Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006.

To cite this article: C. Chiccoli , P. Pasini , F. Semeria & C. Zannoni (1992): Monte Carlo Simulations of Model Nematic Droplets, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 212:1, 197-204

To link to this article: http://dx.doi.org/10.1080/10587259208037260

Mol. Cryst. Liq. Cryst. 1992, Vol. 212, pp. 197–204
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Printed in the United States of America

MONTE CARLO SIMULATIONS OF MODEL NEMATIC DROPLETS

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(*Received May 8, 1991*)

Abstract We present Monte Carlo computer simulations of model nematic droplets with radial boundary conditions and various anchoring strengths and we investigate the orientational order and the molecular organizations in these systems that mimic polymer dispersed liquid crystals (PDLC). We find a hedgehog organization at high anchoring strengths and that an ordered domain is created in the droplet center at lower strengths.

Keywords: nematic, droplets, Monte Carlo, simulation

INTRODUCTION

Polymer dispersed liquid crystals (PDLC) consist of liquid crystal droplets of submicron to micron size embedded in a polymer matrix. They have received a great deal of attention, both for their applications in display technology[1–4] and for their fundamental interest concerning the behavior of mesophases and the structure of defects[4–8] in a restricted environment.

The molecular organization inside the droplets can be strongly influenced by varying the properties of the polymer outside and the preparation method, i.e. the boundary conditions at the droplet surface. These in turn will influence the orientation of molecules near to the surface and the aligning effect will tend to propagate inside the droplet. In general there will be a competition between the molecular orientation induced by the surface boundary condition, the ordering effects 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 depend on a number of factors, including the strength of the surface interaction, the temperature and so on, so that it is not easy to predict it with microscopic theories and even, especially for the smaller sizes, to investigate experimentally.

We believe that Monte Carlo simulations can be a particularly effective tool to predict the combined effect of these factors without resorting to continuum theory,

whose applicability on such small scales is not obvious, and we plan to investigate this systematically. In two recent papers we have studied, using Monte Carlo simulations, the molecular organization in droplets with radial[9] and tangential[10] boundary conditions. In particular in[9] we have considered radial boundary conditions with a rather strong anchoring energy, i.e. with a surface interaction of the same strength as that existing between the nematogen particles and we have investigated temperature and size effects. Here we wish to examine the effect of changing the anchoring strength in droplets with radial boundary conditions.

THE MODEL

Our model droplet is an irregular sphere $\mathcal{S}$ obtained from a cubic lattice by considering all the molecules falling within a given distance from the center. Clearly our sample is not exactly spherical, even though it becomes more and more so as the droplet size increases, but then true cavities in the polymer will hardly be spherical too at very small sizes.

The particles at the cubic lattice sites interact through the attractive nearest neighbours Lebwohl - Lasher[11] pair potential and the different boundary conditions are mimicked assuming a layer of outside particles $\mathcal{G}$ with an orientation determined by the specific type of boundary conditions. We keep the orientations of the particles outside the box fixed with the long axis aligned in the direction of the droplet center. Thus in practice we let the particles interact with a pair potential:

$$U_{i,j} = \begin{cases} -\epsilon_{ij} P_2(\cos\beta_{ij}), & \text{for } i,j \in \mathcal{S} \\ -\epsilon_{ij} J P_2(\cos\beta_{ij}), & \text{for } i \in S, j \in \mathcal{G} \end{cases} \tag{1}$$

where ϵ_{ij} is a positive constant, ϵ, for nearest neighbours 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 and J determines the strength of coupling to the external environment. When the interaction between molecules inside and outside is the same ($J = 1$) and when of course the orientation of the particles outside is not frozen the model reduces to the usual Lebwohl - Lasher (LL) model, which in turn is the prototype one for nematic type orientational phase transitions[12,13]. The effect of boundaries on the simulation is in principle distinct from that of finite size, simply due to limited number of particles as we have shown in[9,10] using the Cluster Monte Carlo method.[12]. These calculations showed that even with a few hundred particles we obtain a reasonable approximation to macroscopic, bulk, behavior with cluster updating boundary conditions, while different results are obtained when free or different kinds of fixed boundary conditions are employed.

THE SIMULATIONS

We have performed a set of independent simulations for radial boundary conditions with different anchoring strengths by changing the parameter J that couples molecules inside and outside, while keeping the number of particles constant to $N = 304$. All the simulations were started from a system with the particles pointing toward the center. At higher temperatures we have taken the starting configuration to be an equilibrium one at a lower temperature. We have then employed the standard Metropolis Monte Carlo to update the lattice for a certain number of cycles i.e. of sets of N attempted moves. The details of the calculation have beed described in full in[9,10] and will not be repeated here. We calculate the dimensionless heat capacity C_V^* from a differentiation of the average energy with respect to temperature and second and fourth rank order parameters $< P_2 >_\lambda$, $< P_4 >_\lambda$ defined over the whole droplet from the maximum eigenvalue of the ordering matrix[13] as discussed previously[9-10]. We have also calculated a *radial order parameter* $< P_2 >_R$[9] defined as:

$$< P_2 >_R = \frac{1}{N} \sum_{i=1}^{N} P_2(\mathbf{u}_i \cdot \mathbf{r}_i), \tag{2}$$

where N is the number of particles contained in the sphere, $\mathbf{u}_i$ is the direction cosine of the i-th particle and $\mathbf{r}_i$ is its radial vector. This expresses disordering from the perfect hedgehog organization and is a maximum when all the particles point exactly toward the center of the sphere. We have also investigated how the order parameters change from the center of the droplet to the surface [6-8]. To do that we have divided our droplet into concentric shells in an onion skin fashion and we have evaluated the orientational order parameters $< P_2 >_\lambda$ and $< P_2 >_R$ in these different shells.

RESULTS

In fig. 1 we show the energy and heat capacity (top) and the total and radial order parameter for droplets of 304 particles and for anchoring strengths $J = 0.25$, $J = 0.5$, $J = 1$ and $J = 2$.

In Table I we summarize the values of the heat capacity peaks and the temperatures at which they occur. As we can see there are no major changes in the behavior of the heat capacity, except for a flattening of the heat capacity peak as J increases. The global $< P_2 >_\lambda$ is strongly reduced, while at the same time $< P_2 >_R$ increases as the anchoring strength increases. This hints that a hedgehog organization with no average director exists at high J [9].

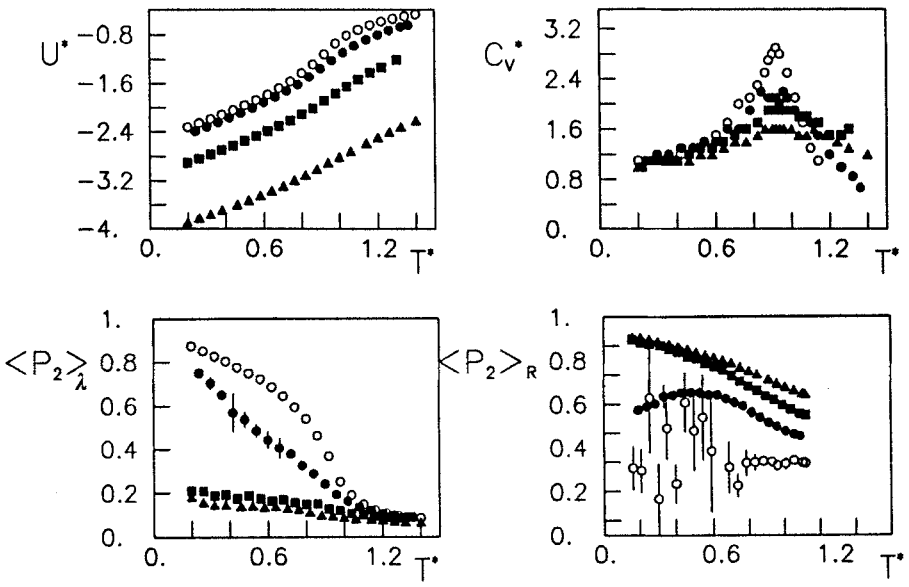

FIGURE 1 The dimensionless energy per particle U^*, heat capacity $C_V{}^*$, total order parameter $< P_2 >_\lambda$ and radial order parameter $< P_2 >_R$ for droplets with RBC as a function of reduced temperature $T^* = kT/\epsilon$. We show Monte Carlo results for $J = 0.25(\bigcirc)$,$0.5(\bullet)$, $1(\blacksquare)^9$, $2(\blacktriangle)$.

TABLE I The peak values of the heat capacity $C^*_{V_{max}}$ and the temperatures at which they occur, $(T^*)_{C_V}$, for radial boundary conditions droplets with N particles and anchoring strength J. We also report for comparison the values previously obtained by us[9] for $J = 1$.

N	J	$C^*_{V_{max}}$	$(T^*)_{C_V}$
304	2.0	1.7	0.91 ± 0.03
304	1.0	2.04	0.99 ± 0.03
1568	1.0	2.7	1.10 ± 0.03
7616	1.0	3.5	1.10 ± 0.02
304	0.5	2.2	0.97 ± 0.03
304	0.25	2.9	0.93 ± 0.03
304	0.0	3.26	0.98
304 CMC	1	17.8	1.12

The observables calculated over the entire sample do not give much insight

on the molecular organization, so in fig. 2 we present instantaneous equilibrium configurations both as perspective views and as equatorial sections showing the orientations of the droplet particles together with the fixed external ones at a rather low temperature ($T^* \approx 0.2$).

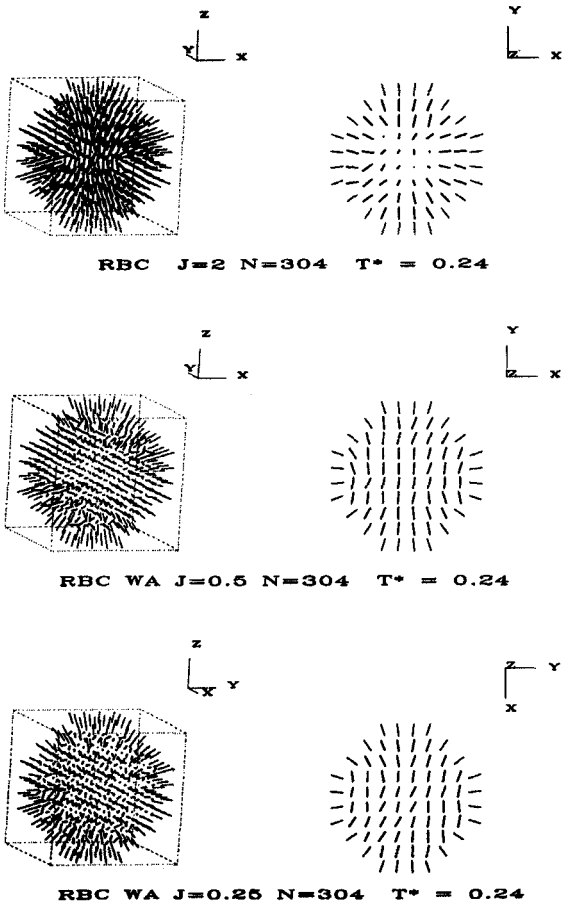

FIGURE 2 Perspective views and radial sections of typical droplet configurations for and anchoring strength $J = 2, 0.5, 0.25$ and temperature $T^* = 0.24$

We see that a hedgehog defect is formed at the higher anchoring strength. However, it is interesting and maybe more unexpected to see that even at this low temperature the hedgehog distribution does not seem to propagate all the way to the center of the sample. As the strength of the interfacial interaction is lowered from $J = 2$ to $J = 0.25$ (top to bottom in the figure) we see that the molecules prefer to order one with respect to the other, rather than to follow the boundary constraint. At high temperatures and particularly above the heat

capacity anomaly, the system is disordered and the radial boundary conditions do not propagate inside, as expected. The propagation of boundary condition ordering inside the sample is well represented by calculating order parameters $< P_2 >_\lambda$ and $< P_2 >_R$ at different coupling strengths and different temperatures as a function of the distance from the drop center.

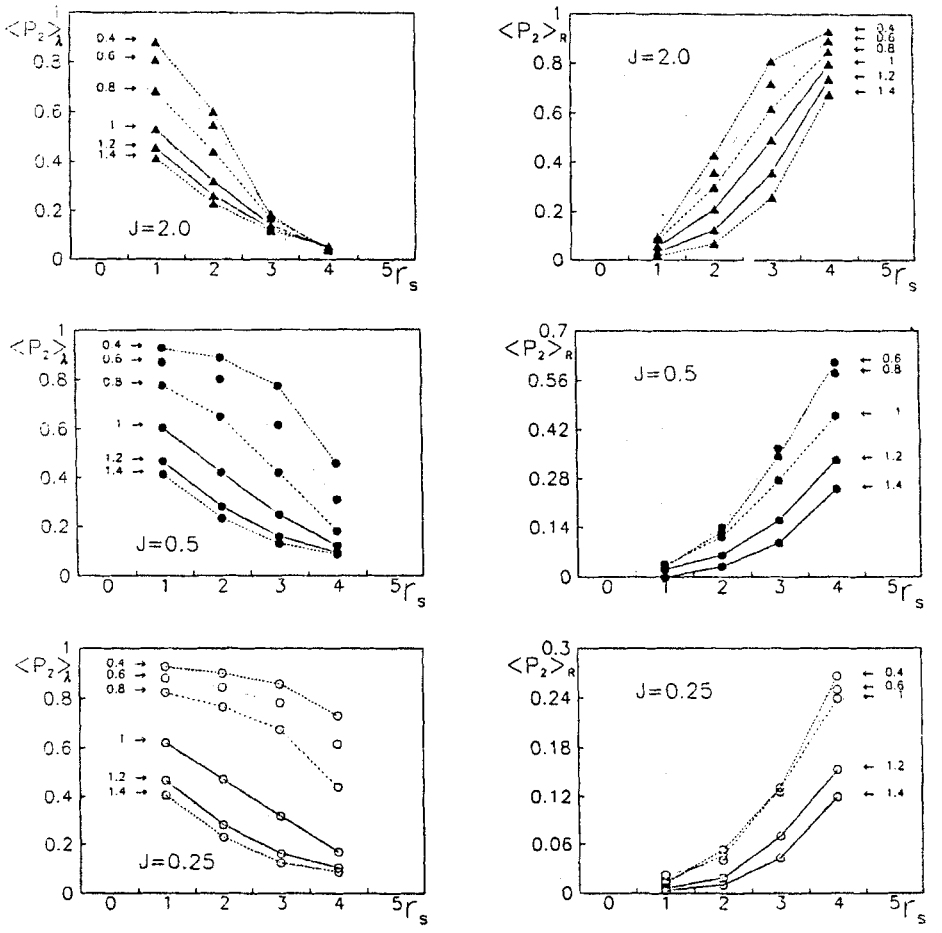

FIGURE 3 The second rank order parameter $< P_2 >_\lambda$ (left) and the radial order parameter $< P_2 >_R$ (right) against distance r_s from the droplet center in lattice units for three anchoring strength J and at different temperatures T^*, indicated in the plot near every curve.

In fig.3 r_s numbers the shells, giving their distance from the center. We

have a unit shell thickness, so that the shell at r_K contains all the particles with $r_{K-1} \leq r < r_K$ from the center. Here we have an even number of lattice points along x, y, z so that the center of the sphere does not correspond to a particle. At high J the eigenvalue order parameter $< P_2 >_\lambda$ is essentially zero for the outer shell which contains the molecules directly interacting with the outside. As we move toward the center the effect of boundary conditions weakens and the molecules try to align according to a common director. The central shell (core) can form a domain which becomes more ordered as the temperature is lowered. The radial order parameter on the right shows a somewhat opposite trend, that at high anchoring strength resembles that predicted by Schopohl and Sluckin[6] using Landau-de Gennes theory, with an increase in ordering on moving from a disordered core towards the drop surface. It has been suggested that the structure of the central core is biaxial.[7-8] We cannot answer this point at present and we plan to investigate this in a separate work.

CONCLUSIONS

We have studied by Monte Carlo a nematic droplet with radial boundary conditions and various anchoring strengths. We have shown that at weak anchoring strength an ordered domain tends to form in the center of the drop at low temperature, rather than the hedgehog defect appearing at higher strengths.

ACKNOWLEDGMENTS

We thank Consorzio INFM for support through Progetto Polimeri Liquido Cristallini. Support from MPI and CNR is also acknowledged.

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