phase containing smaller droplets should be less stable than one of the same composition containing larger droplets. However, this is not the case, as can be observed in the phase diagrams obtained from the simulations, see figures 1 (*a*) and 1 (*b*). Indeed, we see the opposite behaviour at all temperatures, that the nematic becomes unstable at relatively low concentrations for the system containing large droplets, and only at higher concentrations for systems containing smaller droplets. In contrast, the composition of the coexisting isotropic phase is relatively large for the large sphere system compared with that for the small sphere system at each temperature. This is a clear indication that it is not only the number of spheres that is important in determining the stability of the nematic, but the 'disordering strength' of the spheres, which clearly depends on the droplet size.

To conclude, we have seen that the phase diagram for two model and one experimental nematic systems are topologically equivalent. However, the phase diagrams for the two model systems are quantitatively different and this is shown to depend on the size of the dispersed droplets. The critical sphere concentration at which the

nematic is no longer stable is at significantly lower values for systems containing larger spheres compared with systems containing smaller ones.

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