Mol. Cryst. Liq. Cryst., 1992, Vol. 221, pp. 19–28
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Computer Simulations of Nematic Droplets with Toroidal Boundary Conditions†

C. CHICCOLI, P. PASINI and F. SEMERIA
INFN Sez. di Bologna and CNAF, Viale Ercolani, 8, 40138 Bologna, Italy

and

C. ZANNONI
Dipartimento di Chimica Fisica ed Inorganica, Universita', Viale Risorgimento, 4, 40136 Bologna, Italy

(Received January 10, 1991)

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

PACS: 02.50 Monte Carlo studies
PACS: 61.30.Jf Defects in liquid crystals
PACS: 61.30.Gd Orientational order of liquid crystals
PACS: 64.70.M Liquid Crystals phase transitions.

Keywords: polymer dispersed liquid crystals, PDLC, Monte Carlo, boundary conditions

1. INTRODUCTION

The preparation of sub-micron size nematic liquid crystal droplets dispersed in a polymer matrix has been demonstrated by Doane *et al.* (cf.[1] and References therein) using phase separation techniques. The investigation of these polymer dispersed liquid crystals (PDLC) is quite fascinating for a number of reasons. For one it is interesting in itself to study the behaviour of matter in a small confined environment and here the droplet size can be so small that cooperative phenomena are strongly affected. For example the nematic-isotropic phase transition is shifted in temperature or suppressed altogether and replaced by a continuous change as the droplet size becomes small enough.[2] The rounding and shifting of a transition indicator, e.g., of the heat capacity peak is well known in computer simulations, where one

---

† Work presented at the 3rd meeting Italy-USSR on the Physics of Liquid Crystals and Langmuir-Blodgett films, 1990.

Correspondence to Prof. C. Zannoni.

is forced to deal with small finite samples.[3,4] The effect is known to be important also in real experiments, at least for first order phase transitions. For instance the melting point of benzene and other organic materials in "controlled pore glass" decreases with pore diameter[5] and shifts of even 10–20 degrees are observed for cavities of 0.02 μm to 0.004 μm diameter. The behavior at a second order transition or at weak first order one, like the nematic-isotropic one, is less clear, although a shift of the transition to lower temperatures has been found for para azoxy anisole in small silica pores.[6] Another reason of great interest in these PDLC systems lies in their extremely large surface to volume ratio. It is well known that nematic liquid crystals can be aligned by surface effects[7] and indeed this is behind their usefulness in display applications. Thus the molecular organization in 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. For example radial, toroidal and bipolar molecular organizations have been obtained.[1,8] It appears that radial configurations, where molecules inside the drop point on average toward the centre of the sphere, are harder to obtain experimentally, especially in small droplets.[8] Often a tangential orientation is obtained with epoxy polymers.[1,8] Two surface boundary conditions compatible with tangential anchoring are the bipolar and the toroidal one.[9–12] In the bipolar configuration the molecules at the surface lie tangent to the sphere and are directed towards the pole along the meridians. In the toroidal or circular boundary conditions the particles at the interface lie in plane perpendicular to the z axis while having orientations tangential to the droplet surface.

The surface boundary conditions will tend to influence the orientation of molecules near the surface and the aligning effect may propagate inside the droplet. In general there will be competition between the molecular orientation induced by surface boundary condition, the effects of ordering on the liquid crystal itself due to the molecules trying to arrange parallel to each other, and the disordering effect of temperature.

Thus on one hand PDLC offer the stimulating opportunity of being able to condition the molecular organization of a large but not macroscopic ensemble of molecules. On the other hand the actual result obtained for a certain boundary condition will depend on a number of factors, including the strength of the surface interaction, the temperature and so on.

We believe that Monte Carlo simulations can be a particularly effective tool to predict the combined effect of these factor and we plan to investigate this systematically. In a separate publication[13] 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.

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.[14] The "bulk" LL model has been studied with a variety of theoretical techniques as well by periodic boundary conditions (PBC)[14,15] and Cluster Monte Carlo (CMC)[16] simulations and it has been found to give a weak first order orientational phase transition at temperature $T^* \equiv kT/\varepsilon \approx 1.1232$,[14] 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 to see how they affect the behaviour of the system.

Here we wish to investigate another important boundary condition: that of tangential anchoring with a toroidal configuration (TBC). We think of the effect of the polymer interface as determining the orientation of molecules at the boundary independently from what happens inside the sample and independently of temperature. Thus we have chosen to mimic the effect of polymer on the liquid crystal by assuming that the orientation of the first shell of particles outside the drop, i.e. of the "ghosts," as they are called in Monte Carlo jargon, is fixed along a direction dictated by the boundaries.

2. THE MODEL

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 $\mathbf{r}_i$ inside the sphere. The jagged sphere S realized in this way is our model droplet. 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[14] pair potential and the different boundary conditions are mimicked assuming a layer of outside particles G with an orientation determined by the specific type of boundary condition.

Thus in practice we consider that the particles interact with a pair potential:

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

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.[14,15] 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,[16] with the same number of particles but with updating boundary conditions to see how well macroscopic behaviour can be a result of the different way of treating boundaries.

3. MONTE CARLO SIMULATIONS

We have performed a full temperature scan for four jagged droplets of $N = 304$ particles interacting with the simple P_2 potential in Equation 1 for different values of the strength parameter J, i.e. $J = 1.$, $J = 0.5$, $J = 0.25$ and $J = 0$. We have also simulated over a large temperature range a bigger system of 1568 particles for $J = 1.$, mainly to try and understand the dependence of our results from the size of the sample. For the same reason we looked at two selected temperatures for $J = 1$ and $N = 7616$ particles.

Another full simulation of the Lebwohl-Lasher model system using the Cluster Monte Carlo method[16] has been performed on the small droplet to obtain, as already mentioned, a comparison with pseudo-bulk results independent from the toroidal boundary conditions.

The TBC calculations at each J are started at low temperatures from a system with the orientations of the sample particles inside arranged in onion-skin like fashion parallel to the outside toroidal ghosts. At higher temperatures the starting configuration has been taken from an already equilibrated configuration at a lower temperature. The usual Metropolis Monte Carlo procedure is then used to update the lattice for a certain number of cycles i.e. of sets of N attempted moves. Each particle is selected at random for trial move at every cycle using a random shuffling algorithm.[15] A new trial orientation of the chosen particle is then generated by a controlled angular variation from the previous one using the Barker-Watts technique.[17] We have checked that a rejection ratio not too far from 0.5 is achieved. The energy of the system is then recalculated and evolution proceeds as before. Second rank order parameters over the whole sample have been evaluated by diagonalization of the ordering matrix[4] and the fourth rank order parameters have been computed with the algorithm introduced in Reference 15.

We have used at least 30000 equilibration cycles for the simulation of the $N = 304$ systems with Toroidal Boundary Conditions, while for the $N = 1568$ and $N = 7616$ systems simulations we have discarded at least 40000 equilibration cycles before starting production. For the Cluster Monte Carlo simulation we have discarded about 18000 equilibration cycles.

After equilibration, production runs of varying length, according to the system studied, were followed. Thus 20 Kcycles have been used for the 1568 droplet, and up to 12 Kcycles for the other simulations. Each calculation was divided in chains of 1000 to 2000 cycles. Statistical errors were estimated as standard deviations from the average over these runs. During the production run various observables have been calculated in addition to the internal energy and second rank order parameters calculated at every cycle as already described. Every property of interest, A, is evaluated at every cycle. After a certain number of cycles m_J has been accumulated an average A^J is calculated thus providing an effective coarse graining of the trajectory. A further grand average is then computed as the weighted average over M such supposedly uncorrelated segments. The attendant weighted standard deviation from the average σ_A is also calculated and gives the error estimates shown in the figures. We have calculated for each simulation energy, second and fourth rank order parameters.

4. RESULTS

The energy-temperature plot for the models studied is shown in Figure 1A.

We see that the energy plots are rather different but that the curves are essentially

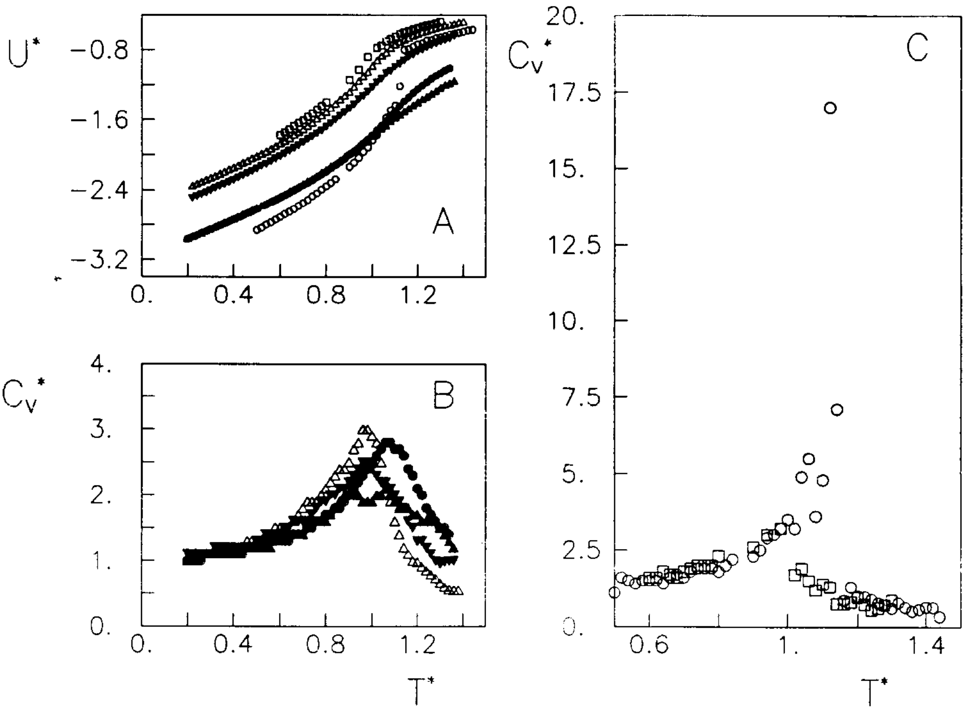

FIGURE 1 The dimensionless energy per particle U^* (A) and heat capacity C_V^* (B, C) of a droplet with TBC as a function of reduced temperature $T^* = kT/\varepsilon$. We show results for $N = 304$ particles and strength parameter J, $J = 1.$ (▲), $J = 0.5$ (▼), $J = 0.25$ (△) (plate A). We also show on plate C a CMC (○) and an empty space boundary, $J = 0$, (□) simulation and a $N = 1568$, $J = 1$ (●).

TABLE I

Heat capacity peak values and the temperatures at which they occur

N	J	$C^*_{v_{max}}$	$(T^*)_{C_v}$
304	1.0	2.1 ± 0.2	1.06 ± 0.02
1568	1.0	2.8 ± 0.2	1.08 ± 0.02
304	0.5	2.5 ± 0.2	0.98 ± 0.02
304	0.25	3.0 ± 0.2	0.98 ± 0.02
304	0.0	3.3 ± 0.2	0.98 ± 0.02
304 CMC	1	17.8 ± 0.3	1.12 ± 0.02

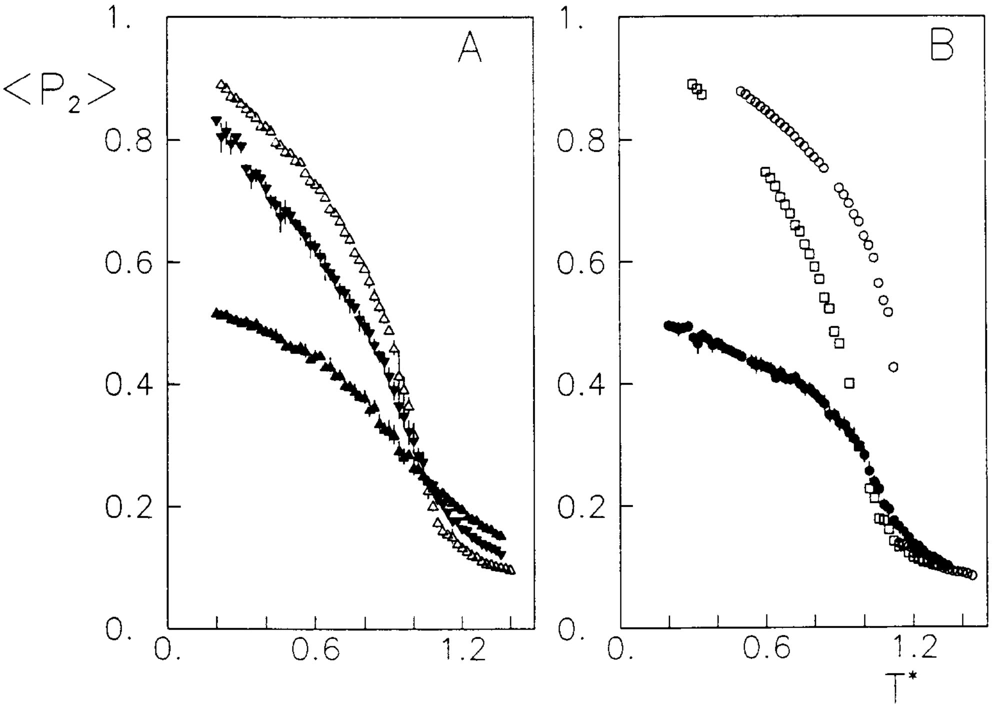

FIGURE 2 The second rank order parameter $\langle P_2 \rangle_\lambda$ vs reduced temperature of a TBC droplet with $N = 304$ particles and strength parameter J, $J = 1$. (▲), $J = 0.5$ (▼), $J = 0.25$ (△) (plate A). We also show on plate B a CMC (○) and an empty space boundary, $J = 0$, (□) simulation and a $N = 1568$, $J = 1$ (●) against reduced temperature $T^* = kT/\varepsilon$.

parallel to each other, so that the dimensionless heat capacity C_V^* shown in Figure 1B for the different strengths of interaction with the outside are rather similar, giving in all cases a small heat capacity anomaly around $T^* = 1$. The temperatures corresponding to these peak capacities and the peak value of the heat capacity itself are shown in Table I.

We also show in Figure 1C (○) the pseudo-bulk peak obtained updating the ghosts with the Cluster Monte Carlo prescription.[16] This procedure is designed to try and reproduce bulk behavior based on a limited number of particles and indeed we find a very sharp peak at $T^* = 1.12 \pm 0.02$, i.e. quite near to the value obtained with large 30 × 30 × 30 lattice and periodic boundary conditions simulations.[15] Thus given the same number of particles, the effect of what is outside the droplet is extremely important.

The other calculation shown in Figure 1C (□) is for empty space outside the droplet. Here the peak is at $T^* = 0.98$, i.e. lower than the bulk. Looking at Table I we see that decreasing the coupling constant with $J = 1$ to $J = 0.25$ tends to move the heat capacity peak temperature down toward the empty space value, even though the difference between 0.5, 0.25 and 0 cannot be appreciated with the present simulations.

Second and fourth rank order parameters $\langle P_2 \rangle_\lambda$ and $\langle P_4 \rangle_\lambda$ have been calculated by setting up and diagonalizing the ordering tensor as discussed in detail earlier in

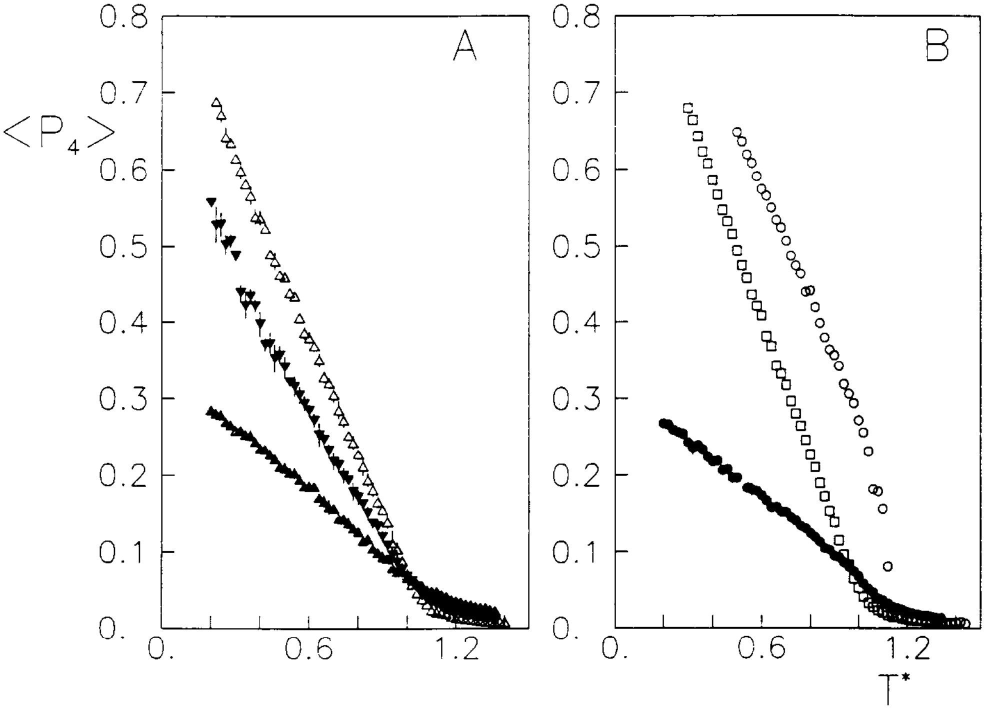

FIGURE 3 The fourth rank order parameter $\langle P_4\rangle_\lambda$ vs reduced temperature of a TBC droplet. Same cases and symbols as in Figure 1.

References 4 and 15. The order parameters $\langle P_2\rangle_\lambda$ for the various systems studied are shown in Figure 2.

On the left (plate A) we see the effect of changing the strength of the coupling from $J = 1$ to $J = 0.5$ to $J = 0.25$. We recall that $\langle P_2\rangle_\lambda$ gives the average order with respect to the instantaneous director present in the sample. If this order parameter is high it means that the molecules tend to point along a common direction at any time, even though this overall director may well fluctuate from a configuration to another.[4] Here we see that the order with respect to a common director increases as the coupling is reduced and becomes more and more similar to that of the system with empty space outside ($J = 0$), shown on the right (□). The effect of size is relatively less important. Indeed the order parameter for the $N = 1568$, $J = 1$ is so similar to that for $N = 304$, that we have plotted it on the right hand plate (●) to avoid overlap. We also plot as a reference $\langle P_2\rangle_\lambda$ for the pseudobulk (○), calculated for $N = 304$ particles with Cluster Monte Carlo lattice updates. In Figure 3 we see that $\langle P_4\rangle_\lambda$ yields similar results.

We can understand the behavior of the order parameters as the result of a compromise between boundary and aligning effects. In Figure 4 we report some typical instantaneous configurations for low temperature ($T^* = 0.24$) and high temperature ($T^* = 1.36$).

We show both perspective views and equatorial sections showing both the orientations of the fixed external ghosts and that of the particles inside. At $T^* =$

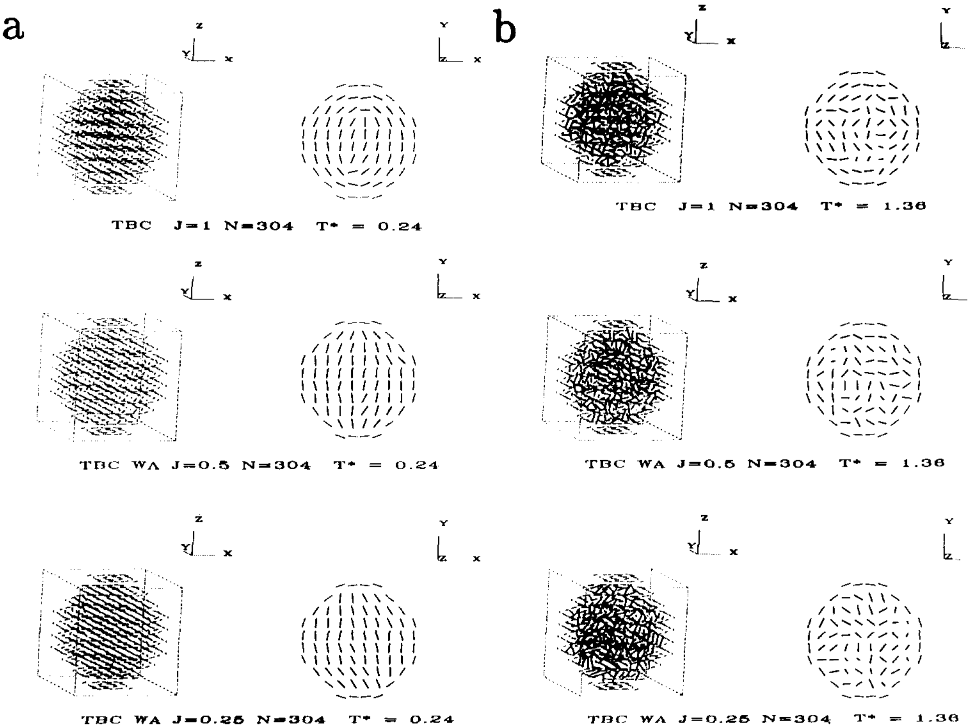

FIGURE 4 A perspective view of a typical molecular organization for a droplet with TBC and N = 304 at reduced temperature T^* = 0.24 (a) and 1.35 (b). We show the effect of reducing the anchoring strength from J = 1 (top), J = 0.5 (middle), J = 0.25 (bottom).

1.36, above the heat capacity anomaly, the tangential boundary conditions do not propagate inside, as expected. However, it is interesting and somewhat unexpected to see that even at low temperature the onion skin distribution of molecules does not seem to propagate all the way to the centre of the sample. As the strength of the interfacial interaction is lowered from J = 1 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 J = 0.25 even the first layer is already quite decoupled from the surface. This is of course consistent with what we have found earlier for $\langle P_2 \rangle_\lambda$. Next we have looked at the effect of changing sample size, keeping the interfacial interaction fixed. In Figure 5 we see equatorial sections of the droplets with J = 1 for N = 304 (the one just examined), 1568 and 7616 particles.

Here again it seems that the system is not really assuming a uniform organization with the director arranged in concentric shells. Instead we see an oriented domain at the centre growing as the sample size grows. There is no external field applied in the simulation so the absolute orientation of the domain is irrelevant and, as we see from Figure 5, it changes for the three simulations shown.

The obtainment of rather complex molecular organizations that change qualitatively as well as quantitatively with temperature illustrates the power of the present approach to the microscopic study of PDLC. The treatment has also the

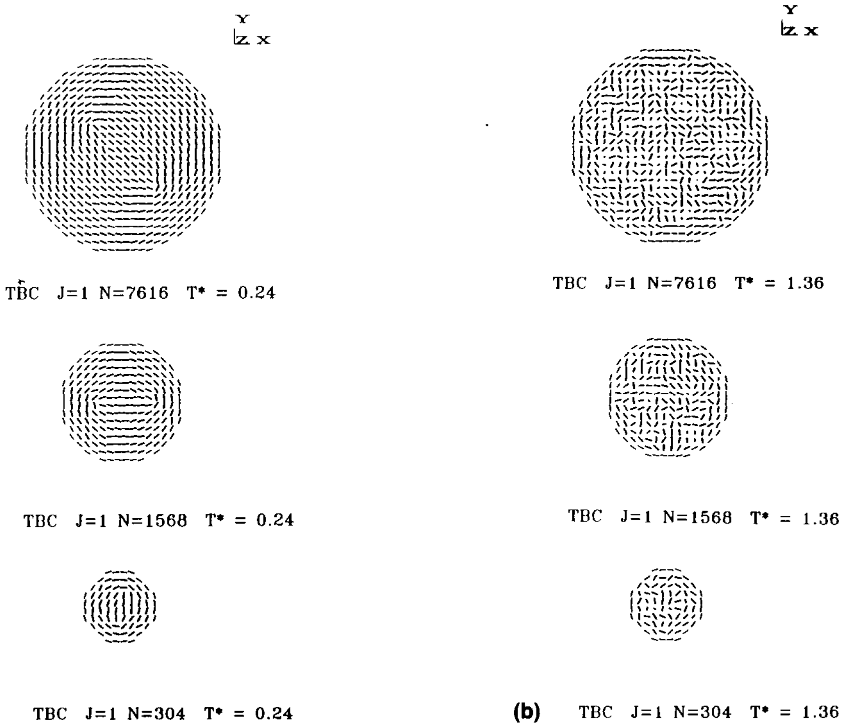

FIGURE 5 Equatorial sections showing projections of typical instantaneous configurations for N = 304 (bottom), 1564 (middle), 7616 (top) at temperatures T^* = 0.24 (left), 1.36 (right).

advantage of making use only of microscopic, molecular level, quantities without assuming the validity of continuum theory concepts that might be hard to justify on the present mesoscopic scale.

Acknowledgment

We wish to thank CNR (Rome) for supporting this work under P.F. "Sistemi informatici e Calcolo Parallelo," Sottoprogetto 1: "Calcolo Scientifico per grandi sistemi" and MURST for general support. We also thank Professors G. Chidichimo and A. Golemme (UNICAL) for stimulating discussions.

References

1. J. W. Doane, A. Golemme, J. L. West, J. B. Whitehead and B.-G. Wu, *Mol. Cryst. Liq. Cryst.*, **165**, 511 (1988).
2. A. Golemme, S. Žumer, D. W. Allender and J. W. Doane, *Phys. Rev. Lett.*, **61**, 2937 (1988).
3. H. Müller-Krumbhaar, *Monte Carlo Methods in Statistical Physics*, K. Binder editor, Springer-Verlag, Berlin, 195 (1979).
4. C. Zannoni, *The Molecular Physics of Liquid Crystals*, G. R. Luckhurst and G. W. Gray eds., Academic, Chap. 9, 191 (1979).
5. C. L. Jackson and G. B. McKenna, *J. Chem. Phys.*, **93**, 9002 (1990).
6. D. Armitage and F. P. Price, *Chem. Phys. Lett.*, **44**, 305 (1976).
7. P. G. de Gennes, *The Physics of Liquid Crystals*, Oxford, U.P., London (1974).

8. A. Golemme, Ph.D. thesis, Kent State University, (1987).
9. R. D. Williams, *J. Phys. A,* **19**, 3211 (1986).
10. S. Žumer, M. Vilfan and I. Vilfan, *Liq. Cryst.*, **3**, 947 (1988).
11. I. Vilfan, M. Vilfan and S. Žumer, *Phys. Rev. A.*, **40**, 4724 (1989).
12. O. D. Lavrentovich and V. V. Sergan, *Nuovo Cim. D.*, **12**, 1219 (1990).
13. C. Chiccoli, P. Pasini, F. Semeria and C. Zannoni, *Phys. Lett. A.*, **150**, 311 (1990).
14. P. A. Lebwohl and G. Lasher, *Phys. Rev. A.*, **6**, 426 (1972).
15. U. Fabbri and C. Zannoni, *Mol. Phys.*, **58**, 763 (1986).
16. C. Zannoni, *J. Chem. Phys.*, **84**, 424 (1986).
17. J. A. Barker and R. O. Watts, *Chem. Phys. Lett.*, **3**, 144 (1969).