C. Chiccoli, P. Pasini, F. Semeria, C. Zannoni, A Computer Simulation of nematic droplets with radial boundary conditions, Phys. Lett. A, 150, 311-314 (1990).

A computer simulation of nematic droplets with radial boundary conditions

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Received 23 July 1990; accepted for publication 10 September 1990
Communicated by A.A. Maradudin

We present Monte Carlo simulations of nematic droplets with radial boundary conditions and we investigate the orientational order and the molecular organizations in these systems that mimic polymer dispersed liquid crystals (PDLC).

1. Introduction

Polymer dispersed liquid crystals (PDLC) formed of liquid crystal droplets embedded in a polymer matrix have recently been prepared [1,2] and have immediately received a great deal of attention, both in view of their applications in large area displays [3,4] and of their fundamental interest concerning the behaviour of mesophases in a restricted environment. The size of liquid crystal droplets can be adjusted and typically ranges from radii of a few hundred angstroms to micron size [5]. The orientation of the nematic at the droplet boundary can also be controlled to a good extent by a suitable choice of the host polymer. For example radial, toroidal and bipolar boundary conditions have been realized [1–4]. One of the most interesting aspects in very small droplets is the suppression of the first order nematic–isotropic transition and its replacement with a continuous transition shifted to lower temperature [6]. Such a phenomenon has been experimentally observed first in nematics adsorbed in porous silica [7]. From the point of view of computer simulations PDLC systems offer an interesting opportunity because the size of the dispersed droplets can be so small as to contain just a few thousand molecules, thus not too far from the range accessible to simulations and in any case reducing the usual need for extrapolation to macroscopic dimensions. In this communication we wish to show that computer simulations can indeed be particularly suited for treating this problem and we present the results of a first application to the case of radial boundary conditions (RBC).

We have studied the problem using Monte Carlo simulation of an approximate spherical sample carved from a cubic lattice of particles interacting through a Lebwohl–Lasher (LL) potential [8–10]. The "bulk" LL model has been studied with a variety of theoretical techniques as well by periodic boundary conditions (PBC) [8,9] and cluster Monte Carlo (CMC) [10] simulations and it has been found to give a weak first order orientational phase transition $T^* \equiv kT/\epsilon \approx 1.1213$ [9], with features similar to those of real nematics. In the simulation of a nematic droplet we do not really want to eliminate the effect of boundaries but rather see how they affect the behaviour of the system. We could think of the effect of surface as determining the orientation of molecules at the boundary independently from

0375-9601/90/$ 03.50

what happens inside the sample and independently of temperature. Thus we have chosen to mimic the effect of the polymer on the liquid crystal by assuming that the orientation of the first shell of particles outside the drop (i.e. of ghosts) is fixed along a direction dictated by the boundaries. The effect of boundaries on the simulation is in principle distinct from that of finite size, simply due to limited number of particles. To examine this point we have used our cluster Monte Carlo method [10], with the same number of particles but with updating boundary conditions to see how well macroscopic behaviour can be a result of the different ways of treating boundaries.

Another point of great interest is that of the configurations adopted by the director in the systems. This problem is normally tackled by elastic type calculations [11,12] thus on one hand employing macroscopic continuum concepts that have to be proved to be valid in such small systems and on the other masking the molecular aspects of the problem. Here again we think computer simulations can be quite useful to visualize molecular organizations at different temperatures.

2. The simulation

We consider a virtual sphere of a given radius measured from a point at the centre of the lattice and consider as belonging to the sample only the particles at positions r_i inside the sphere. The jagged sphere realized in this way is our model droplet. Clearly it is not exactly spherical, but then true cavities in the polymer will hardly be spherical too. The particles at the cubic lattice sites interact through the attractive nearest neighbour Lebwohl–Lasher [8] pair potential:

$$U_{i,j} = -\epsilon_{ij} P_2(\cos\beta_{ij}) \,, \qquad (1)$$

where ϵ_{ij} is a positive constant, ϵ, for nearest neighbour particles i and j, β_{ij} is the angle between the axis of these two molecules. As already mentioned we represent the effect of the boundaries by keeping the orientation of the first shell of ghosts outside the drop as fixed, in the present case with the long axis pointing to the centre of the lattice.

The calculation is started at the lowest temperature from a system with all the molecules pointing toward the centre. At higher temperature we start from an already equilibrated configuration at a lower temperature. The lattice is updated using the Metropolis algorithm. Each particle is selected for trial move at every cycle using a random shuffling algorithm [9]. A new trial orientation is then generated by a controlled variation from the previous one to get a rejection ratio near 0.5. The energy of the system is calculated as a sum of pair interactions (1). The dimensionless heat capacity C_V^* is obtained by differentiating the average energy with respect to temperature as previously described [13]. Second and fourth rank order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ have been calculated by setting up and diagonalizing the ordering tensor as discussed in detail earlier [9]. We now describe briefly the system studied. We have simulated three jagged spherical droplets contained in the three cubic lattices with linear dimensions $L=10$, 16, 26 respectively. This corresponds to $N=304$, 1568, 7616 particles inside the sphere and to $N_G=200$, 576, 1632 ghost respectively.

3. Results

In fig. 1 we show the reduced heat capacity $C_V^* \equiv C_V/kN$ at various droplet sizes.

We notice that there are no major changes in behaviour and that the peak does slowly increase with

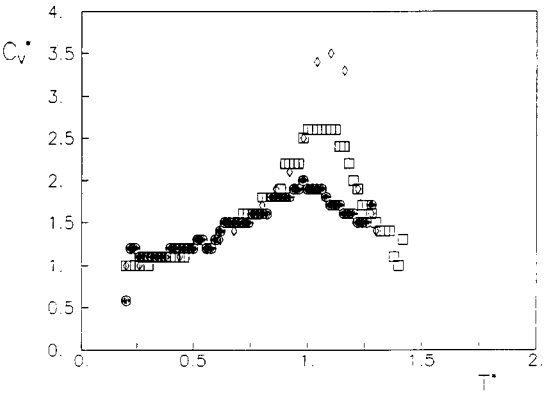

Fig. 1. The dimensionless heat capacity of a droplet with RBC containing (●) 304, (□) 1568 and (◇) 7616 particles as a function of reduced temperature $T^* = kT/\epsilon$.

increasing the number of particles. The peaks are centred at $T^* \approx 0.99$, 1.10, 1.10 and the maxima $(C_V)_{max}$ are ≈ 2.0, ≈ 2.7 and ≈ 3.5 respectively for the three lattice sizes studied, with the width at half height quite comparable. Although the behaviour of the bulk LL model is known [8–10], we have performed a complete cluster Monte Carlo simulation [10] of a LL model for the smallest droplet size, to get a reference value for this spherical geometry. In this calculation the ghost orientations are generated according to the CMC procedure and updated regularly. As already mentioned the method constitutes an alternative to periodic boundary conditions and allows mimicking a bulk system starting from a relatively small system. Here we obtain a maximum of 16.2 in dimensionless units at about $T^* = 1.12$. Thus the small peak observed with the radial conditions is not due to the small number of particles but seems to indicate the absence of a true phase transition in the nematic droplet.

It is interesting to look at the second rank order parameter of the droplet relative to the instantaneous director (i.e. $\langle P_2 \rangle_\lambda$) as calculated from the ordering matrix diagonalization procedure [9]. As we show in fig. 2 $\langle P_2 \rangle_\lambda$ is very low even in the whole temperature range (even at very low temperatures) and decreasing with drop size.

$\langle P_2 \rangle_\lambda$ actually tends to increase with temperature up to the heat capacity anomaly and after that it takes on an isotropic-like value. The effect is clearly due to the influence of boundary conditions and is illustrated by the instantaneous configurations in figs. 3 and 4.

In fig. 4 we show equatorial sections of the droplet for the three sizes studied and at low and high temperature respectively. The largest droplet shows more clearly the central defect at low temperatures and the rapid smearing of the boundary condition influence at $T^* = 1.3$.

At low temperatures the particles are mostly radially directed and there is very low ordering with respect to a unique axis. As the temperature increases and we arrive near the transition region it becomes possible to acquire an instantaneous director and the order referred to that direction grows. Increasing the temperature again the order decreases again because the molecular orientations are randomized (cf. fig. 4). On the other hand the star-like

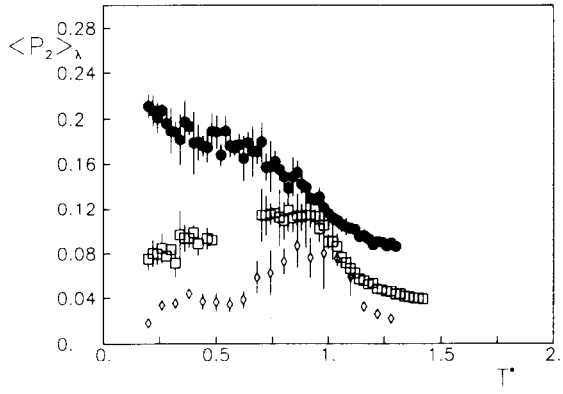

Fig. 2. The second rank order parameter $\langle P_2 \rangle_\lambda$ versus reduced temperature for (•) 304, (□) 1568 and (◇) 7616 particles.

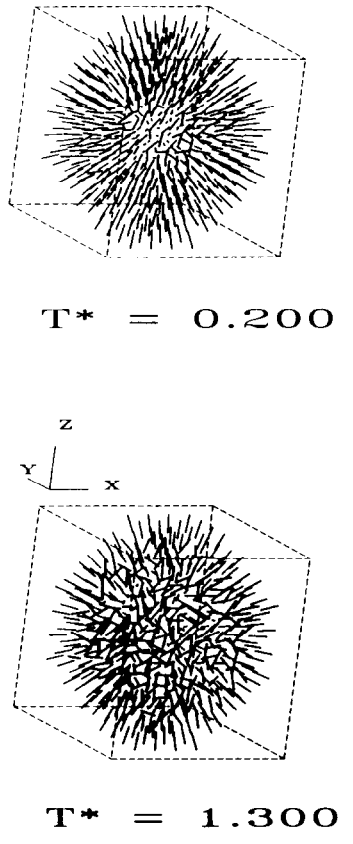

Fig. 3. A perspective view of a typical molecular organization for a droplet with RBC and $N = 304$ at reduced temperatures $T^* = 0.2$ and 1.3.

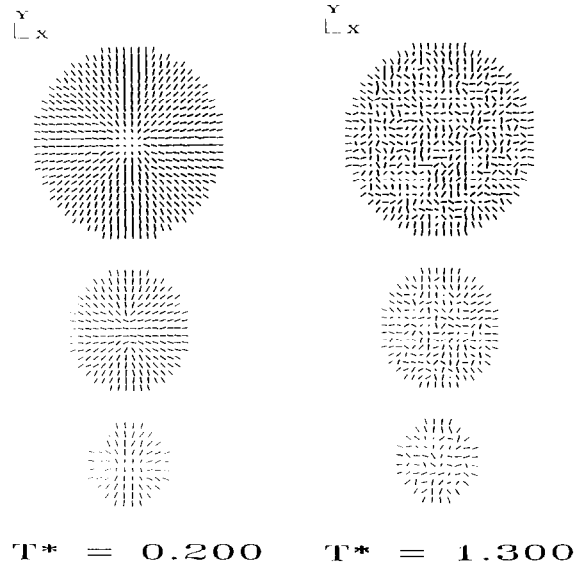

Fig. 4. Equatorial sections showing projections of typical instantaneous configurations for $N=304$ (bottom), 1564 (middle), 7616 (top) at temperatures $T^*=0.2$ and 1.3.

configuration at low temperature represents itself a kind of regular arrangement and we could try to quantify the disordering from a perfectly regular star distribution. Thus we introduce a radial order parameter $\langle P_2\rangle_R$ as follows:

$$\langle P_2\rangle_R = \frac{1}{N}\left\langle \sum_{i=1}^{N} P_2(\boldsymbol{u}_i\cdot\boldsymbol{r}_i)\right\rangle, \qquad (2)$$

where $\boldsymbol{u}_i$ is the direction cosine of the ith particle and $\boldsymbol{r}_i$ is its radial vector. In fig. 5 we show the change of this order parameter with temperature.

We see that the change in order parameter now has a more familiar appearance, decreasing with temperature and showing an order–disorder change that becomes more pronounced as the number of particles increases.

In conclusion we have shown that MC simulation affords a useful way of studying the influence of specific boundary conditions in liquid crystal droplets as those present in PDLC. The possibility of visualizing the molecular organization inside the droplets should be of help in rationalizing the various kinds of experiments currently performed on these

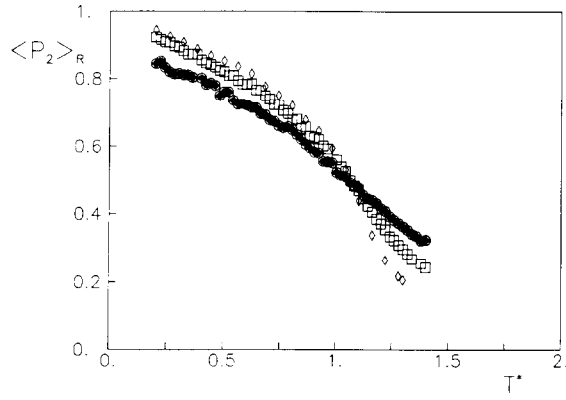

Fig. 5. The second rank order parameter $\langle P_2\rangle_R$ referred to the local radius plotted versus reduced temperature for (●) 304, (□) 1568 and (◇) 7616 particles.

important systems. It is worth pointing out that simulations also have the advantage of showing how the molecular organization changes with temperature.

We wish to thank MURST and CNR (Rome) for supporting this work.

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