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Biaxial Nematic Droplets and their Optical Textures. A Lattice Model Computer Simulation Study

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Monte Carlo simulations of polarizing microscope textures for confined nematic droplets are presented. We consider uniaxial and biaxial cases with various boundary conditions and different values of the molecular biaxiality. The analysis of these optical textures should be of interest in assigning and characterizing biaxial nematic system, an issue of great current interest.

Keywords Computer simulation, Monte Carlo, biaxial nematics, topological defects

INTRODUCTION

Lattice spin models consist of systems of interacting centers (“spins") placed at the sites of a certain regular lattice. They have been the first successful models to simulate the orientational ordering and the clearing transition of liquid crystals (c.f. the pioneering work of Lebwohl and Lasher (LL) [1]). As long as the properties of interest are purely orientational, there are several

advantages in using simple lattice models, with respect to more realistic potentials, like those employed in the molecular level approaches, with translational degrees of freedom, or in the atomistic simulations [2] and particularly the possibility of performing "computer experiments" on a larger number (often 10^2 - 10^3 times larger!) of particles. This is particularly useful when the system is confined and the number of molecules of the sample is finite, albeit large, so that periodic boundary conditions cannot be employed. We have shown that this technique is useful in investigating sub-micron droplets with fixed (homeotropic and planar) surface anchoring mimicking polymer dispersed liquid crystals (PDLC), twisted nematic displays and thin nematic films [3]. The large number of particles which can be simulated on a lattice allows us also to simulate the optical textures, as can be obtained by a polarized microscopy experiment, with a sufficient number of pixels.

Biaxial nematics are currently a subject of great interest [4,5] and the question of how to identify a biaxial nematic is still a major problem. One of classical approaches is to examine the optical texture between crossed polarizers and a suggestion originally made by deGennes [6] was that, due to the different symmetry, biaxial nematics should present only two brushes stable defects in schlieren films. Experiments by Chandrasekhar et. al [7] and, more recently, investigations on lyotropic [8] and thermotropic [4,5,9] systems seem to support this hypothesis which we have also

verified by computer simulations of a schlieren texture, at least in some biaxial nematic films [10]. The problem of the molecular organization and of the optical texture of biaxial nematics in spherical droplets is also of interest in view of the expected differences in topological defect structure [11]. In particular a point hedgehog central defect should not be stable in a biaxial nematic [11], differently from the uniaxial case. Here we shall consider droplets formed by either uniaxial or biaxial nematics devoting particular attention to the less studied biaxial nematic case and to the differences from the uniaxial one, including the presence of a hedgehog defect.

THE MODEL DROPLETS

Our model biaxial and uniaxial nematics are obtained from a discretized version of the orientational biaxial potential put forward many years ago by Luckhurst et al. [12,13] and whose phase diagram has already been studied in detail by us through extensive computer simulations of bulk systems [14]. This lattice model reproduces the rich phase diagram of a biaxial nematic system with isotropic, uniaxial and biaxial phases and it reduces to the well known Lebwohl-Lasher (LL) uniaxial one [1] for nematics when the molecular biaxiality vanishes. The biaxial model Hamiltonian is the following:

$$U_N = (1/2) \sum_{\substack{i,j \in \mathcal{F} \\ i \neq j}} \Phi_{ij} + J \sum_{\substack{i \in \mathcal{F} \\ j \in \mathcal{S}}} \Phi_{ij} \qquad (1)$$

where $\mathcal{F}$, $\mathcal{S}$ are the set of particles in the bulk and at the surfaces, respectively, and the parameter J models the strength of the coupling with the surfaces. The particles interact through the second rank attractive pair potential:

$$\Phi_{ij} = - \varepsilon_{ij} \{ P_2 (\cos \beta_{ij}) + 2 \lambda [R_{02}^2(\omega_{ij}) + R_{20}^2(\omega_{ij})] + 4 \lambda^2 R_{22}^2(\omega_{ij}) \} \qquad (2)$$

where ε_{ij} is a positive constant, ε, for nearest neighbour molecules i and j and zero otherwise, $\omega \equiv (\alpha,\beta,\gamma)$ is the set of Euler angles specifying molecular orientations and R_{mn}^L are symmetrized combinations of Wigner functions [15]. The biaxiality parameter λ takes into account the deviation from molecular cylindrical symmetry, so that when λ is different from zero the particles tend to align not only their major axis, but also their short ones.

While in simulating bulk systems [13,14] periodic boundary conditions are employed, in the case of confinement the boundaries are implemented by considering additional layers of particles, kept fixed during the simulation, with suitable orientations chosen to mimic the desired surface alignment. In previous work we have studied uniaxial nematic droplets, employing an approximately spherical sample carved from a cubic lattice, with radial, bipolar and toroidal boundary conditions [16] and thin films with hybrid

[17] and schlieren anchoring geometries [10]. Here we present an investigation of biaxial nematic droplets with various selected boundary conditions. The starting configurations of the lattice were chosen to be completely aligned along the *z* direction and the evolution of the system was followed according to the classic Metropolis Monte Carlo procedure [18]. Polarizing microscope textures were simulated by means of a Müller matrix approach [19], assuming the molecular domains represented by the spins to act as retarders on the light propagating through the sample [20].

SIMULATIONS AND RESULTS

All the simulations for the various model droplets have been performed on samples carved from a 50×50×50 cubic lattice and containing N=54474 particles. The parameter J, denoting the coupling with the surface, is taken equal to one, which means that the interaction between the nematic and the surrounding polymer has the same strength of the nematic-nematic interaction. The following parameters were employed for computing the optical textures: droplet diameter d = 5.3μm, ordinary and extraordinary refractive indices n_o = 1.5 and n_e = 1.66, and light wavelength λ_o = 545nm.

As mentioned before we have investigated uniaxial and biaxial droplets with different anchoring at the surfaces and now we report results for the various cases studied.

Uniaxial nematic droplets

The first case we present is that of a droplet with radial boundary conditions, where the spins at the surface are directed towards the centre of the sphere.

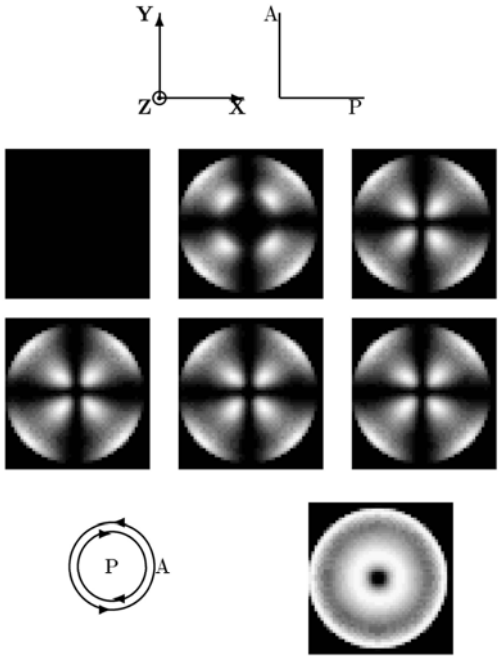

Figure 1. Simulated polarized microscopy images as obtained from Monte Carlo configurations of a uniaxial nematic droplet with radial boundary conditions carved from a 50×50×50 lattice at the reduced temperature $T^* = 0.1$. The axis on top indicate the observer point of view together with the orientation of the crossed polarizers (P, A). The upper images are taken after 0, 5000, 10000, 20000 and 60000 MC cycles with the sample between crossed polarizers left to right. The bottom right frame indicates the image after 60000 MC cycle as observed between circular polarizers (P, A) (bottom left sketch).

We have simulated the optical textures as observed between crossed and circular polarizers. The crossed polarizers textures are quite similar to those observed in real experiments with the typical cross pattern, see, e.g. [20,21]. In the case of circular polarizers the core of the droplet is also dark, consistently with the presence of an aligned region, while the maximum in the light transmission appears in an intermediate position of the droplet radius and close to the surface. In fact the distribution of maxima and minima in the optical textures, shown in Fig. 2, depends only on the distance from the centre of the droplet.

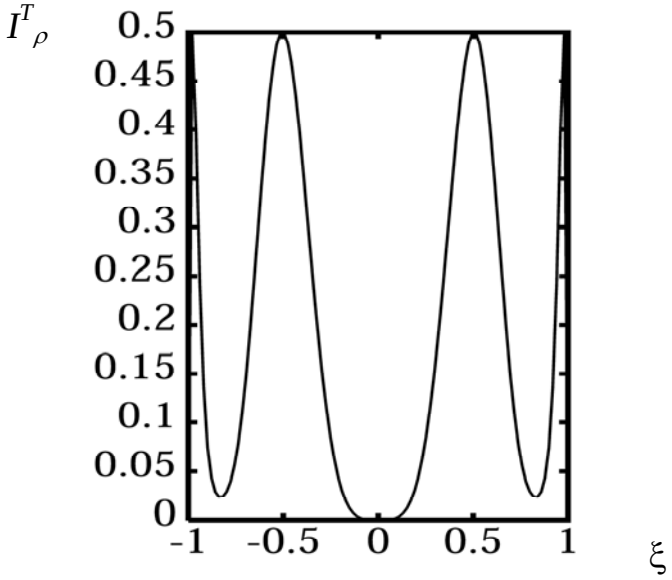

Figure 2. The intensity variation as ξ deviates from the centre.

This means that the local optical axis orientation, i.e. its spherical coordinates ($\sin\varphi\cos\theta$, $\sin\varphi\sin\theta$, $\cos\varphi$), do not depend on Z but only on the distance from the centre of the projection of the optical axis onto the XY plane. The transmitted light intensity I^T_ρ is then:

$$I^T_\rho = \tfrac{1}{2} \sin^2\{ n_0 [1-n_e (n_e^2(1-\xi^2)+ n_0^2 \xi^2)^{-1/2}] L (1+ \xi^2)^{1/2} \} \qquad (3)$$

Where L is the droplet radius and $\rho = L\xi = \sqrt{(x^2+y^2)}$ is the distance from the centre of the particle having (x, y) coordinates.

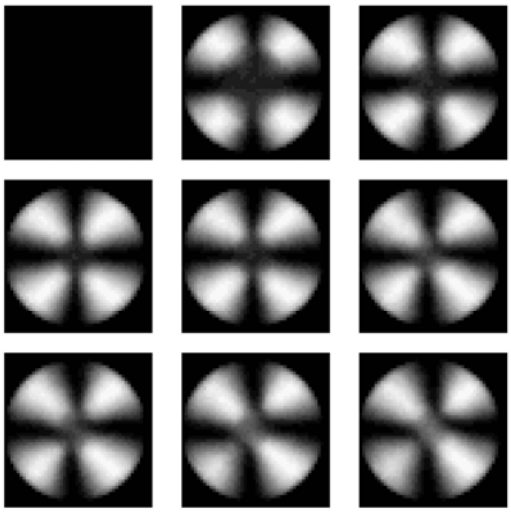

Figure 3. Simulated optical patterns for a droplets containing biaxial particles ($\lambda = 0.2$). The boundary conditions are radial for the long molecular axis and random for the short one. The images (from top left to bottom right) are taken at 0, 20, 50, 100, 200, 300, 400 and 500 MC kcycles respectively.

Biaxial nematic droplets

We have studied nematic droplets with three values of molecular biaxiality, i.e. $\lambda = 0.2$, 0.25 and $\lambda = 0.3$ and two different boundary conditions. The first case presented here is that of a droplet formed by particles with biaxiality $\lambda = 0.2$ and where the molecules at the surface have their long axis directed radially toward the centre of the sphere while the short axis are tangent to the sphere and randomly oriented. We started from a configuration where all the long molecular axes were vertically aligned along Z and we have performed very long runs reaching a total amount of 500000 MC cycles.

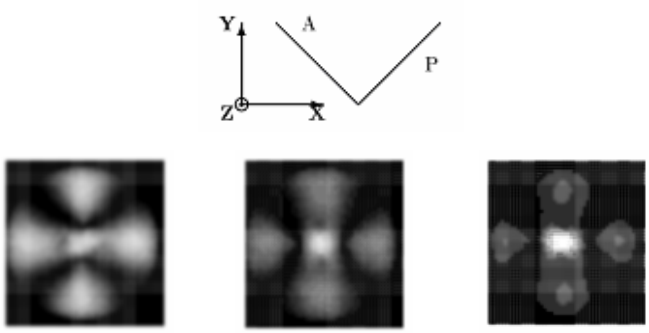

Figure 4. Droplets containing particles with different molecular biaxiality ($\lambda = 0.2, 0.25, 0.3$ from left to right) with radial boundary conditions for the long molecular axis and bipolar for the short one. The optical textures are taken after 60000 MC cycles. The upper sketch indicates the observer point of view together with the orientation of the crossed polarizers (P,A).

The results, reported in Fig. 3 show that the pattern changes from a configuration similar to the uniaxial case, where at the centre of the droplet a four leaves point defect is present, to a final pattern where the defect tends to move to the surface according to the

predictions by Mermin [11], Kurik and Lavrentovich [22] and Sukumaran and Ranganath [23].

We have then examined a droplet with a different type of boundary conditions: radial for the long axis and bipolar (i.e. directed along the local meridians while being tangential to the surface) for the short ones. In this case the dependence on the molecular biaxiality has been examined considering three different values of λ : λ = 0.2, 0.25, 0.30 . The results are presented in Fig. 4 and Fig. 5.

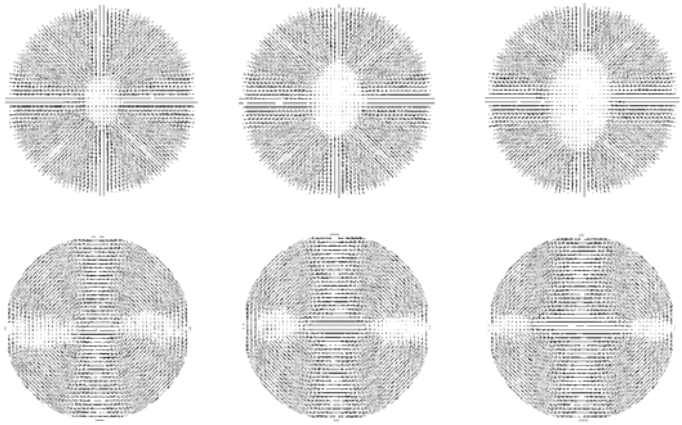

Figure 5. Side view snapshots of the central layer for the long (top) and short (bottom) molecular axes for different molecular biaxiality (λ = 0.20, 0.25, 0.30 from left to right) , corresponding to the images shown in Fig 4.

The snapshots of the central layer of the droplet, shown in Fig. 5, are consistent with the presence of a boojum at the surface. In particular the snapshots of the long axes configurations (Fig. 5 top) are consistent with the fountain configuration predicted in

[11,22,23]. As the molecular biaxiality increases the fountain width increases. Correspondingly the short axes snapshots (bottom plates in Fig.5) change.

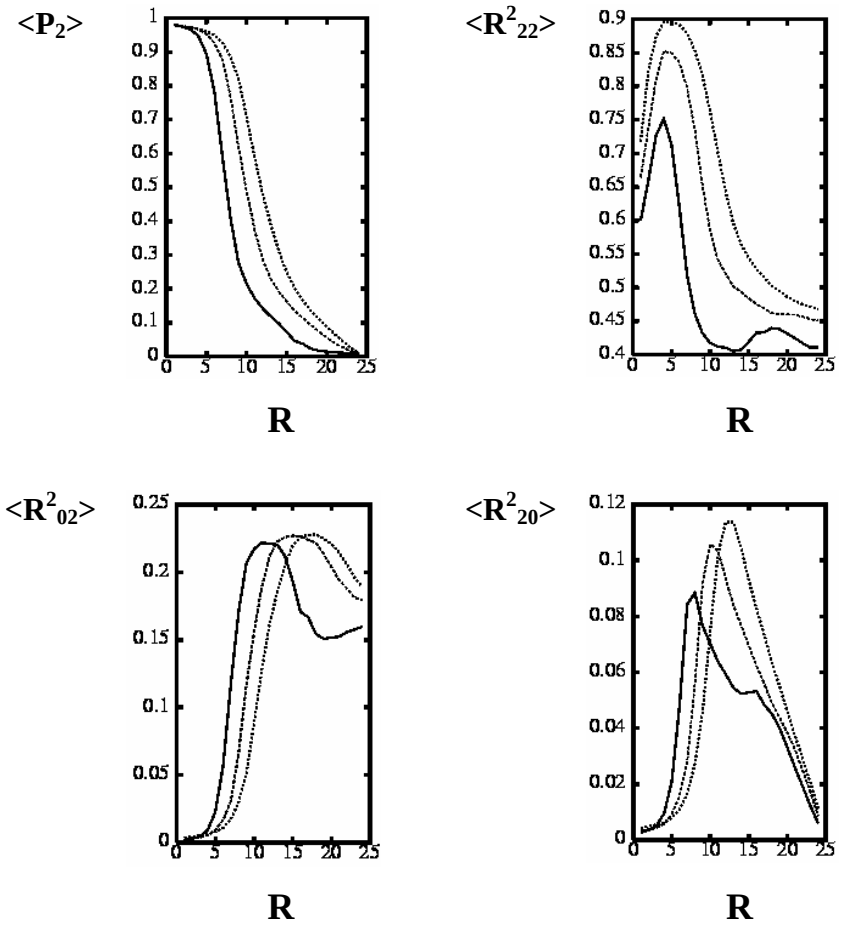

Figure 6. Uniaxial and biaxial order parameters versus lattice units, starting from the centre of the droplet, for the case presented in Fig. 4 and Fig. 5 The molecular biaxiality is $\lambda = 0.2$ continuous l*ine,* $\lambda = 0.25$ dashed line, $\lambda = 0.3$ dotted line.

We have also calculated the full set of order parameters [6] to quantify the different kind of ordering across the sample. To do that we have divided the droplet in concentric shells, starting from the centre of the system, and calculated the observables by averaging only on the molecules belonging to the chosen shell. The results, shown in Fig. 6, indicate that there is a uniaxial nematic ordering at the center of the droplet, which increases as the molecular biaxiality increases. This quantitative determination is qualitatively evident by looking at the snapshots in Fig. 5.

CONCLUSIONS

Lattice spin models, now a classical tool in the study of a variety of liquid crystalline systems, offer interesting opportunities for investigating the molecular organization of anisotropic materials and their optical textures. This is particularly helpful for investigating the structures of topological defects in confined systems. Here we have shown some cases of simulations of models for polymer dispersed liquid crystals formed by uniaxial and biaxial molecules. The effect of the surface alignments combined with the molecular biaxiality can produce different molecular organizations and accordingly different kinds of topological defects. Lattice models are also useful to describe the molecular ordering when simulated images, similar to the real experimental ones, are found (as for the uniaxial cases) or to predict the

polarized optical patterns for experiments which have not yet been performed (as for the biaxial nematic droplets).

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References

1. P.A. Lebwohl and G. Lasher, *Phys. Rev. A,* **6** , 426 (1972).
2. P. Pasini and C. Zannoni (Eds.) *Advances in the Computer simulations of Liquid Crystals* (Kluwer, Dordrecht, 2000).
3. C. Chiccoli, I. Feruli, P. Pasini, and C. Zannoni, in *Defects in Liquid Crystals: Computer simulations, Theory and Experiments* O.D. Lavrentovich, P. Pasini, C. Zannoni and S. Žumer (Eds.) (Kluwer, Dordrecht, 2001) Ch.4.
4. L.A. Madsen, T.J. Dingemans, M. Nakata and E.T. Samulski, *Phys. Rev. Lett.* **92**, 145505 (2004)
5. B.R. Acharya, A. Primak and S. Kumar, *Phys. Rev. Lett*. **92**, 145506-1 (2004).
6. P.G. De Gennes, *The Physics of Liquid Crystals*, (Clarendon Press, Oxford, 1972).
7. S. Chandrasekhar *et al*., *Current Sci*., **75**, 1042 (1998).
8. A.R. Sampaio, A.J. Palangana and R.C. Vescovili, *Mol. Cryst. Liq. Cryst.*, 408, 44 (2004).
9. T.J. Dingemans and E.T. Samulski, *Liq. Cryst.* **27**, 131 (2000).
10. C. Chiccoli, I. Feruli, O.D. Lavrentovich, P. Pasini, S. Shiyanovskii and C. Zannoni, *Phys. Rev. E*, **66**, 030701 (2002).
11. N. Mermin, Rev. Mod. Phys. 51, 647 (1979).
12. G.R. Luckhurst, C. Zannoni, P.L. Nordio, U. Segre, *Mol. Phys.*, **30,** 1345 (1975).
13. G.R. Luckhurst and S. Romano, *Mol. Phys.* **40**, 129 (1980)

14. F. Biscarini, C. Chiccoli, P. Pasini, F. Semeria and C. Zannoni, *Phys. Rev. Lett.*, **75,** 1803 (1995).
15. M.E. Rose, *Elementary Theory of Angular Momentum*, Wiley, New York , (1957).
16. C. Chiccoli, P. Pasini, F. Semeria, E. Berggren, C. Zannoni: *Mol. Cryst. Liq. Cryst.* **266**, 241 (1995).
17. C. Chiccoli, O.D. Lavrentovich, P. Pasini and C. Zannoni, *Phys. Rev. Lett.*, **79**, 4401 (1997).
18. N. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth, A.H. Teller and E. Teller, *J. Chem. Phys.* **21**, 1087 (1953).
19. A. Killian, *Liq. Cryst.*, **14**, 1189 (1993).
20. R. Ondris-Crawford, E.P. Boyko, B.G. Wagner, J. H. Erdmann, S. Žumer and J.W. Doane, *J. Appl. Phys* **69**, 6380 (1991).
21. D. Harrison and M.R. Fisch, *Liq. Cryst.* **27**, 737 (2000*) and references therein*.
22. M.V. Kurik and O.D. Lavrentovich, *Sov. Phys. Usp.* **31**, 196 (1988).
23. S. Sukumaran and G.S. Ranganath, *J. Phys II France* **7**, 583 (1997).