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Monte Carlo study of the molecular organization in model nematic droplets. Field effects

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The Monte Carlo technique is used to investigate the orientational order and the molecular organization of model nematic droplets with radial boundary conditions subject to an external field. The effect of varying field strength on these model systems of polymer dispersed liquid crystals (PDLC) is also investigated.

1. Introduction

The study of polymer dispersed liquid crystals (PDLC), formed of sub-micron or micron size liquid crystal droplets embedded in a polymer matrix is attracting increasing attention, both for their fundamental interest and for their applications in display technology [1–6]. PDLC possess an extremely large surface-to-volume ratio so that the aligning effect of surface boundary conditions, which has a profound effect on the orientation of molecules near the surface, has a possibility of propagating inside the droplet. In general there will be a competition between the molecular orientation induced by the surface boundary, the effects of ordering of the liquid crystal itself due to the molecules trying to arrange parallel to each other, and the disordering effect of temperature. The resulting molecular organization for a certain boundary condition will thus depend on a number of factors, including the strength of the surface interaction, the temperature, and so on. Even though these factors can to a good extent be controlled, it is not easy to predict the molecular organization with microscopic theories or even, especially for the smaller sizes, to investigate it experimentally [5,6]. The situation is further complicated in the practically important case that an external field is applied.

We have shown in recent papers that Monte Carlo simulations provide a particularly effective tool for predicting the combined effect of these factors on a purely microscopic basis, without resorting to continuum theory. What is done in practice is to choose an interaction potential between particles inside the drop as well as with the boundary ones and perform a computer simulation to determine equilibrium configurations at various temperatures. In particular we have investigated, using Monte Carlo simulations, the molecular organization in droplets with radial boundary conditions [7] and various anchoring strengths [8] as well as tangential boundary conditions [9]. Here we investigate how the application of a field influences the ordering inside a droplet with radial boundary conditions and the modifications that the field induces on the phase transition behaviour. We also calculate polydomain NMR lineshapes [5,6] corresponding to the configurations found.

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2. The model

Our model droplet is a jagged sphere obtained from a cubic lattice by considering all the molecules falling within a given distance from the centre [7–9]. The radial boundary conditions can be mimicked assuming a layer of outside particles (ghosts) with fixed orientation and long axis aligned in the direction of the droplet centre. The particles are assumed to interact through the attractive nearest-neighbours Lebwohl–Lasher pair potential which has proved to be extremely useful in modelling nematics and has been extensively studied by computer simulations [10–13]. The effect of an external field is modelled by adding a term with a form similar to that of a magnetic orientational energy [12,13]. Thus the model Hamiltonian is

$$U_N = -\sum_{i<j} \epsilon_{ij} P_2(\cos\beta_{ij}) - \epsilon\xi \sum_{i=1}^{N} P_1(\cos\beta_i) , \qquad (1)$$

where ϵ_{ij} is a positive constant, ϵ, for nearest-neighbour particles i and j and zero otherwise, β_{ij} is the angle between the axis of the two molecules, P_2 is a second-rank Legendre polynomial, β_i is the angle between the field direction and the molecular symmetry axis and ξ determines the strength of coupling with the field $\boldsymbol{B}$, which is assumed to be homogeneous across the drop. The parameter ξ would depend in a real situation on the anisotropy of the electric or magnetic susceptivity and on the field intensity. Here we consider positive ξ so that the field has the effect of favouring alignment of the particles parallel to its direction.

The system in eq. (1) has been studied, with a view to investigate the effect of an external field on a bulk nematic, employing Monte Carlo on a lattice and mean field theory [12,13]. The same Hamiltonian has also been used as a model for studying, using mean field theory, laser self-focusing in liquid crystals [14] and the effect of cholesterol in lipid membranes [15]. There a critical field where the usual nematic–isotropic transition is suppressed was found. Here the situation is complicated by size and surface effects and the transition is smeared and continuous even in the absence of the field [7–9] and we shall presently concentrate on the effects on the molecular organization.

2.1. Computer simulations

In this preliminary study we have performed three completely independent simulations for radial boundary conditions (RBC) with different effective field strengths, i.e. $\xi=0.01$, 0.2 and 0.5, of a droplet carved from a $10\times10\times10$ cubic lattice. The values of 0.2 and 0.5 are similar to those of previous studies of field effects on bulk nematics [12,13] and are useful to see the trend obtained. They correspond to extremely large and possibly unrealistic magnetic fields for the bulk [13]. However, in PDLC applications electric fields rather than magnetic fields are normally used and fields of the order of 1 V/μm correspond, given, e.g., the magnetic and dielectric anisotropy of the liquid crystal E7, to about 10 T [6]. Thus, given the sub-micron size of the droplets we consider, even these rather large model parameters may be not completely unreasonable. The number of particles belonging to the jagged sphere is 304 and is sufficient to obtain reasonable results as shown in our previous studies [7,8]. Two simulations with a much larger size (5832 particles) have also been run at $T^*=0.4$ and $T^*=1.2$. All the simulations have been started at the lowest temperature from a perfect aligned radial configuration and the metropolis algorithm has been applied to update the lattice. At all the higher temperatures the runs have been produced in cascade starting from an equilibrium configuration at the closest lower temperature. Equilibrium runs of typically 18000 cycles have been discarded and a similar number of production cycles has been taken into account to produce the observable averages. We calculate energy U, second- and fourth-rank order parameters $\langle P_2\rangle_\lambda$, $\langle P_4\rangle_\lambda$, obtained from the largest eigenvalue of the ordering matrix [11], and the dimensionless heat capacity C_V^*. $\langle P_2\rangle_\lambda$, $\langle P_4\rangle_\lambda$ describe the ordering with respect to an instantaneous director. They are less meaningful when a hedgehog rather than a uniformly aligned configuration is produced. We have thus also calculated a *radial order parameter* $\langle P_2\rangle_\mathrm{R}$ as defined in refs. [7,8]:

$$\langle P_2\rangle_\mathrm{R} = \frac{1}{N}\sum_{i=1}^{N} P_2(\boldsymbol{u}_i\cdot\boldsymbol{r}_i) , \qquad (2)$$

where N is the number of particles contained in the sphere, $\boldsymbol{u}_i$ is the direction cosine of the ith particle and $\boldsymbol{r}_i$ is its radial vector. $\langle P_2\rangle_R$ is one for a perfect hedgehog and in general becomes lower when the organization deviates from this structure. We also consider yet another order parameter, $\langle P_2\rangle_B$, expressing the molecular alignment with respect to the field direction that is useful to estimate the changes in molecular organization produced by a field

$$\langle P_2\rangle_B = \frac{1}{N}\sum_{i=1}^{N} P_2(\boldsymbol{u}_i\cdot\boldsymbol{B}) , \qquad (3)$$

where $\boldsymbol{B}$ is the field direction (in the present study we have chosen the field along the z direction so $\boldsymbol{B}=(0, 0, 1)$). We expect $\langle P_2\rangle_B$ to be vanishingly small when the field applied is very low, while it should become closer and closer to the value of the usual order parameter $\langle P_2\rangle_\lambda$ as the field increases.

We have also investigated how these order parameters change going from the centre of the droplet to the surface. To do that we have divided our droplet into concentric shells in an onion skin fashion. Then the orientational order parameters $\langle P_2\rangle_\lambda$, $\langle P_2\rangle_R$ and $\langle P_2\rangle_B$ have been calculated for these different regions.

Another important aspect of the simulations is that we can have as results the molecular organization of the droplet. These data are available off line to calculate other quantities of interest. E.g. from the configurations, given as direction cosines, we have calculated the polydomain deuterium NMR lineshapes for a system of fictitious molecules with an axis of effective molecular uniaxial symmetry as obtained for our configurations. The full details of the calculation will be reported elsewhere [16]; here we only mention that diffusion effects are neglected and that every lineshape is an average obtained from a set of different configurations at the same temperature. Each particle provides a couple of transitions at

$$\omega_Q(\cos\beta_i) = \pm\tfrac{3}{4}\nu_Q P_2(\cos\beta_i)P_2(\cos\theta) , \qquad (4)$$

where β_i is the angle between the molecular and field axes, ν_Q is the quadrupole coupling constant and θ is the angle between the CD axis and molecular axis. (We have used $\nu_Q=175$ kHz and $\theta=59.45°$ as appropriate to the 4'-methoxy-4-cyanobiphenyl-d_3 (1OCB) molecule employed by Doane et al. [5].) We take the contribution of every particle to the spectrum as

$$\mathcal{S}[\omega, \omega_Q(\cos\beta_i), T_2^{-1}] = \frac{T^{-1}}{[\omega-\omega_Q(\cos\beta_i)]^2+(T_2^{-1})^2} + \frac{T_2^{-1}}{[\omega+\omega_Q(\cos\beta_i)]^2+(T_2^{-1})^2} , \qquad (5)$$

i.e. we assume for each line a Lorentzian shape with the intrinsic line width $T_2^{-1}=200$ Hz. The total spectrum is then calculated as the sample average

$$\mathcal{S}(\omega) = \langle \mathcal{S}[\omega, \omega_Q(\cos\beta_i), T_2^{-1}]\rangle_S , \qquad (6)$$

by summing over the N particles and then further averaged over a number of configurations.

3. Results

The energy versus temperature curves for the various field strengths (not shown to save space) show essentially a decrease of the energy in absolute terms upon increasing the field. The heat capacity, determined as the derivative of the energy with respect to the temperature, has the same behaviour for the three cases: the peaks have essentially the same intensity at the present resolution ($\approx 2.0\pm0.1$ in reduced units) and are shifted to higher temperatures (from $T^*\approx 0.99$ at $\xi=0$ [7] to $T^*\approx 1.06$ at $\xi=0.2$ and $T^*\approx 1.11$ at $\xi=0.5$) as the field increases. The shift to higher pseudo-transition temperatures is to be expected because of the stabilization of the ordered phase caused by the field.

The results for the order parameters $\langle P_2\rangle_\lambda$, $\langle P_2\rangle_R$ and $\langle P_2\rangle_B$ calculated over the entire droplet at effective field strengths $\xi=0.01$, 0.20 and 0.50 are shown as a function of temperature in fig. 1. We notice that at very low values of ξ (left plate) the radial order parameter is high, at least at low temperatures, indicating that a good hedgehog is formed. On the contrary, the field order parameter $\langle P_2\rangle_B$ fluctuates around zero, since there is no well-defined preferred direction in the laboratory frame. The order parameter referred to the instantaneous director, $\langle P_2\rangle_\lambda$, is also low, again consistently with lack of a uniform domain even in each configuration. Increasing the intensity of the external field, the two-order parameters related to instantaneous director and field tend to approach each other and at $\xi=0.5$ they are essen-

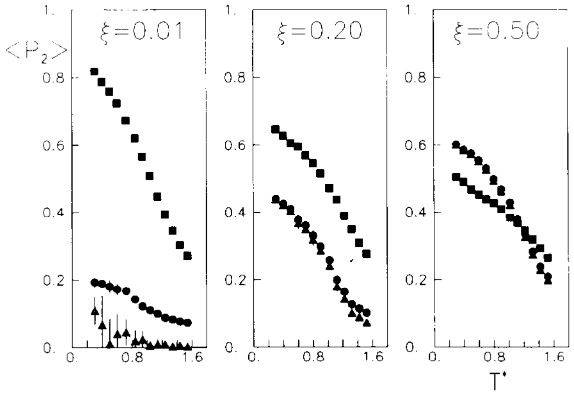

Fig. 1. The total order parameter $\langle P_2\rangle_\lambda$ (●), field order parameter $\langle P_2\rangle_B$ (△) and radial order parameter $\langle P_2\rangle_R$ (■) for droplets with RBC as a function of reduced temperature $T^*=kT/\epsilon$. We show Monte Carlo results for the different field strengths $\xi=0.01$ (left), $\xi=0.20$ (middle) and $\xi=0.50$ (right).

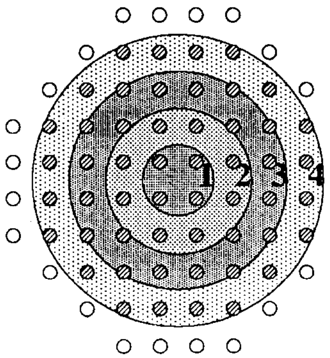

Fig. 2. A two-dimensional schematic representation of the shells for a droplet with 304 particles. The molecules in white are the surface particles defining the boundary conditions: they have orientations fixed toward the centre.

tially superimposed (right-hand plate in fig. 1). The radial order parameter remains relatively high, hinting that the organization still has some hedgehog character.

As mentioned before, we have calculated the various order parameters for shells at various distances from the centre as schematically sketched in fig. 2. We have discretized the radius to allow four shells for the droplet with $N=304$ (fig. 2) while for the larger droplet ($N=5832$) 11 shells have been defined. This kind of investigation is essential to examine the defects in the droplet and compare, e.g. with continuum theory predictions [17–19]. In fig. 3 we report a collection of results for the various order parameters versus r_S at selected temperatures for the various fields ξ as obtained for the smaller system studied.

We observe that the values of the radial parameter $\langle P_2\rangle_R$ are near zero for the first shells (i.e. near the centre) and are approaching their maximum at the greatest r_S where the influence of the radial boundary conditions dominates over the effect of the field. Increasing the strength of the field, the region with low $\langle P_2\rangle_R$ becomes larger and larger and the curves for the various temperatures collapse on top of each other.

The usual order parameter $\langle P_2\rangle_\lambda$ has an opposite behaviour: it shows a certain alignment of the molecules near the centre that vanishes at the surface. The field order parameter $\langle P_2\rangle_B$ is well characterized only at the higher values of ξ, when it becomes,

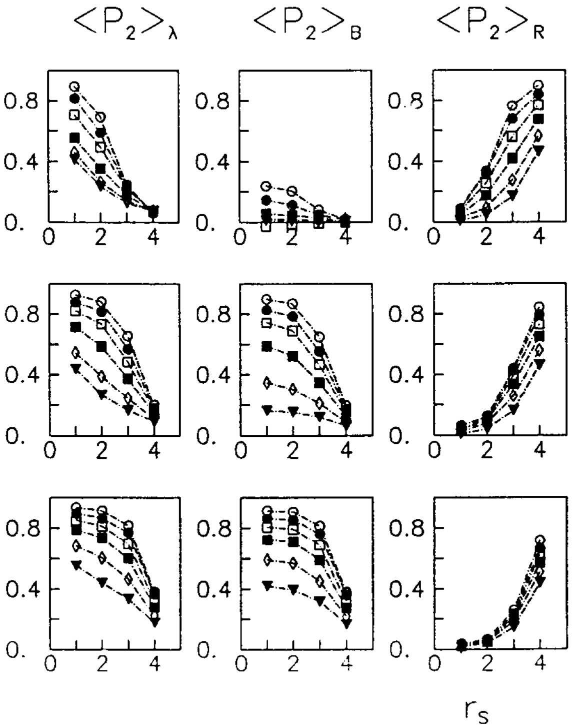

Fig. 3. Order parameters $\langle P_2\rangle_\lambda$, $\langle P_2\rangle_B$ and $\langle P_2\rangle_R$ against distance from the centre r_S (in lattice units) for field strengths $\xi=0.01$ (top), 0.20 (middle), 0.50 (bottom). We show results for $N=304$ particles and various temperatures $T^*=kT/\epsilon$, i.e. (○) $T^*=0.4$; (●) $T^*=0.6$; (□) $T^*=0.8$; (■) $T^*=1.0$; (◇) $T^*=1.2$; (▼) $T^*=1.4$.

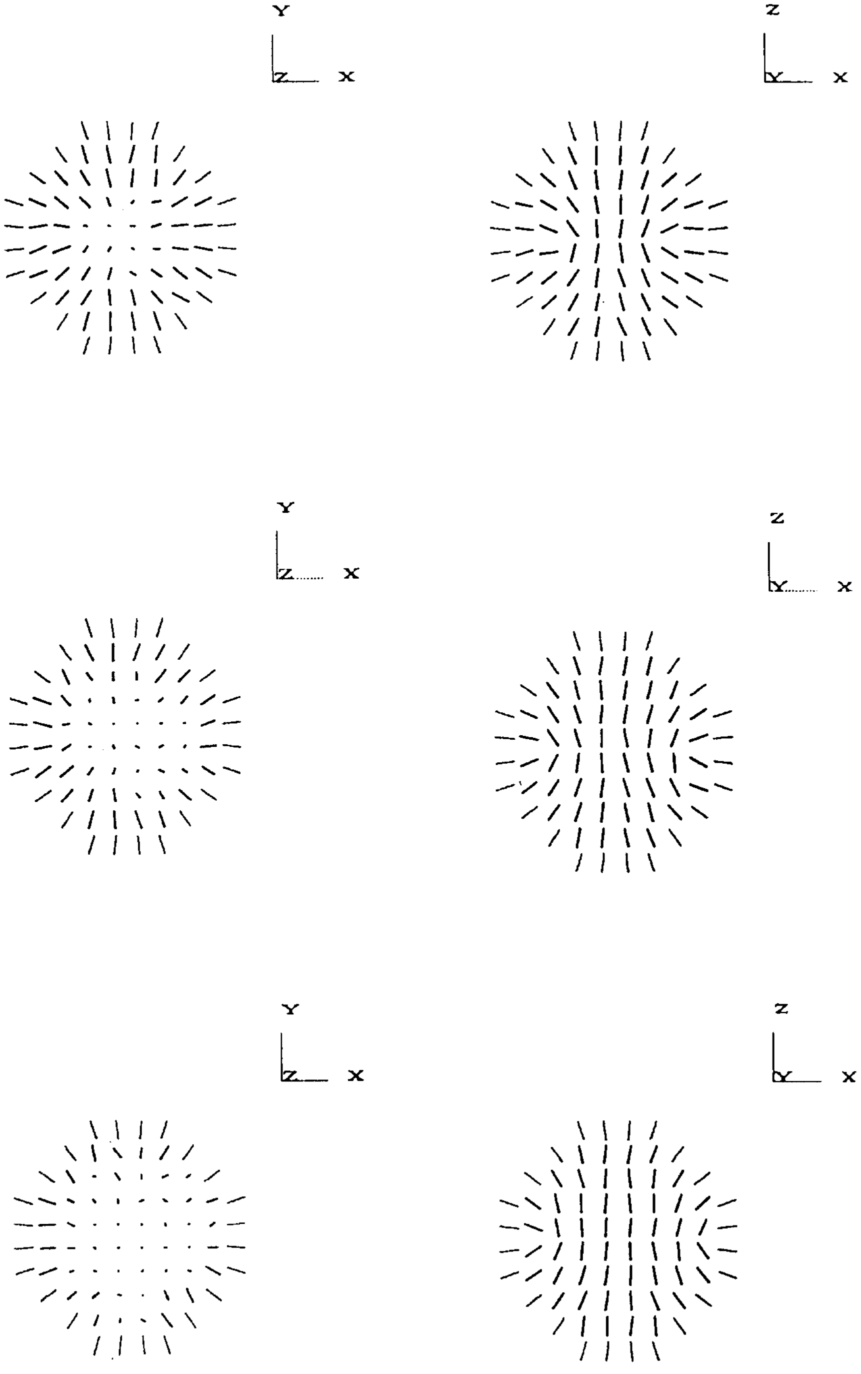

Fig. 4. Snapshots of typical droplet configurations for field strengths $\xi=0.01$, 0.20, 0.50 at a temperature $T^*=0.2$. For each case an equatorial and a vertical section are reported.

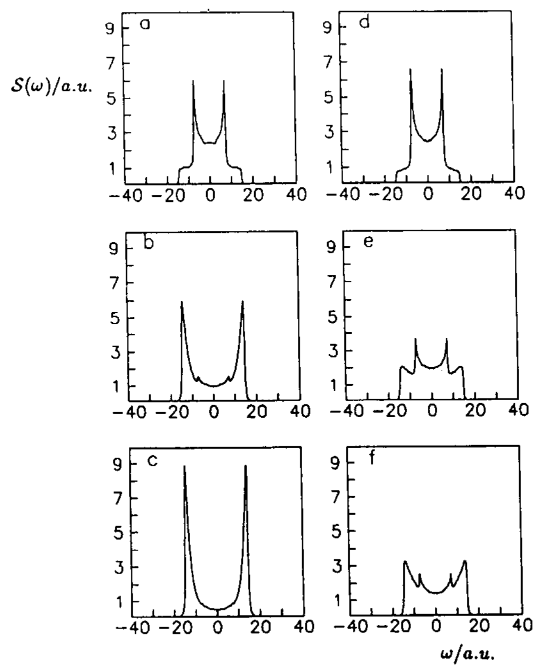

Fig. 5. Polydomain deuterium NMR lineshapes calculated from the molecular organizations obtained by the Monte Carlo method. Results for field strengths $\xi=0.01$ (top), $\xi=0.20$ (middle) and $\xi=0.50$ (bottom) are shown at a "low" ($kT/\epsilon=0.4$) and a "high' temperature ($kT/\epsilon=1.2$). Frequency is in kHz (see text).

as for the global one shown in fig. 1, more similar to $\langle P_2\rangle_\lambda$.

In the absence of a field the radial order parameter was predicted to saturate with r_S by Schopohl and Sluckin [17] and we find this supported by the present simulations and by preliminary work on the larger number of particles [16]. The field and temperature effects can be qualitatively seen from some snapshots of the molecular organization obtained from the simulations reported in fig. 4. Two section views are plotted for each value of ξ, one is the xy plane and the other one the zx plane. From these plots the competition between the ordering induced by the boundary conditions and the effect of the field is apparent. When the strength of the field is low (top) only a limited number of particles, at the centre of the droplet, tends to align with the direction of the field, while the radial alignment for the molecules nearer to the surface induced by the "ghosts" propagates toward the centre. Increasing the field, the "aligned core" becomes larger and the director configuration assumes a bifocal structure.

Since in real experiments the actual configurations as shown in fig. 4 are not accessible and the technique most often employed is deuterium NMR [4–6], we have chosen to calculate also deuterium NMR lineshapes corresponding to the different organizations.

The NMR line shapes calculated from an average over ten droplet configurations of the large ($N=5832$) droplets at different field strengths and at two temperatures are in fig. 5. The deuterium NMR spectrum corresponds to a superposition of doublets originating from each molecule in the droplet. The deuterium splitting has the greatest magnitude when the molecules have their principal axis parallel to the applied field. For the low-temperature case, at the lowest field (fig. 5a), the droplet configurations give rise to a lineshape including contributions from an essentially three-dimensionally isotropic distribution of molecules with respect to the direction of the applied field. At stronger fields the population of molecules parallel to the field increases and, as we see in fig. 5c, the lineshape essentially reduces to a doublet corresponding to the parallel splitting. For the isotropic case, i.e. the high-temperature case (figs. 5d–5f), the lineshape obtained from the lowest field has still the characteristics of a powder spectrum (fig. 5d). However, even for the high-temperature case the population of molecules aligned with the field increases when higher fields are applied to the system, leading to the more complex pattern in figs. 5e and 5f.

4. Conclusions

The Monte Carlo method has been applied to study the effect of an external field on the molecular organization of a nematic droplet with radial boundary conditions. We have calculated the order parameters across the droplet as well as deuterium NMR lineshapes corresponding to the molecular organizations obtained at various field strenghts.

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