Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Anchoring Transitions in Biaxial Nematic Droplets: A Monte Carlo Study

B. Kamala Latha [a], G. Sai Preeti [b], N. Satyavathi [c], K. P. N. Murthy [a] & V. S. S. Sastry [a]

[a] School of Physics, University of Hyderabad, Hyderabad, India
[b] Department of Chemistry, University of Bologna, Bologna, Italy
[c] Department of Physics, Osmania University, Hyderabad, India

Version of record first published: 30 Jun 2011

To cite this article: B. Kamala Latha, G. Sai Preeti, N. Satyavathi, K. P. N. Murthy & V. S. S. Sastry (2011): Anchoring Transitions in Biaxial Nematic Droplets: A Monte Carlo Study, Molecular Crystals and Liquid Crystals, 545:1, 230/[1454]-241/[1465]

To link to this article: http://dx.doi.org/10.1080/15421406.2011.572022

Mol. Cryst. Liq. Cryst., Vol. 545: pp. 230/[1454]–241/[1465], 2011

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.572022

Anchoring Transitions in Biaxial Nematic Droplets: A Monte Carlo Study

B. KAMALA LATHA,[1] G. SAI PREETI,[2]
N. SATYAVATHI,[3] K. P. N. MURTHY,[1] AND
V. S. S. SASTRY[1]

[1]School of Physics, University of Hyderabad, Hyderabad, India
[2]Department of Chemistry, University of Bologna, Bologna, Italy
[3]Department of Physics, Osmania University, Hyderabad, India

Equilibrium order parameters of a liquid crystal micro-droplet of biaxial molecules, with radial anchoring conditions at the boundary, are computed based on Monte Carlo simulations. Their spatial variation within the droplet, and their temperature dependence covering uniaxial and biaxial nematic phases, are reported as a function of the biaxiality parameter. Central core, known to form for minimizing the energy cost of the boundary-induced distortion at low curvature regions, is characterized from these studies by estimating its size and spatial variation of relevant order parameters. Anchoring induced configuration transition in biaxial phases, and its dependence on the biaxiality parameter are studied.

Keywords Anchoring transitions; biaxial nematics; liquid crystal droplet; Monte Carlo simulations

1. Introduction

Polymer Dispersed Liquid Crystals (PDLC) attracted considerable attention over the last decade due to their potential applications for display purposes, and in optically engineered diffractive structures and devices [1–5]. They are also interesting from the point of view of anisotropic diffusion of light through such systems [6] and orientational multiplicity and transitions in these droplets [7] for possible use in photonic devices. Director distributions in PDLCs are very sensitive to the nature of the boundary conditions,and such systems composed of uniaxial nematic medium were earlier investigated based on Lebwohl-Lasher model [8]. In particular the application of radial boundary conditions at the surface of the spherical droplet produces a defect core at itscenter which has bulk-like nematic symmetry independent of the boundary condition and size of the actual droplet [9,10].

The extent of core region and its physical properties are dependent only on the elastic properties of the medium, determined by the temperature and the underlying

Address correspondence to B. Kamala Latha, School of Physics, University of Hyderabad, Hyderabad, India. Tel.: + 91 - 40 - 23011033; Fax: + 91 - 40 - 23010227; E-mail: kklata@gmail.com

model accounting for inter-molecular interactions. The coupling of the liquid crystal molecules with the surrounding bounding medium however requires a minimum threshold value before the bulk-like nematic structure in the droplet changes over to the anchoring-induced distorted structure with the central core (anchoring driven configuration transition). In the case of a droplet of uniaxial molecules confined to a radially anchoring boundary, splay elasticity of the medium mediates the formation of this core [11,12].

More recently such a micro-droplet comprising of biaxial molecules was investigated based on Monte Carlo simulations using a lattice based model [13], reporting interesting optical textures generated from different molecular biaxiality parameter values (λ), and qualitatively different boundary conditions but under strong anchoring conditions. The interest in the present work is to complement this study with detailed information on director configurations in such a biaxial droplet under radial boundary conditions, as a function of biaxiality parameter λ and temperature, as the anchoring strength at the bounding surface is varied. We adopt an identical Hamiltonian [14] for this purpose, and observe the formation of the droplet (parameterized by the uniaxial and biaxial order parameters) as the sample is cooled from the isotropic phase to the biaxial phase via the intermediate uniaxial phase. We report our results for four different λ values representatively spanning the relevant part of the phase diagram reported for this model [15].

In the second set of computations we investigate the effect of the surface (radial) anchoring strength onthe droplet formation at different temperatures in the biaxial phase. These studies also compare the elastic response of the uniaxial phases formed by the inherently biaxial constituents at different λ values (at appropriate high temperatures), with the results on the pure uniaxial system (Lebwohl-Lasher model) providing the reference for such purposes [12]. In the following, Section 2 briefly introduces the lattice model for the biaxial system and provides details of our simulations. The results are presented and discussed in Section 3, while the main conclusions are presented in Section 4.

2. Model and Details of Simulations

The present lattice model assumes the dispersion approximation, as has been the case with the earlier work [13], thus requiring one parameter (λ) to assign the biaxiality at molecular level. The resulting phase diagram predicts, on cooling the sample from the isotropic phase, successive formation of uniaxial and biaxial nematic phases for non-zeroλ values, with the isotropic-nematic transition temperature (all reported in appropriate reduced units) being essentially independent of the molecular biaxiality. The spread of the intermediate uniaxial nematic phase however is diminished gradually with increase in λ, finally culminating in the possibility of a direct transition to biaxial phase from the isotropic fluid ($\lambda \sim 0.4$). The Hamiltonian is given by

$$U(\omega_{ij}) = -\varepsilon_{ij}\{R^2_{00}(\omega_{ij}) + 2\lambda[R^2_{02}(\omega_{ij}) + R^2_{20}(\omega_{ij})] + 4\lambda^2 R^2_{22}(\omega_{ij})\}. \quad (1)$$

Here, $\omega(\alpha, \beta, \gamma)$ is the set of Euler angles specifying the orientation of the molecule, and ω_{ij} represents the relative orientation of the ijth pair of molecules. $R^2_{m,n}$ are combinations of Wigner functions, symmetry-adapted for the D_{2h} group of the two interacting particles. ϵ_{ij} is the strength of interaction between the molecules, which sets the

scale of the energy and hence the reduced temperature used in such simulations. We take it to be independent of the choice of the specific pair ($\epsilon_{ij} = \epsilon$) and set its value to this constant for nearest neighbors on the lattice, and zero otherwise. The above expression is conveniently recast as a function of inner products of different vectors specifying the orientations of different molecules (x_i, y_i, z_i) with those of the chosen laboratory frame (X, Y, Z), and is expressed as [16]

$$U_{IJ} = -\varepsilon\left\{\frac{3}{2}V_{33} - \sqrt{6}\lambda(V_{11} - V_{22}) + \lambda^2(V_{11} + V_{22} - V_{12} - V_{21}) - \frac{1}{2}\right\}. \quad (2)$$

Here $V_a b = (u_a . v_b)^2$, and the unit vectors u_a, v_b,[a,b = 1,2,3], are the three axes of the two interacting neighboring molecules. The value of λ sets the relative importance of the biaxial interaction in the Hamiltonian, while ϵ (set to unity in the simulations) defines the temperature scale ($T = k_B T^*/\varepsilon$), where T^* is the laboratory temperature.

Simulations on confined systems, based on lattice models, start by carving out the desired geometry from a sufficiently big cubic lattice. One treats the lattice sites within this geometry as liquid crystal constituents participating in the Monte Carlo simulation (namely performing a Markov chain Monte Carlo random walk), while the others are treated as substrate molecules with fixed orientations appropriate to the boundary conditions, referred to in literature as the ghost molecules [17]. The value of ϵ_{ij} involving liquid crystal and substrate molecules (on the condition of being nearest neighbours), relative to that between nearest neighbour liquid crystal molecules (set to unity in the present case), represents the degree of influence of the surrounding medium imposing boundary conditions on the droplet. We focus on the effect of a medium which enforces variable degree of such anchoring in the radial direction towards the center of the droplet. In the first set of the computations, where we investigate the equilibrium director structures across the phase diagram (by varying temperatures over the liquid crystalline phases at different biaxiality parameter values), we assume strong anchoring, and set the corresponding $\epsilon_{ij} (= \epsilon_s)$ also to be unity. In the second part, we focus on the effect of variation of this coupling on the director structures in the biaxial phase, at a few temperatures.

A droplet of radius 20 (in lattice units) was considered, carved out of a cube of sufficient dimension, to allow for the ghost molecules. The equilibrium ensembles were constructed following the Metropolis algorithm for different combinations of temperature and biaxiality parameter (in the strong anchoring limit), with typically 4×10^5 microstates collected in each ensemble after ensuring equilibration. In this set of simulations with strong anchoring, λ was chosen at four different values (0.20, 0.25, 0.30, and 0.35); this provides essentially constant isotropic-uniaxial nematic transition temperature ($T_{IN_U} \sim 1.1$), while the transition temperature from the uniaxial to biaxial nematic phase ($T_{N_U N_B}$) varies from about 0.15 to about 0.5 as λ changes from 0.2 to 0.35 [15]. The temperature T at each of these λ values is varied from 1.2 to 0.1 in steps of 0.1. The physical parameters of interest in this system are the four order parameters which essentially quantify the uniaxial order (along the primary director), the phase biaxiality (originating from the lack of azimuthal symmetry of the long axes of the molecules), and the molecular contribution to the biaxiality of the medium ($< R^2_{00} >, < R^2_{20} >, < R^2_{02} >, < R^2_{22} >$).From the data we find that only $< R^2_{00} >$ and $< R^2_{22} >$ have appreciable values and reflect effectively the changes in the configuration of the droplet.

For examining the formation of the core closely, we extract from the equilibrium ensembles the values of these parameters (and their fluctuations) for different concentric spheres within the droplet, as the radius of this sphere is varied by a lattice unit starting with an initial sphere of radius 2 lattice units. This helps in the identification of the core region, and its exclusive characteristics once formed. The second set of simulations are carried out primarily under the conditions of high molecular biaxiality ($\lambda = 0.35$ and 0.30), and in the biaxial region (below $T_{N_U N_B}$), for differing values of ϵ_S involving the liquid crystal and substrate molecules. These are varied from zero (free boundary condition on the droplet surface) in steps of 0.05, up to the strong limit value of unity. These form the latter part of the results presented below.

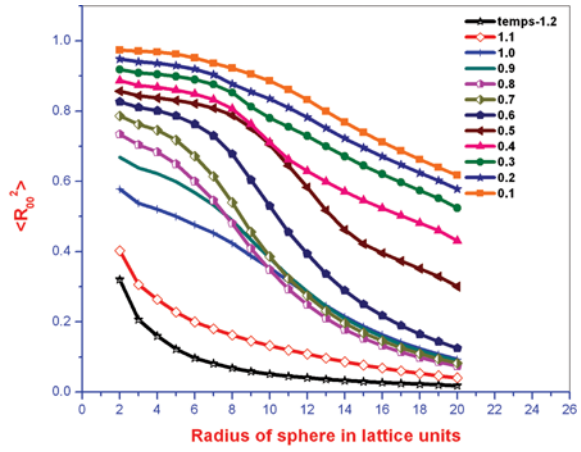
3. Results and Discussion

Figures 1–4 summarize the variation of different interesting parameters in the limit of $\epsilon_S = 1$. Figure 1(a)–1(c) depict the temperature variation at $\lambda = 0.35$ of the uniaxial order, $<R^2_{00}>$, biaxial order due to molecular origin $<R^2_{22}>$ and its susceptibility (expressed in the usual way in terms of the variance and the temperature) – all shown as a function of the radius of concentric spheres built within the droplet, while Figure 2(a)–2(c) present in the same format the results for $\lambda = 0.30$. We contrast this strong anchoring case by depicting in Figure 3(a) and 3(b), the variation of $<R^2_{22}>$ and $<R^2_{00}>$, across the droplet (averages over spheres of increasing radius) in the biaxial phase (at $T = 0.1$) for an intermediate value of the anchoring strength $\epsilon_S = 0.25$, to focus on the competition between the intermolecular aligning interactions and the disordering surface coupling for moderate anchoring values.

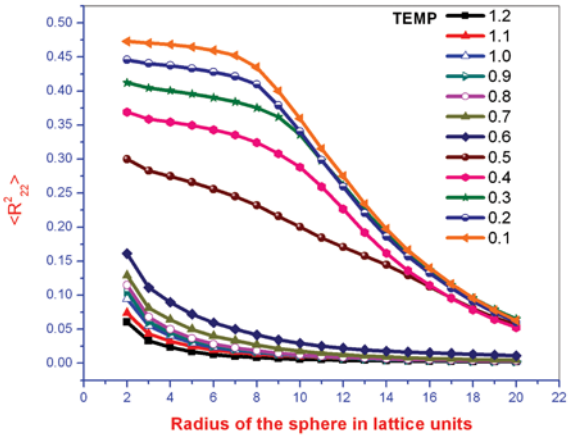
The variation of susceptibility of $<R^2_{00}>$ across the droplet in the strong anchoring limit, at two representative temperatures within the uniaxial phase,is shown in Figure 4(a) and 4(b), as the molecular biaxiality parameter is varied spanning the phase diagram of interest. Finally, the effect of variable anchoring leading to a configuration transition is presented in Figure 5 - 6, by showing the variation across the droplet at two temperatures ($T = 0.4$ and 0.2), of the two order parameters $<R^2_{00}>$ and $<R^2_{22}>$ as well as susceptibility of $<R^2_{22}>$, as ϵ_S is varied between 0 and 0.25. These represent a subset of the data collected on order parameters and their susceptibility, of different director configurations, under different conditions of temperature, molecular biaxiality, and anchoring strength.

Focusing on Figure 1(a) ($\lambda = 0.35$) and 2(a) ($\lambda = 0.30$) representing the evolution of the droplet director structureas a function of temperature, (and based on similar results for the other values of λ not shown here), we observe that in the uniaxial nematic region of temperature a core with appreciable uniaxial order but of variable size forms, its size decreasing as λdecreases (from about 10 units in Fig. 1(a) to 7 in Fig. 2(a)). This value asymptotically reduces to about 4-5 lattice units as λ is decreased to 0.2, and is very close to the value observed in the case of uniaxial molecules (Lebwohl-Lasher potential) [10]. Thus the uniaxial phases of differing λ seem to enforce significantly different core sizes (all other experimental conditions being the same), signaling subtle changes in the appropriate elastic property of the medium (even within the macroscopically uniaxial bulk phase).

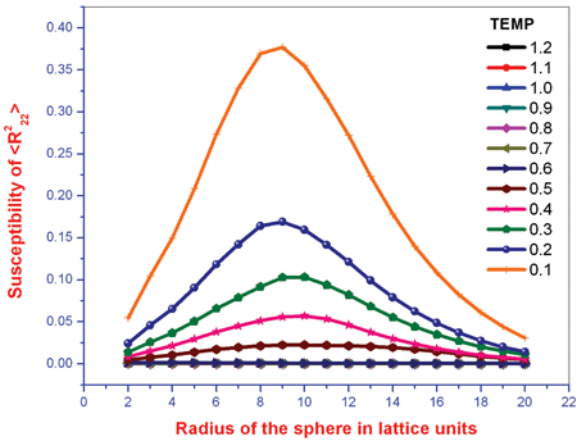
For a medium of uniaxial molecules such core changes are attributed to changes in the splay elastic energy [12].



(a)

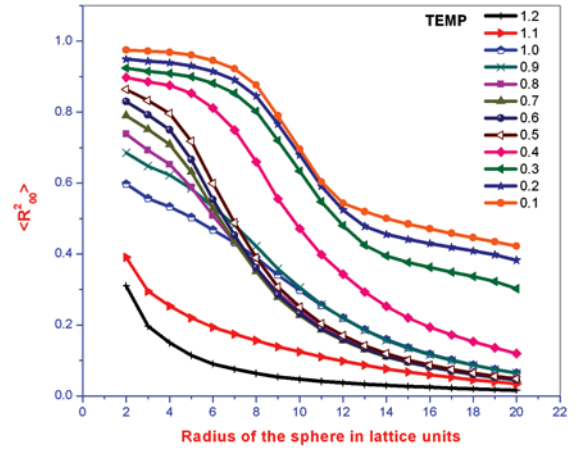


(b)

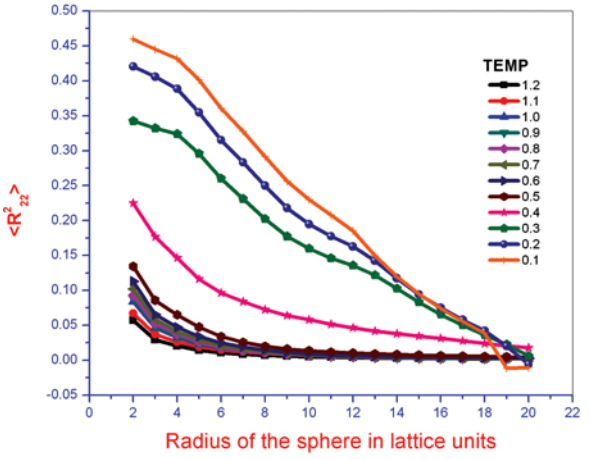


(c)

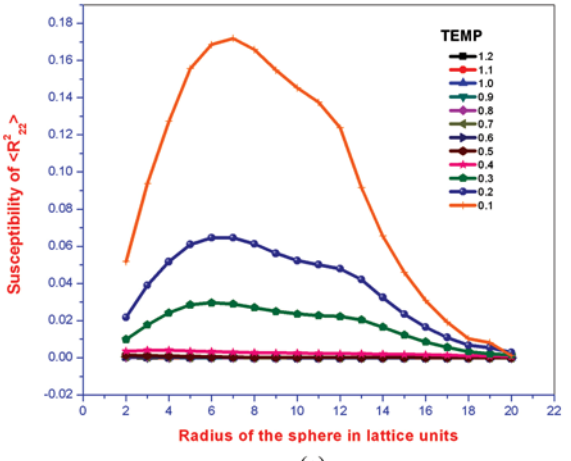
Figure 1. Spatial dependence of **(a)** $<R_{00}^2>$, **(b)** $<R_{22}^2>$ and **(c)** fluctuations in $<R_{22}^2>$ at $\lambda = 0.35$, at different temperatures. (Figure appears in color online.)



(a)



(b)



(c)

Figure 2. Spatial dependence of **(a)** $<R^2_{00}>$, **(b)** $<R^2_{22}>$ and **(c)** fluctuations in $<R^2_{22}>$ at $\lambda = 0.30$, at different temperatures. (Figure appears in color online.)

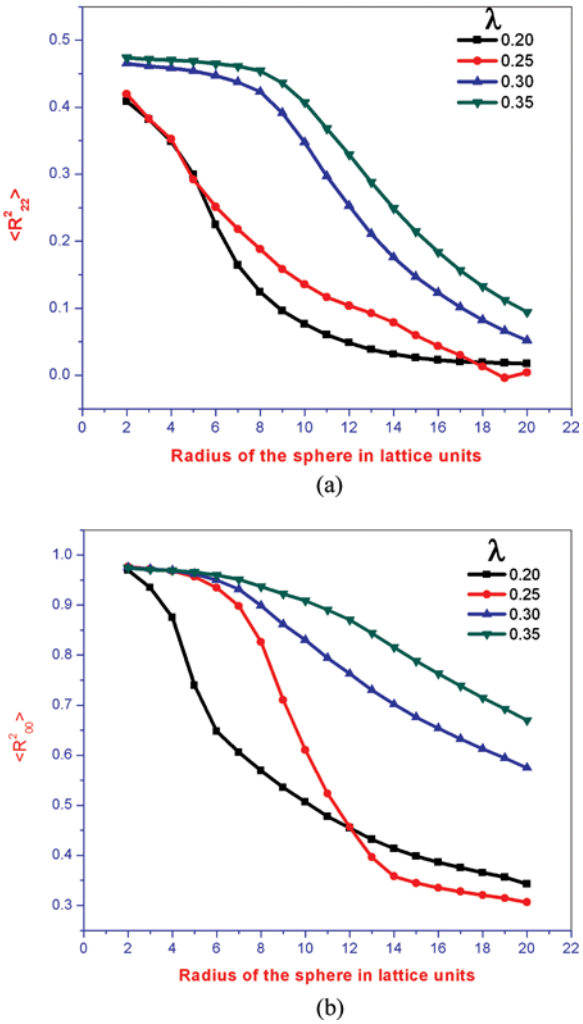


Figure 3. Effect of variation of λ on the spatial dependence of **(a)** $<R_{22}^2>$ and **(b)** $<R_{00}^2>$. (Figure appears in color online.)

Figures 1(b) and 2(b) show differing resistances of the medium ($<R_{22}^2><R_{22}^2>$ within biaxial regime of temperature) to allow the surface induced disorder to percolate to the center, for the two λ values. At $\lambda = 0.35$ a biaxial core forms once a biaxial phase sets in (size estimated to be about 8 lattice units, Figure 1(b)), while a slight decrease of its value to 0.3, at this strong anchoring limit, shows that only a uniaxial core is possible under these conditions.

The results at lower values of λ only confirm this observation. An interesting contrast is provided in Figures 3(a) and 3(b), where $<R_{00}^2>$ and $<R_{22}^2>$ are plotted for different concentric spheres at $T = 0.1$ (lowest temperature in the biaxial region) for different λ values, but for a reduced anchoring strength of $\epsilon_S = 0.25$.

We immediately see that at this reduced degree of surface-induced disorder, the biaxial medium at $\lambda = 0.3$ has enough elastic resistance to sustain a biaxial core of

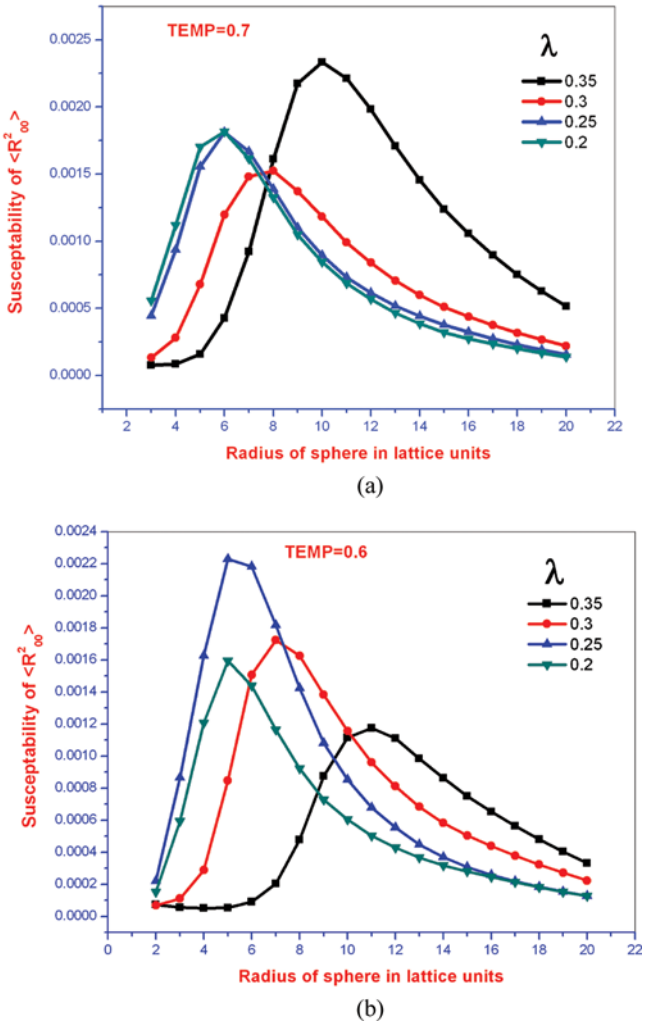


Figure 4. Spatial dependence of fluctuations in $<R^2_{00}>$for different λ at **(a)** $T=0.7$ and **(b)** $T=0.6$. (Figure appears in color online.)

approximately comparable magnitude to that at 0.35. Figure 3(b) provides an interesting contrast showing that the droplet manages to have a uniaxial core of high order and perceptible dimension for all value of λ, but for the lowest value of $\lambda=0.2$. At this value it tends to the asymptotic LL limit. Figure 1(c) and 2(c) show susceptibilities of $<R^2_{22}>$ across the droplet, exhibiting a peak at the interfacial regions between the central core and the surrounding medium. The earlier observation, that the formation of the biaxial core (under strong anchoring limit, $\epsilon_S=1.0$) was clearly evident at $\lambda=0.35$ relative to 0.30, was further borne out by a comparison of its susceptibility profiles at these two values, depicted in these two figures.

In Figure 4(a) and (b) we present a similar comparison of data in the uniaxial phase of the medium at two different temperatures ($T=0.6$ and 0.7), the relevant parameters being the susceptibilities in $<R^2_{00}>$, for different λ values. The location

of the interfacial region between the uniaxial core and the rest of the droplet in this high temperature uniaxial nematic phase, and its progressive shift towards outer regions as the inherent molecular biaxiality is increased in the model, are again supportive of the observations made earlier based on Figure 1(a) and 2(a).

We study the formation of the core region in the biaxial phase at two temperatures ($T=0.4$ and 0.2) at $\lambda=0.35$, as a function of ϵ_S (varying between 0.0 and 0.25 in steps of 0.05). We present the variation of $<R^2_{00}>$ and $<R^2_{22}>$ for different anchoring strengths, and the corresponding variation of the susceptibility of $<R^2_{22}>$, at $T=0.4$ in Figure 5 and at $T=0.2$ in Figure 6. From Figure 5(a) we notice that both the order parameters show a qualitative change in their spatial distribution as ϵ_S changes from 0.1 to 0.15. Figure 5(b), depicting the spatial variation of the

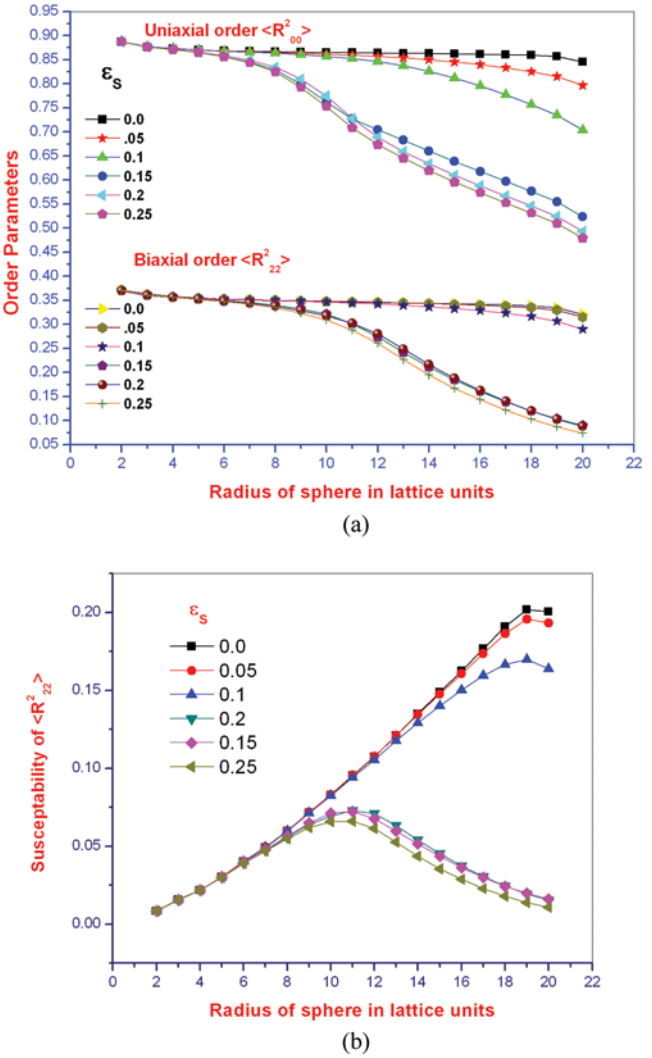
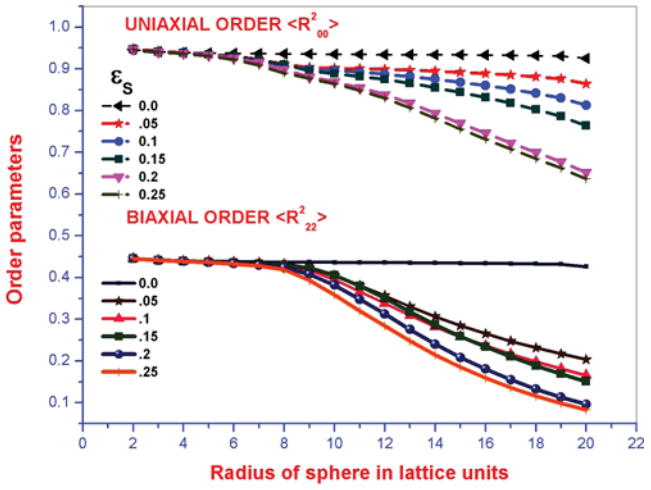
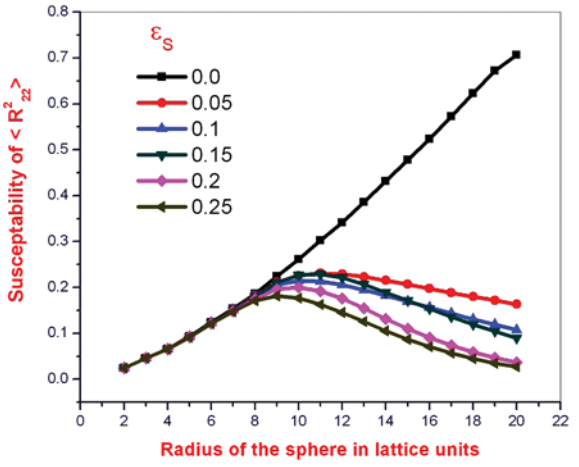


Figure 5. Variation of **(a)** order parameters and **(b)** susceptibility in $<R^2_{22}>$, bracketing the anchoring transition for various values of ϵ_S at $\lambda=0.35$, $T=0.4$. (Figure appears in color online.)



(a)



(b)

Figure 6. Variation of **(a)** order parameters and **(b) s**usceptibility in $<R_{22}^2>$, bracketing the anchoring transition for various values of ϵ_S at $\lambda = 0.35$, $T = 0.2$. (Figure appears in color online.)

susceptibility in $<R_{22}^2>$, interestingly indicates that the interfacial region forms only when ϵ_S increases beyond 0.1, below which it monotonically increases towards the edge of the droplet as is expected in a simple bulk-like medium with weak antagonistic boundary conditions at the boundaries of this geometry. Both these results together indicate that the droplet undergoes a configuration transition at some threshold lying in between these two values at this high value of λ. These suggest that the droplet splits into a biaxial core region with a size of about 10 lattice units (see Fig. 5(b)), and the core is characterized by typical value of order parameters: $<R_{00}^2> \sim 0.85$ and $<R_{22}^2> \sim 0.35$, at $T = 0.4$. Figures 6(a) and 6(b) depict such variations at a lower temperature $T = 0.2$ (at the same biaxiality parameter). We notice that at this temperature qualitative changes have taken place even at a low

value of $\epsilon_S = 0.05$ itself. As may be seen from Figure 6(a), $<R_{22}^2>$ shows a dramatic decrease from a nearly uniform biaxial distribution (at a higher value of $<R_{22}^2> \sim 0.45$) of an unperturbed system ($\epsilon_S = 0$) at the slightest of perturbation from the surface.

The uniaxial order of the core (with $<R_{00}^2> \sim 0.95$) also shows a qualitative change with this slightest increase in ϵ_S (from 0.0 to 0.05). Further, the profiles of $<R_{00}^2>$ (Fig. 6(a)) also seem to betray the possibility of a second anchoring driven transition also, between 0.15 and 0.20, with such accompanying changes in $<R_{22}^2>$ as well. Figure 6(b) brings out the qualitative difference between the same droplet at the two different temperatures more clearly. Unlike at $T = 0.4$, the susceptibility in $<R_{22}^2>$ shows evidences of an interfacial region (dividing the droplet into two distinct parts) even at $\epsilon_S = 0.05$, supporting the results of Figure 6(a).These observations, coupled with data at this value of biaxiality but at $\epsilon_S = 1.0$ (Fig. 1(b)), suggest that as the biaxiality sets in to higher values (at a given biaxiality parameter, say), the droplet is less compatible, from energetic considerations obviously, to even the slightest antagonistic perturbation of the medium from the bounding surface, forcing the medium to undergo anchoring driven transition(s). And the droplet size seems to shrink (though nominally, see Fig. 1(b), at the strong anchoring limit) as the biaxial order firms up more at low temperatures. This makes an interesting and contrasting comparison with a medium comprising of uniaxial molecules, wherein for a given anchoring strength and big enough droplet, the core grows in size with decrease of temperature since the corresponding $<R^2{}_{00}>$ increases, and so does its elastic resistance.

4. Conclusions

We studied a spherical droplet ofa liquid crystal comprising of biaxial molecules whose phase diagram, which includes a low temperature biaxial nematic phase also, can be varied by a single parameter (λ) in the interaction terms. We investigate the formation of different director configurations, quantifying them with spatial variations of relevant order parameters and their fluctuations. We in particular focus on the formation of a central core bearing the characteristics of the nematic region compatible with the corresponding experimental conditions, spanning the phase diagram (i.e., as a function of λ and T). We examine the spatial variation of the uniaxial ($<R_{00}^2>$) and biaxial ($<R_{22}^2>$) order parameters (and their fluctuations) to infer about subtle changes in its structure. We supplement this effort by varying the anchoring strength at chosen values of λ (we present results for $\lambda = 0.35$ here), and make an attempt to correlate its behavior under different experimental conditions. We find that the uniaxial phases formed at high temperatures at different λ values are quantitatively different in their elastic behavior, and tend to the Lebwohl-Lasher behavior as λ tends to zero. It is also known in uniaxial regime that a higher inherent order (by, say, lowering the temperature) leads to bigger core (conditions of anchoring being the same) owing to anincrease in the relevant elastic energy density. In the biaxial regime, this does not seem to be true, and if at all it seems to be the opposite.

Acknowledgment

We thank the Centre for Modeling, Simulation and Design (CMSD) at the University of Hyderabad for providing computational facilities. BKL would like

to thank the University Grants Commission for the award of a Research Fellowship through CAS/RFSMS Scheme.

References

[1] Crawford, C. P., *et al*. (1996). *Liquid Crystal in Complex Geometries formed by Polymer and Porous Network*, Taylor and Francis: London.
[2] Drzaic, P. (1986). *J. Appl. Phys.*, *60*, 2142.
[3] Doane, J. W., Vaz, N. A., Wu, B. G., & Zumer, S. (1986). *Appl. Phys. Lett.*, *48*, 269.
[4] Drzaic, P. S. (1988). *Liq. Cryst.*, *11*, 1543.
[5] Hadjichristov, G. B., Marinov, Y. G., & Petrov, A. G. (2010). *Mol. Cryst. Liq. Cryst.*, *525*, 128.
[6] Alenka, Mertelj, & Martin, Copic. (2007). Phy. *Rev. E*, *75*, 011705.
[7] Goyal, Rajesh K., & Denn, Martin M. (2007). Phy. *Rev. E*, *75*, 021704.
[8] Lebwohl, P., & Lasher, G. (1972). *Phy. Rev. A.*, *6*, 426.
[9] Berggren, E., Zannoni, C., Chiccoli, C., Pasini, P., & Semeria, F. (1992). *Chem. Phy. Lett.*, *197*, 224.
[10] Chiccoli, C., Pasini, P., Skacej, G., Zumer, S., & Zannoni, C. (2005). *Lattice spin Models of Polymer Dispersed Liquid Crystalsin Computer Simulations of Liquid Crystals and Polymers*, Kluwer, Dordrecht, 1–23.
[11] Luckhurst, G. R., & Romano, S. (1999). *Liquid Crystals*, *26*, 871.
[12] Sai Preeti, G., Satyavathi, N., Murthy, K. P. N., & Sastry, V. S. S. (2009). *Liq. Cryst.*, *36*, 1379.
[13] Chiccoli, C., Pasini, P., Feruli, I., & Zannoni, C. (2005). *Mol. Cryst. Liq. Cryst.*, *441*, 319.
[14] Luckhurst, G. R., & Romano, S. (1980). *Mol. Phys.*, *40*, 129.
[15] Biscarini, F., Chiccoli, C., Pasini, P., Semeria, F., & Zannoni, C. (1995). *Phy. Rev. Lett.*, *75*, 1803.
[16] Chiccoli, C., Pasini, P., Semeria, F., & Zannoni, C. (1999). *Int. J. Mod. Phys. C*, *10*, 469.
[17] Pasini, P., Chiccoli, C., & Zannoni, C. (2000). *Advances in the Computer Simulations of Liquid Crystals*, Kluwer: Dordrecht.