

Influence of flexibility on the biaxial nematic phase of bent core liquid crystals: A Monte Carlo simulation study

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The influence of flexibility on the phase behavior of bent core biaxial nematic liquid crystals is investigated using Monte Carlo simulation. A generic model for rigid V-shaped molecules is extended to include a bending potential, which allows us to investigate the relationship between the flexibility of a bent core molecule and its ability to form a biaxial nematic phase. The simulation results indicate that, as the flexibility is increased, the biaxial nematic phase is typically forced to lower temperatures. In contrast, the stability of the uniaxial nematic phase with respect to the isotropic phase is not significantly affected. The Landau point is split into a line of first order phase transitions between two different uniaxial phases. In some cases, the uniaxial nematic to biaxial nematic transition becomes first order, and a shape change is observed at this transition.

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I. INTRODUCTION

There has been considerable interest in the liquid crystal phases formed by bent core or V-shaped molecules since this is one of the predicted molecular topologies that should form a biaxial nematic phase. Many liquid crystalline materials have molecules which are approximately rodlike in shape and these exhibit the common uniaxial nematic phase, in which the long axes of the molecules tend to be aligned in a common direction. The small deviations from molecular uniaxial symmetry possessed by all known rod shaped liquid crystal molecules are not enough for biaxiality to be observed in the nematic phase. However, when a molecule deviates significantly from this rodlike shape, the possibility of a second axis aligning arises, and thus a biaxial nematic could be formed [1]. A number of different molecular shapes that deviate from uniaxial symmetry have been proposed [2–5], although the majority of these appear not to exhibit a biaxial nematic phase [6]. Samulski and his colleagues [7,8] have prepared a range of bent core molecules in which different cores or linking groups are used to vary the bend angle, to explore the extent to which a molecule might deviate from linearity and still retain its liquid crystallinity. Some of their bent core molecules exhibit nematic phases and one particular example has been shown to have an optical texture with two brush patterns [9]. This optical texture is an indicator that the nematic phase may be biaxial [10] although the use of further techniques are necessary to unambiguously demonstrate this [9]. More recent studies that include deuterium NMR spectroscopy [11] and x-ray scattering [12] appear to indicate that this system does exhibit a biaxial nematic phase. Evidence for biaxiality in a nematic phase has also been observed in systems of symmetric bent core molecules but with lateral chains on the arms to lower the melting point [13]. Yelamagad *et al.* [14] have also used optical measurements to investigate the phase behavior of a nonsymmetric V-shaped molecule with two very different arms, one of which contains a flexible spacer. Their results suggest that the nematic phase of this system could also be biaxial.

The uniaxial and biaxial nematic phases exhibited by bent core molecules have been studied theoretically using a num-

ber of techniques. These include a molecular field analysis for a symmetric bent core molecule interacting via a continuous potential [6], a bifurcation analysis of a symmetric bent spherocylinder with purely repulsive interactions [15], and, more recently, a simulation study based on a bent core Lebwohl-Lasher model in which symmetric models and deviations from these were investigated [16]. For the symmetric models, all three of these studies agree that the Landau point, at which the isotropic phase undergoes a transition directly to the biaxial nematic, is predicted to occur when the link between the arms is at the tetrahedral angle ($109^{\circ}28'$). This is somewhat different to the value of approximately 140° , the angle estimated for the symmetric bent core molecules recently reported having a biaxial nematic phase [11,12]. We may wonder why this difference is observed between theoretical models and experimental realizations of biaxial molecules. The simulation study for the nonsymmetric models [16], in which the anisotropies of the two arms are different, indicates that, within the assumption of a continuous point interaction potential between the molecules, the phase behavior for all ratios in the anisotropies of the two arms can be mapped onto the symmetric model, with a shift in the angle at which the two arms are linked. In particular, this study showed that the angle at which nonsymmetric arms must be linked to exhibit a Landau point must be strictly less than the tetrahedral angle and that the critical angle drops as the deviation of the arms from the symmetric case increases. Thus, small differences in the arms cannot account for the molecule requiring a larger bend angle.

So far, these investigations have considered rigid molecules only, that is, ones with fixed bend angles. However, real molecules may adopt more than one conformation and the different conformations of the molecule may have different molecular biaxialities. A system of such molecules can be expected to behave in a different way to a system of molecules that have a fixed shape. We may, therefore, wonder what effect the flexibility has on the topology of the phase diagram and on the Landau point. To help understand how the flexibility of a bent core molecule influences its ability to form a biaxial nematic phase, we have extended the bent core lattice model so that it includes a bending potential

between the two arms. The phase behavior of the model together with certain key properties of the nematic phases have been determined using Monte Carlo simulations.

The layout of this paper is the following. In the next section, the model is described together with the Monte Carlo simulations used to investigate its properties. The results of the simulations are given in Sec. III where they are compared with those of equivalent rigid molecules. Our conclusions are presented in Sec. IV.

II. THE MODEL AND SIMULATIONS

In order to explore the phase behavior of bent core molecules which can adopt a range of conformations, we have constructed a simple lattice model based on the Lebwohl-Lasher (LL) model [17]. The LL model was recently extended to investigate the liquid crystalline behavior of symmetric and nonsymmetric bent core molecules, by allowing each lattice site to host two rather than one mesogenic unit [16]. In this extended model, a molecule is located at each site in a cubic lattice and interacts with the six nearest neighbors, as in the original LL model [17]. The difference is that each molecule consists of two rods of type A and B joined at a fixed angle, rather than one. The potential between two identical, neighboring molecules can be written as a sum over all distinct pairs of rods

$$U_{ij} = - \sum_{\alpha=A,B} \sum_{\beta=A,B} \epsilon_{\alpha\beta} P_2(\cos \beta_{\alpha\beta}), \quad (1)$$

in which the indices α and β run over the two rods in molecules i and j , respectively. $P_2(x) = \frac{3}{2}x^2 - \frac{1}{2}$ is the second Legendre function, which gives a minimum in the potential energy function for neighboring rods with parallel (or antiparallel) alignment and a maximum when they are perpendicular. For symmetric molecules, the anisotropy in the interactions for each arm is the same and we have $\epsilon_{AA} = \epsilon_{AB} = \epsilon_{BB}$. For nonsymmetric molecules, the anisotropy in the interactions for a pair of rods of type A is different to that for a pair of type B (i.e., $\epsilon_{AA} \neq \epsilon_{BB}$) and, for the mixed interaction, a Berthelot-like combining rule $\epsilon_{AB} = \epsilon_{BA} = \sqrt{(\epsilon_{AA}\epsilon_{BB})}$ can be used to reduce the number of variable parameters [18]. When considering flexible bent core molecules, we shall consider only symmetric arm models, although the extension to nonsymmetric molecules is trivial but necessarily introduces a further parameter to the model. To introduce the possibility of different conformations in the flexible model, we use a simple harmonic bending potential based on the angle between the two arms

$$U_i = \epsilon_k (\theta_i - \theta_0)^2, \quad (2)$$

where ϵ_k is a bending force constant, θ_i is the angle between the two rods in molecule i and θ_0 is the preferred angle, at which the bending potential term is at a minimum. This assumption, of course, implies that the distribution of conformations that a molecule can adopt in the gas phase is continuous and peaked about a single angle, rather than being peaked around two or more distinct angles. To reduce the number of variables in the model, as we are considering only

symmetric models ($\epsilon_{AA} = \epsilon_{AB} = \epsilon_{BB}$) we scale the potentials by ϵ_{AA} and introduce the single parameter $\epsilon_k = \epsilon_k / \epsilon_{AA}$ to represent the strength of the bending potential. The temperature is naturally scaled in the same way, so that $T^* = k_B T / \epsilon_{AA}$. This means that the two parameters in the model are the equilibrium angle θ_0 and the reduced bending force constant ϵ_k which is related to the flexibility of the bent core molecule; the lower ϵ_k , the more flexible the molecule and the wider the distribution of angles the molecule is expected to adopt. We should point out that, since the two-arm model for bent core molecules can be mapped onto the single site pair potential proposed by Luckhurst *et al.* [19], an equivalent model to the flexible bent core molecule could be constructed by using the single site model in which the molecular biaxiality, rather than the bending angle, is allowed to fluctuate. However, it makes more physical sense to relate the flexibility of a bent-core molecule directly to a bending potential in a two arm model rather than using the more abstract view of a single site biaxial molecule with variable biaxiality. We should also point out that it is possible to use an off-lattice model to investigate the effect that flexibility has on the phase diagram of a bent core molecule. Indeed, one study has been performed for a system of such molecules, in which two Gay-Berne mesogens are linked together through stretch, bend and twist potentials [20]. Limited simulations using a few different parameter sets, including some to model nonsymmetric molecules, did not show any evidence for biaxial nematics, although evidence for biaxial smectic phases was observed. The use of a lattice model to investigate the influence of flexibility clearly has a number of advantages. Only a very limited number of simulations can be performed if an off-lattice model is used, since off-lattice models are significantly more computationally demanding than lattice ones. Not only is the computational power necessary to investigate a single model important, but just as important are the number of parameters which must be studied to be able to construct the global phase diagram. For example, not only can the three force constants and their associated equilibrium values be varied, but so can the four Gay-Berne parameters and the pressure or density. This means that there is a large number of variables for such models, and each parameter set may exhibit a different phase behavior. Thus the same values for a set constants chosen to model the flexibility may give different results depending on the lengths of the arms, the anisotropy in the dispersion forces, and so on. In the simple lattice model described, only the two parameters already discussed need to be varied to construct the full phase diagram. This means that the generic behavior for the model, albeit a more simple model, can be determined more efficiently. Once the influence of flexibility is understood for the more simple model, off lattice models may give more insights into the stability of the biaxial nematic phase with respect to phases with higher translational order or to investigate interesting regions of the phase diagram. Another reason for using a lattice model is more subtle [16] and is based on the fact that liquid crystal models composed of rotating particles at fixed lattice sites cannot, by their very nature, change in their translational structure. This can be used to our advantage since we may probe regions of a phase diagram where off-lattice systems may form a smec-

tic phase or crystallize thus blocking the phase of interest. Since the phase diagram for the lattice model for fixed angle bent core molecules is known to contain a biaxial nematic phase [16], this is a sensible starting place to investigate the generic effect of flexibility on the biaxial nematic phase, as we know that one of the limiting cases of the model actually has a biaxial nematic phase. The biaxial nematic phase has not been seen in linked arm off-lattice models and so the influence of flexibility on the biaxial nematic phase cannot be examined. We can thus observe how deviations from the rigid model influence the stability of the biaxial nematic phase with respect to the uniaxial nematic and isotropic phases. Of course, for real systems, locating the biaxial nematic phase is still a difficult task and for any particular molecule the biaxial nematic may not be stable with respect to, for example, the smectic or crystalline phases. Moreover, the results of such simple models (or, indeed, of combined Gay-Berne models) cannot be used to study or suggest particular molecular structures simply because the chemical structure is coarse-grained out of the model. However, the simple lattice model is still useful in that we can investigate how flexibility might influence the biaxial nematic phase in real or other model systems, and use this information to decide whether target molecules should be rigid or more flexible and investigate what sort of transitions could be observed if varying the flexibility is an option.

Simulations were performed for a number of different parameters to map out the phase diagram as a function of both ϵ_K and θ_0 . The simulations for each set of model parameters were performed using sensibly large systems of $N=40^3$ lattice sites to locate the transitions. As we shall see, both cooling and heating runs were necessary as some of the models exhibit a small amount of hysteresis in their equation of state at the transitions, especially where shape changes occur. Monte Carlo trials were made by selecting a molecule i at random and then (i) randomly selecting one of the two rods at this site and randomly changing its orientation or (ii) randomly changing the orientation of both rods. Equilibration runs were typically of 20 000–50 000 cycles (where 1 cycle= N trials) and were followed by a production run of 50 000 cycles, although longer equilibration runs were used near transitions where appropriate. In the vicinity of the transitions where the equation of state exhibits hysteresis, significantly longer runs were found necessary to fully equilibrate the systems. As already pointed out, the phase behavior as a function of angle for the rigid model is known [16]; this corresponds to using an infinite force constant for the bending potential. The other extreme, $\epsilon_K=0$, is less interesting. In the zero force constant limit, the phase behavior will not depend on the equilibrium bend angle as there is no bending potential. The model becomes a Lebwohl-Lasher model in which two uncorrelated spins are located at each site. This will therefore exhibit only isotropic and uniaxial nematic phases as for the original Lebwohl-Lasher model. The only difference would be a scaling of the overall interaction energy between neighboring sites and thus the nematic-isotropic transition temperature.

To characterize the phases, we need to determine the principal order parameters that can distinguish between the biaxial and uniaxial nematic phases and the isotropic phase for

one or more axis sets in the molecule. However, as shown for the previous investigation of rigid bent core molecules [16], more useful information can be obtained by viewing the ordering matrices for individual axes in the molecule rather than the principal order parameters derived from these. Note that although these should strictly be called the principal components of the ordering tensor, we shall also use the term order parameters to describe these. The use of these components of the ordering tensor also allows direct comparison with deuterium NMR experiments which are usually taken to be a definitive measure of biaxiality [6]. For bent core molecules with a fixed geometry, the ordering matrix for an axis along the arms was found to be the most useful to determine the orientational nature of the nematic phase and will use this as our primary measure of biaxiality. However, we also calculate the ordering matrices for three molecular symmetry axes. One of these is the bisecting vector of the arms (y axis), one is the length vector (z axis), and the final one is a vector perpendicular to these (x axis). The labeling of the directors for investigating the uniaxial nematic to biaxial nematic phase transition is crucial. Since any finite uniaxial system will show some biaxiality (just as any finite isotropic system will show some orientational order), it is important to keep track of the labeling of the three directors, rather than reordering them using the magnitude of the order parameters each time the order parameters are calculated. The algorithm to determine the directors and thus the order parameters is discussed in more depth in Ref. [16]. It is also necessary to characterize the shape of the molecule to investigate how the conformation changes with temperature. To do this, we calculate the angular distribution function $f(\theta)$ which is related to the probability of finding a molecule with a bend angle between $\theta-\delta\theta$ and $\theta+\delta\theta$, where $\delta\theta\rightarrow 0$.

III. RESULTS AND DISCUSSION

We start with the most flexible model studied, $\epsilon_K=10$ and determine the phase behavior as a function of preferred angle θ_0 . The phases were identified from the orientational order parameters determined for the three symmetry axes (x , y , and z) of the molecules and for axes parallel to the arms (p) of the molecule; note that since the arms are equivalent, both arms are used to determine the order parameters for the p -axes. These are shown for five values ($\theta_0=98^\circ$, 99° , 101° , 102° , and 103°) in Fig. 1; other values of θ_0 show similar behavior. The angular distribution functions are shown in Fig. 2. We shall base our discussion mainly on the order parameters determined for the p axes of the molecules. For $\theta_0=103^\circ$, we observe that, on cooling past $T^*=1.20$, the long axis of the molecule becomes aligned with the major director of the phase. S_{pp}^{ZZ} increases rapidly from zero at the isotropic (I) – uniaxial nematic (N^+) transition and we observe that $S_{pp}^{XX}=S_{pp}^{YY}=-\frac{1}{2}S_{pp}^{ZZ}$. As this is similar to the behavior expected for a uniaxial nematic phase composed of rodlike molecules, we refer to the average conformations adopted by the molecules as rodlike, although clearly the system will adopt a range of bend angles which, as we will see, contains both rodlike and disklike conformations. As the system is cooled further to below $T^*=0.25$, S_{pp}^{XX} and S_{pp}^{YY} start to differ indicat-

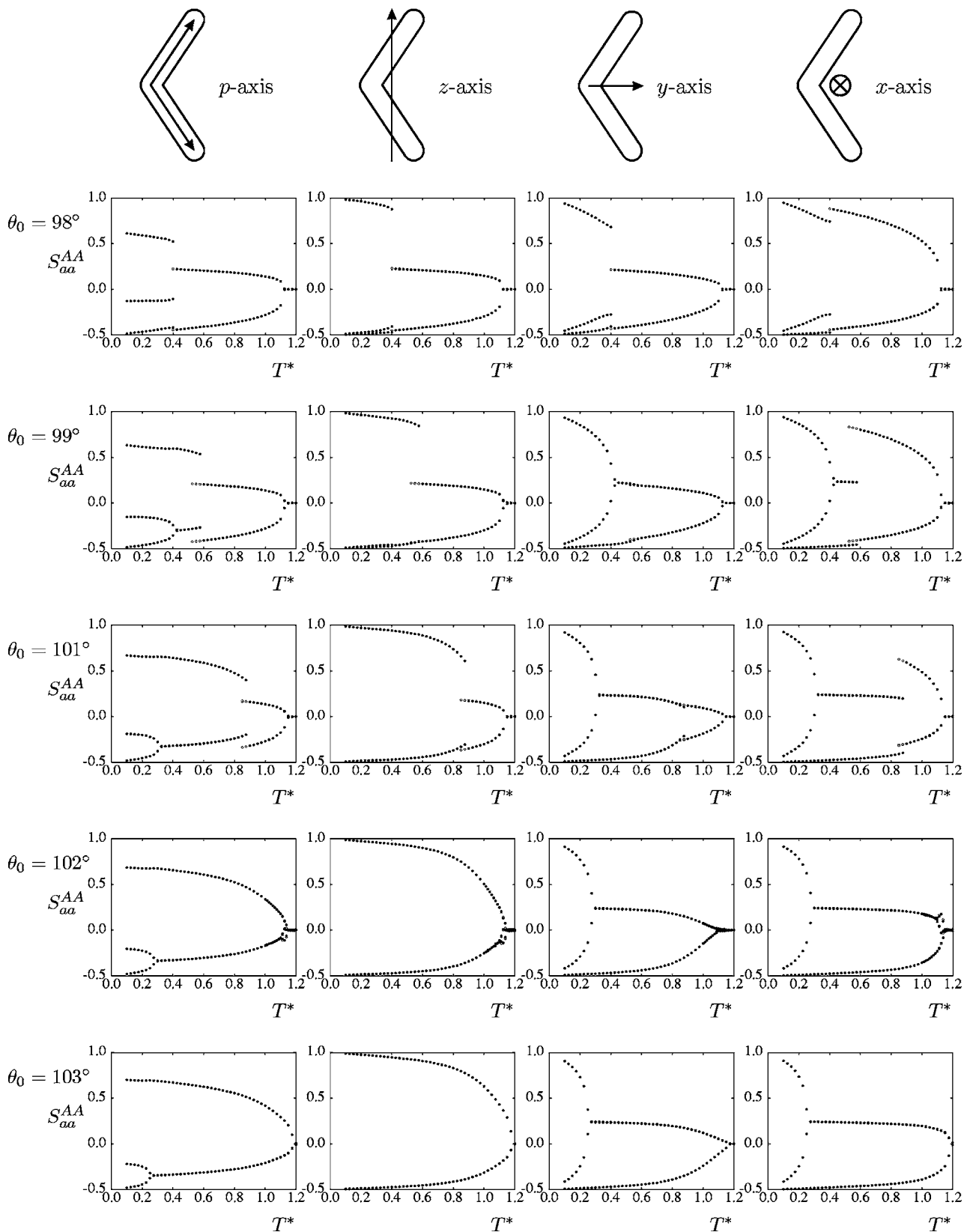


FIG. 1. The temperature dependence of the principal components of the ordering tensor for the arm axis (*p* axis) and the three molecular symmetry axes (*x*, *y*, and *z*), for five different values of the preferred interarm angle θ_0 with bending parameter $\epsilon_K=10$. $A=X, Y, \text{ or } Z$; $a = p, x, y, \text{ or } z$. Gray points are heating, white points are cooling, black points are common to both heating and cooling.

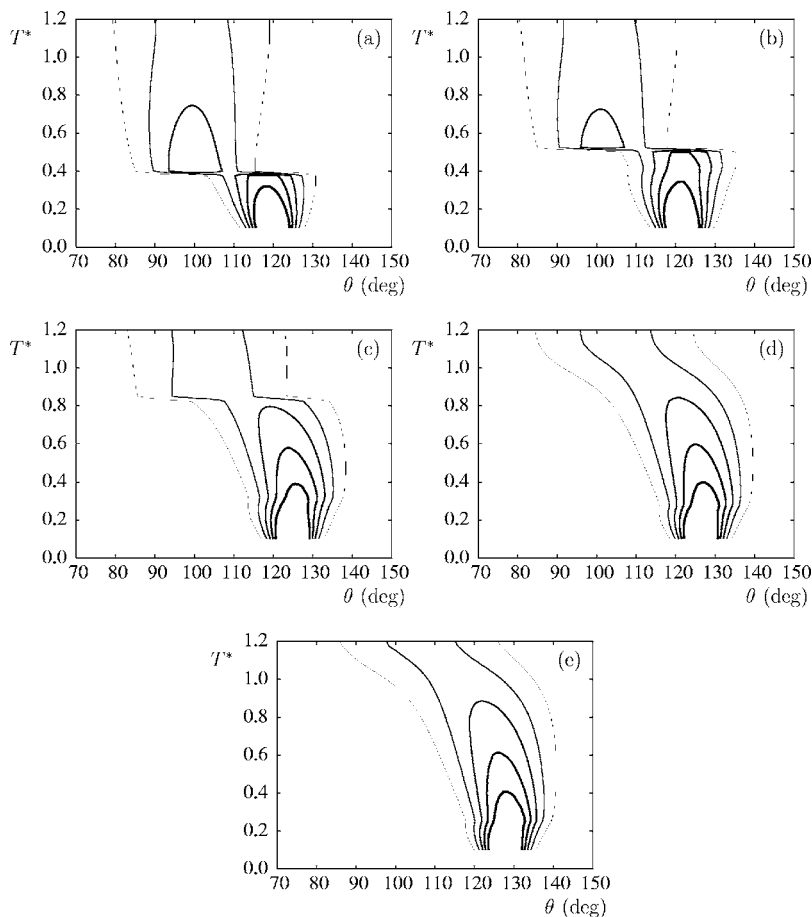


FIG. 2. Contours of the angular distribution function $f(\theta)$ as a function of temperature for the five models with $\epsilon_K=10$ in Fig. 1. (a) $\theta_0=98^\circ$, (b) 99° , (c) 101° , (d) 102° , and (e) 103° . Larger values of $f(\theta)$ are indicated by thicker lines.

ing the onset of biaxiality for this model. The angular distribution is reasonably wide, as we may expect for a relatively flexible molecule, and peaked at approximately θ_0 in the isotropic phase. As the temperature is lowered, the distribution becomes sharper indicating that the range of angles adopted by the molecules is slightly reduced. We also notice that the center of the distribution is shifted to higher values, thus as the temperature is reduced to $T^*=0.25$, just above the transition to the biaxial nematic, the distribution is centered at just below 130° , which is significantly different to the (gas phase) preferred angle of 103° . Thus the conformation depends on the environment the molecule finds itself, and vice versa; there is feedback between the molecular conformation and its environment. This is similar to the effect seen for flexible rodlike mesogens formed from a string of beads [21] and in the bond fluctuation model for nematics [22]. In both cases, straighter molecules enhance the uniaxial nematic phase, and the uniaxial nematic environment enhances the probability to find straighter molecules. As the temperature is lowered in the biaxial phase, the distribution is not affected significantly. The peak is shifted to very slightly lower values, again an indication that structure affects phase and phase affects structure. The biaxial phase appears to prefer a more bent molecule, although this phenomenon is very weak compared to the increase in linearity of the molecule in the uniaxial phase. For larger values of θ_0 , a similar behavior is observed, although the uniaxial nematic phase enters at a higher temperature and the biaxial nematic phase enters at a lower temperature, as we expect for a more linear molecule.

A similar behavior also occurs for $\theta_0=102^\circ$ over the majority of the temperature range. The main interesting difference occurs very close to the clearing point. On cooling from the isotropic phase, S_{pp}^{ZZ} increases as before, but the order parameters for the two other laboratory axes X and Y are not equal. This is observed for both heating and cooling runs, and is also reproducible in smaller and larger systems of 20^3 and 80^3 , respectively. On further cooling, S_{pp}^{XX} and S_{pp}^{YY} become equal. Thus we observe an isotropic-biaxial-nematic (N_B) phase transition, followed by a biaxial-nematic-uniaxial-nematic (N^+) transition. On further cooling a second biaxial nematic phase is observed, at a slightly higher temperature than for $\theta_0=103^\circ$. The behavior in the vicinity of the clearing point can be understood by observing the phase behavior of the $\theta_0=101^\circ$ system. Here, on cooling from the isotropic phase, the largest magnitude order parameter is negative, while the other two are positive and equal to half the magnitude of the first; we label these as $S_{pp}^{ZZ}=S_{pp}^{YY}=-\frac{1}{2}S_{pp}^{XX}$. This behavior is also observed for disklike molecules and rigid bent core molecules in which the angle is less than the tetrahedral angle [16], and so we denote this as an N^- uniaxial nematic. On going from $\theta_0=103^\circ$ to $\theta_0=101^\circ$, we have gone from a system in which the molecules tend to behave, on average, as a rigid bent core molecule on one side of the Landau point (i.e., rodlike) to one located on the other side (i.e., disklike). Thus near the clearing point for $\theta_0=102^\circ$, we have a distribution of molecules, some of which have rodlike conformations, and some of which have disklike conformations. Together, they behave like a mixture

of rodlike and disklike molecules that are very similar and so do not phase separate. This system therefore exhibits a biaxial nematic phase. The angular distribution function indicates that a small drop in temperature shifts the average shape only slightly, but enough so that the system orders in a rodlike rather than a disklike way. Thus on cooling the $\theta_0=102^\circ$, we enter a biaxial nematic phase directly from the isotropic phase, as for rigid molecules at the Landau point in their phase diagram. However, in contrast to the rigid model, on further reduction of the temperature, the biaxial nematic phase is not stable with respect to a uniaxial nematic phase. On further cooling of the $\theta_0=101^\circ$ system, the order parameters undergo a sharp change at approximately $T^*=0.85$. They change from being characteristic of a disk, to those more characteristic of a rod. S_{pp}^{ZZ} becomes the dominant order parameter, while the equivalent order parameters for the laboratory X and Y axes become negative and equal. We also observe a small amount of hysteresis at this transition. The angular distribution function shows that the shape remains largely unchanged on cooling through the isotropic phase into the N^- phase. The distribution is again wide and peaked roughly at $\theta_0=101^\circ$. However, at $T^*=0.85$, there is a large conformation change, the distribution becomes noticeably narrower, but also significantly shifts its center from 101° to about 120° ; that is, from disklike on average to rodlike on average. Clearly, this shape change is associated with the first order transition seen between the two uniaxial N^- and N^+ phases already discussed. On further cooling through the N^+ phase, the peak again shifts to slightly higher values as for the other models. The N^+ uniaxial nematic eventually undergoes a second order transition to the biaxial nematic as the temperature is lowered further, as before. For $\theta_0=100^\circ$ and 99° , similar behavior is observed to $\theta_0=101^\circ$, with the transition between the two uniaxial nematic phases forced to lower temperatures, while the biaxial nematic phase enters at slightly higher temperatures. This latter phenomenon can be explained as the molecules in the uniaxial nematic phase occurring directly above the biaxial nematic are, on average, behaving more as rods than disks. By lowering the bend angle, the behavior is still more rodlike than disklike, but the molecules are more bent and so the biaxial nematic phase occurs at a higher temperature, just as for rigid molecules [16].

As θ_0 is reduced to 98° , the rodlike N^+ uniaxial phase is lost completely; presumably the increased stability of the N_B and N^- phases combined with the decreased stability of the N^+ phase as θ_0 is lowered leads to the loss of the uniaxial phase composed of rodlike conformations. Thus for $\theta_0=98^\circ$, we observe a transition between a uniaxial nematic (N^-) phase and a biaxial nematic phase. However, at this transition, the order parameters do not gradually separate as observed for the N^+-N_B transitions for other values of θ_0 . Rather, there is a large jump in their values at $T^*=0.40$, and a small amount of hysteresis occurs. Therefore, we observe a first order, rather than second order, uniaxial-nematic-biaxial-nematic transition for this model. As for the transitions between rodlike and disklike uniaxial nematic phases, we observe that the first order nature of this transition is associated with a significant conformation change. The peak in the angular distribution shifts from just less than 100° to

120° . The order parameters for the three molecular symmetry axes x , y , and z are also shown in Fig. 1. These order parameters do not change the assignment of the phases in any way. However, note that in some cases transitions may be missed. For example, as discussed for rigid molecules [16], when the primary nematic order parameter S_{zz}^{ZZ} for rodlike molecules is high, the difference between S_{zz}^{XX} and S_{zz}^{YY} is minimal and so the biaxial nematic phase cannot be distinguished from the uniaxial one if a single probe bond directed along the z axis was used for characterization. We also observe that the behavior of the order parameters for the y axis is similar in both the N^+ and N^- uniaxial phases, and the transition between these cannot be readily identified using only the y axis order parameters. Thus we conclude that, as for rigid molecules, the probe bond used for characterizing the phases should be placed as parallel as possible to the arms of the molecules, as this can unambiguously characterize the different uniaxial and biaxial nematic phases.

We now turn to the next bending parameter studied, $\epsilon_K=20$. The order parameters for this model over a narrow range of values for θ_0 are shown in Fig. 3 and the corresponding angular distribution functions are shown in Fig. 4. For $\theta > 106^\circ$, the system exhibits behavior similar to the large angles for $\epsilon_K=10$; that is, a uniaxial N^+ phase is observed on cooling from the isotropic, with a low temperature biaxial nematic. For $\theta_0=106.00^\circ$, we observe behavior similar to the model with parameters $\epsilon_K=10$ and $\theta_0=102^\circ$. On cooling from the isotropic phase, a narrow region of biaxial nematic is observed as the molecules adopt a mixture of rodlike and disklike structures and the ordering is neither characteristic of a rod-dominated or disk-dominated system. This is, again, reproducible in larger systems of 80^3 molecules. On further cooling, the slight shift in conformations adopted to more rodlike is enough to destabilize the biaxial nematic and form a N^+ uniaxial nematic. The biaxial phase reenters at low temperatures. If the preferred angle is reduced by one quarter of a degree to $\theta_0=105.75^\circ$, the system is seen to exhibit a disklike uniaxial N^- phase, and then undergo a transition to a rodlike uniaxial N^+ phase. There are hints of biaxiality in the order parameters on either side of this transition, although clearly this is very weak. Note that at this transition, the width of the angular distribution is essentially unchanged, and accompanied by only a very small shift of less than 2° in the center of the distribution. However, this shift moves the center of the distribution from just below the tetrahedral angle to just above it. Clearly this small change in the average molecular conformation about the tetrahedral angle is enough to significantly influence the phase behavior and thus the order parameters. For $\theta_0=105.50$, the order parameters indicate that an N^- phase forms first on cooling from the isotropic phase. The angular distribution is peaked at about 108° , just lower than the tetrahedral angle. On further cooling there is a relatively smooth change in the center of the angular distribution, through the tetrahedral angle, to larger values. Unlike the sharp transition between two distinct conformations observed for the more flexible molecules ($\epsilon_K=10$), there appears to be a continual shape change from disklike to rodlike on cooling. The order parameters for the p axes indicate that in the temperature range of the crossover, a biaxial nematic phase is observed between the two different

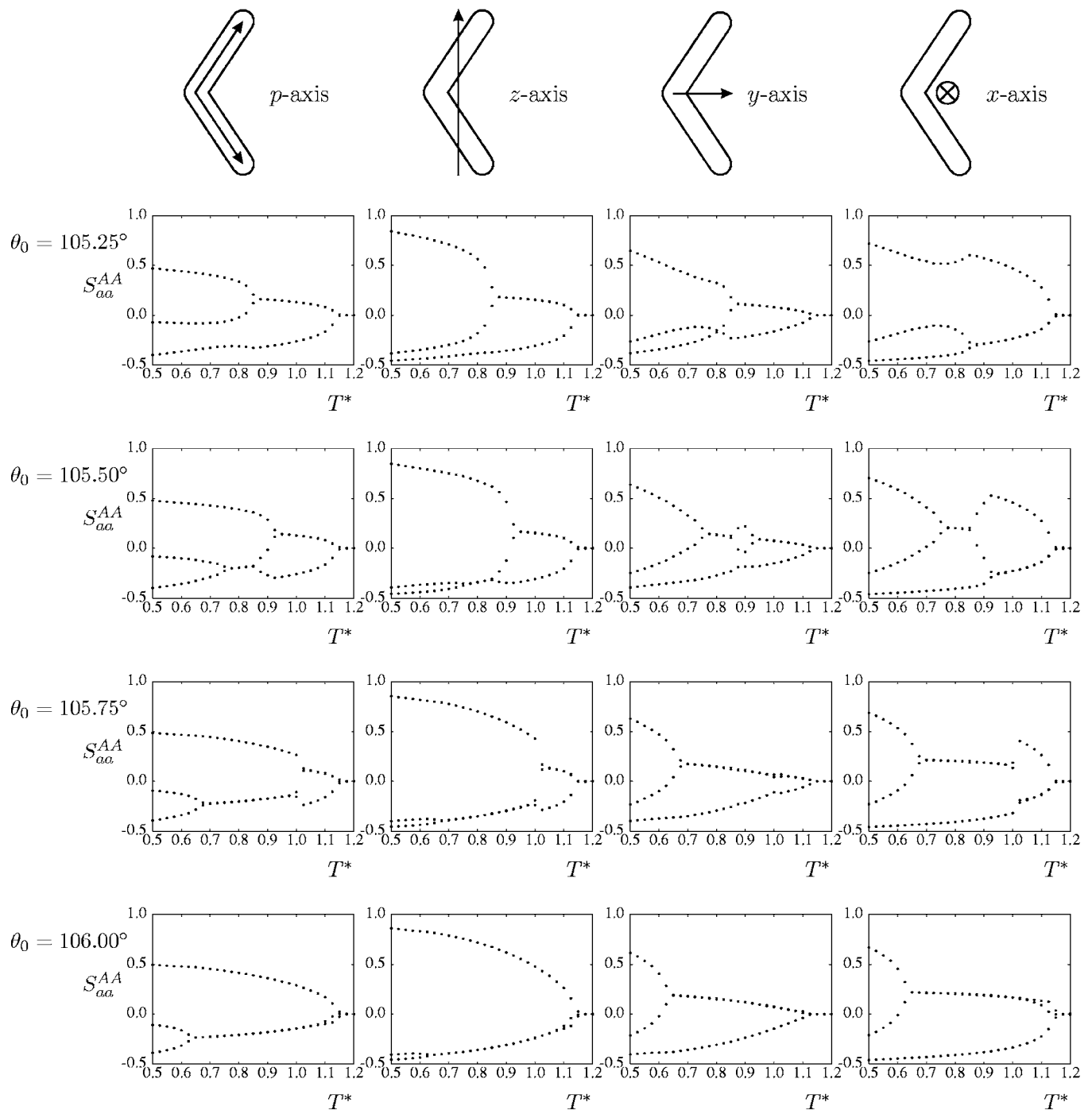


FIG. 3. The temperature dependence of the principal components of the ordering tensor for the arm axis (p axis) and the three molecular symmetry axes (x , y , and z), for four different values of the preferred interarm angle θ_0 with bending parameter $\epsilon_K=20$. $A=X, Y$, or Z ; $a = p, x, y$, or z .

uniaxial N^- and N^+ nematic phases. This behavior is reproducible on heating and cooling, and also in larger systems of 80^3 . Thus the phase behavior observed for this model is $I - N^- - N_B - N^+ - N_B$. The molecules adopt, on average, a disk-like conformation at high temperature which changes to rod-like on cooling, and the corresponding uniaxial nematic phases are observed. In the intermediate regime, the biaxial nematic phase is observed. This may also be the case where the hint of biaxiality was observed at the $N^- - N^+$ transition

for the model with preferred angle $\theta_0=105.75^\circ$, although this transition is clearly much more first order in nature. Lowering the preferred angle to $\theta_0=105.25^\circ$ is enough to lower the temperature at which the rodlike conformation would dominate, and at the same time raise the temperature at which the (low temperature) biaxial nematic phase would occur, and so only a single biaxial nematic phase is observed, which follows a disklike uniaxial N^- phase. As for $\epsilon_K=10$, the order parameters for the molecular x , y , and z symmetry axes do

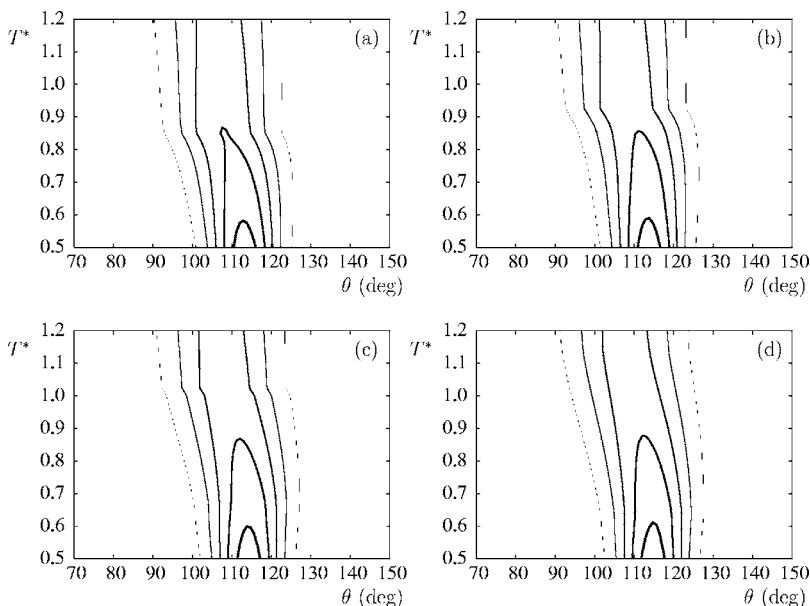


FIG. 4. Contours of the angular distribution function $f(\theta)$ as a function of temperature for the five models with $\epsilon_K=20$ in Fig. 3. (a) $\theta_0 = 105.25^\circ$, (b) 105.50° , (c) 105.75° , and (d) 106.00° . Larger values of $f(\theta)$ are indicated by thicker lines.

not change any phase assignments, but it is interesting to view the behavior of one of these in particular. We have already seen that order parameters for the y axis are not sensitive to the system exhibiting an N^+ or an N^- phase. In both cases, since the molecular y axis is not aligned along the preferred direction of alignment, there is one dominant negative order parameter, and the two minor ones both have a positive value equal to half the magnitude of the dominant one. On cooling between the two uniaxial nematic phases for $\theta_0=105.50$, there is a clear splitting in these, characteristic of the biaxial nematic phase. Thus while a probe aligned along the bisector of the molecule could not distinguish the two uniaxial phases, it can distinguish uniaxial from biaxial.

Similar simulations have been performed for $\epsilon_K=50$ as a function of preferred angle θ_0 . These are found to exhibit only a single uniaxial nematic phase (either N^+ or N^-) and a biaxial nematic phase, in addition to the isotropic. The phase behavior of these three models is collated in Fig. 5, and

compared to that for rigid molecules [16]. Starting with the rigid case, the phase diagram shows that the $N^- - I$ transition temperature is essentially independent of bend angle, whereas the $N^+ - I$ transition temperature increases rapidly as the bend angle is widened. This is exactly as we expect for bent core systems, as the more linear the molecule, the higher the clearing point [6,15,16]. A similar increase in the clearing temperatures was also observed for off-lattice models as the molecule becomes straighter [20]. We can understand this by calculating the intermolecular potential for fixed bend angles as a function of the angle between the molecules. For a pair of molecules in a disklike conformation ($\theta < 109^\circ 28'$) with their x axes aligned (as we expect in a N^- uniaxial nematic, the intermolecular potential is essentially independent of the angle between the other axes). Thus one molecule can rotate about its x axis without changing the intermolecular potential significantly. Moreover, changing the rigid angle also does not significantly influence the mag-

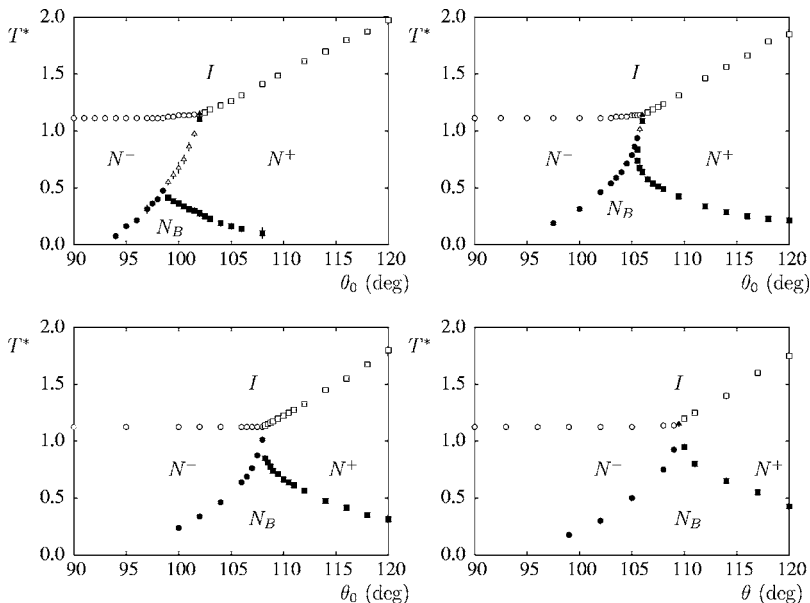


FIG. 5. Phase diagrams for fixed values of the bending parameter (a) $\epsilon_K=10$, (b) 20, (c) 50, and (d) the rigid model ($\epsilon_K=\infty$). White circles: $N^- - I$, black circles: $N_B - N^-$, white squares: $N^+ - I$, black squares: $N_B - N^+$, white triangles: $N^+ - N^-$, and black triangles: $N_B - I$.

nitude of the intermolecular potential for $\theta < 109^\circ 28'$. Thus the intermolecular potential, and hence the transition temperature, is essentially independent of θ for rigid molecules on the disklike side of the phase diagram. In contrast, for rodlike rigid molecules, increasing the bend angle significantly increases the magnitude of the interaction between the rods on neighboring sites as they necessarily become more parallel. This is the reason that the $N^+ - I$ transition temperature rises on the rodlike side of the phase diagram. The biaxial nematic phase is observed over a reasonable range of angles, although only at temperatures significantly lower than the clearing point. The biaxial nematic phase undergoes a transition to the isotropic phase at a single angle only, $\theta = 109^\circ 28'$, known as the Landau point. At this angle, the molecule cannot be described as either rodlike or disklike; there are no uniaxial phases present for this angle, and the molecule does not exhibit behavior characteristic of a rod or a disk at any temperature. For small deviations from this angle, the corresponding uniaxial phase is observed before entering the biaxial nematic phase and the temperature at which the biaxial nematic phase is observed rapidly decreases as the angle deviates from the tetrahedral angle. Here it makes sense, for example, to refer to molecules with an angle larger than the tetrahedral angle as rodlike bent core molecules.

At first glance, the phase diagram for $\epsilon_K = 50$ looks very similar to the rigid case. However, there are subtle points that make it quite different. First, the critical value of θ_0 for which rodlike rather than disklike behavior is observed is not equal to the tetrahedral angle; the actual angle is fractionally over 108° . Second, the behavior in the vicinity of the Landau point has changed. Third, the rate at which the biaxial nematic transition temperature drops is larger on the rodlike side than on the disklike side. All three of these observations can be understood when we consider the interplay between the bending potential and the (intermolecular) orientational ordering potential. If the molecules adopt a disklike conformation, as we have already discussed, the intermolecular potential is not strongly dependent on the bend angle. However, if the molecules adopt a conformation in which the bend angle is larger than the tetrahedral angle, then the magnitude of the intermolecular potential is larger than for the disklike conformation. If the bending potential did not favor conformations on one side of the tetrahedral angle or the other, then the total potential would still favor the higher angle because of the increased magnitude of the orientational ordering potential in this conformation. This explains the first observation that the critical value of θ_0 is not equal to the tetrahedral angle for a flexible molecule. As θ_0 approaches the tetrahedral angle, there comes a point when it is energetically more favorable to become rodlike rather than disklike. The distance between the critical angle and the tetrahedral angle clearly depends on the width of the conformations that can be adopted, and thus on the flexibility of the molecule. Because of this behavior, the traditional Landau point that is approached by steeply rising but continuous $N_B - N^+$ and $N_B - N^-$ transition lines is not observed. However, that is not to say that a biaxial nematic will not be observed where the two uniaxial phases and the isotropic phase meet. The behavior in the vicinity of the Landau point is more apparent for

the models with increased flexibility. Thus for $\epsilon_K = 10$, there is a line of first order transitions between two uniaxial nematic phases, one in which the molecules are disklike, and one in which they are rodlike. These first order phase transitions are accompanied by a change in average molecular conformation. As this line approaches the transition to the isotropic phase, there is evidence for a very narrow range biaxial nematic phase. At the other extreme, the line of first order transitions bifurcates on cooling and a biaxial nematic phase is seen at low temperatures. On the rodlike side of the phase diagram, the transitions between the uniaxial nematic (N^+) phase and the biaxial nematic phase are all second order, as for the rigid bent core models. However, on the disklike side of the phase diagram, the transitions to the biaxial nematic phase are first order and accompanied by a significant change in conformation, as at the $N^- - N^+$ transitions observed for slightly large values of θ_0 at higher temperatures. Thus it appears that the Landau point observed in the rigid model has split into two distinct points, joined by a line of first order phase transitions. At the high temperature end of this line, a small biaxial region is observed, and the transition between the isotropic phase and the biaxial nematic phase appears second order. The shape of the boundaries of this region are not clear, although it appears to be confined to a very narrow region of angles. At the low temperature end of this line, the $N_B - N^+$ transition is second order, as for rigid molecules. However, on the N^- side, the uniaxial-biaxial transition becomes first order, and is accompanied by the change in shape. For $\epsilon_K = 20$, the molecule is somewhat stiffer and so the range of conformations available is narrower. The first order transition line between the two uniaxial N^- and N^+ phases is still observed, but is much shorter and steeper. Note that as this line is approached from below, the $N^+ - N_B$ line is significantly lower in temperature than the $N^- - N_B$ line, echoing the observation in the phase diagram for $\epsilon_K = 50$. Indeed, for one particular value of $\theta_0 = 105.50^\circ$, where the $N^+ - N_B$ line ends, a biaxial phase is observed both above and below the N^+ phase, and a N^- phase above all three of these. Presumably as the bending parameter is increased further from $\epsilon_K = 20$, the $N^+ - N^-$ line becomes both shorter and steeper. By the time $\epsilon_K = 50$, the range of values of θ_0 over which this behavior occurs becomes extremely narrow and it is extremely difficult to determine exactly how the transition lines approach each other.

We can view the influence of flexibility in another way; that is to plot the phase behavior for fixed value of θ_0 as a function of bending parameter ϵ_K . This is done for three angles in Fig. 6. We choose to plot these figures for the tetrahedral angle, one angle below this (100°) and one angle above ($\theta_0 = 112^\circ$). We start this discussion with the larger angle, $\theta_0 = 112^\circ$. For this angle the rigid bent core system exhibits an isotropic phase, a N^+ uniaxial nematic phase, and finally a biaxial nematic phase. As the bending parameter ϵ_K is reduced from the rigid limit, the phase behavior is largely unchanged until the molecule becomes relatively flexible, and the range of angles that can be adopted is widened. This leads to more straightened conformations, due to the favorable orientational interactions arising from the intermolecular potential. Since the conformations adopted tend, on average, to be straighter, this leads to an increase in the

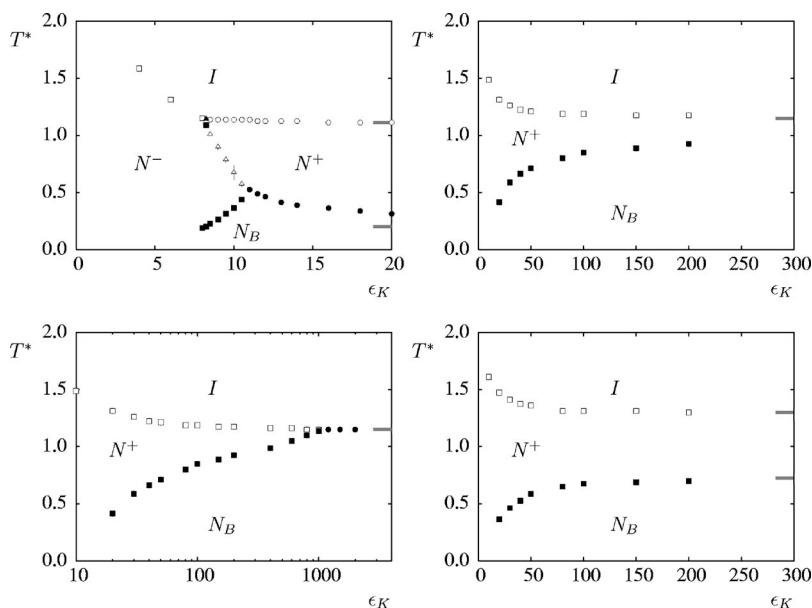


FIG. 6. Phase diagrams for fixed values of the preferred angle (a) $\theta_0=100^\circ$, (b) and (c) $109^\circ 28'$, (d) 112° . Symbols as in Fig. 5. The bars at the right hand side indicate the phase transitions in the rigid limit.

temperature for the N^+-I transition, but a decrease in the N_B-N^+ transition temperature. For the smaller angle, $\theta_0=100^\circ$, we observe the phase behavior N_B-N^+-I for the rigid limit, and so may expect that as the molecule becomes less rigid, the tendency to form less bent conformations may lead to systems with conformations, on average, closer to the tetrahedral angle, and thus stabilize the biaxial nematic phase. This is indeed the case. As ϵ_K is lowered from the rigid limit, the N^-I transition is largely unaffected. We can relate this to the fact that the intermolecular potential between disklike conformations with their x -axis parallel is essentially independent of the bend angle, as already discussed. In contrast, the temperature at which the N_B-N^- transition occurs rises. However, this increase in the stability of the biaxial nematic phase is terminated by the induction of the N^+ phase into the phase diagram. As the molecules have the freedom to become to less bent, this helps stabilize the biaxial nematic phase at higher temperatures. However, at a certain point ($\epsilon_K < 11$) the straightened conformations start to dominate at higher temperatures and an N^+ uniaxial nematic is stabilized. We now turn to flexible models with the preferred angle equal to the tetrahedral angle. As we have seen, the rodlike conformations tend to be more preferred than the disklike ones, because the orientational potential tends to prefer straightened conformations. Thus positive deviations from θ_0 are more favorable than negative ones in the vicinity of the tetrahedral angle. This means that flexible models with $\theta_0=109^\circ 28'$ will tend to behave, on average, more like rodlike systems than disklike ones. This is clearly the case, the phase diagram looks similar to that for $\theta_0=112^\circ$. As ϵ_K is increased from low values, the N^+-I transition temperature rapidly decreases, as the range of straightened conformations accessible to the highly flexible molecules diminishes. Similarly the N_B-N^+ transition temperature increases as the molecules necessarily become more bent as they cannot access the more straightened conformations. The difference between the systems with $\theta_0=109^\circ 28'$ and 112° is that the latter has a uniaxial N^+ phase in the rigid limit, whereas the former has a transition directly from the isotropic into the biaxial nem-

atic phase. Whereas the limiting phase behavior and transition temperatures are reached for $\theta_0=112^\circ$ by about $\epsilon_K=100$, the stiffness of the molecule must be increased much further to $\epsilon_K > 1000$ before the limiting behavior for $\theta_0=109^\circ 28'$ is reached. In particular, this latter point illustrates that even if the molecule has a preferred bend angle equal to the tetrahedral angle, if it is not extremely rigid, then the biaxial nematic phase will be destabilized with respect to the N^+ uniaxial nematic phase. However, that is not to say that such a molecule cannot exhibit a biaxial nematic phase on cooling from the isotropic phase. Indeed, as we have seen for $\epsilon_K=10$ and 20, there may be a narrow temperature range over which the biaxial nematic phase is observed where the rodlike region, the disklike region, and the isotropic phase meet.

IV. CONCLUSIONS

We have developed a two-arm lattice model with a bend potential to investigate how flexibility can influence the phase behavior of biaxial nematics. The defining characteristics of the model are the preferred bend angle, θ_0 and the stiffness of the bending potential ϵ_K . The simulations indicate that flexibility can dramatically influence the phase behavior. As the molecules become more flexible, the range of conformations that they can adopt becomes wider. The orientational ordering potential between the individual arms tends to favor the straighter conformations. This tends to destabilize the biaxial nematic phase of molecules with a bend angle greater than the tetrahedral angle. In contrast, the biaxial nematic phase is enhanced (moved to higher temperatures) for molecules in which θ_0 is less than the tetrahedral angle, since the molecules tend to be less bent. However, eventually the molecules become too straight and exhibit a rodlike uniaxial phase rather than a biaxial one. This suggests that if a molecule has a bend angle larger than the tetrahedral angle, it should be as rigid as possible. In contrast, if the bend angle is less than the tetrahedral angle, it should be flexible to in-

crease the temperature at which the biaxial nematic is observed.

As the flexible molecules can change conformation, they can change their nature as a function of temperature. In particular, a disklike molecule ($\theta_0 < 109^\circ 28'$) can change from being disklike to rodlike on cooling. This introduces a line of first order transitions into the (T^*, θ_0) phase diagram for fixed bending potentials between two different uniaxial nematic phases. At the low temperature end of this line, a biaxial nematic phase is observed. On one side the biaxial region is bounded by a second order transition to a N^+ uniaxial nematic phase. On the other side, a N^- uniaxial nematic phase is observed; this transition may be first or second order depending on the flexibility of the molecule. With increasing stiffness, the line of first order transitions between the two uniaxial nematic phases becomes shorter and steeper, until eventually they merge in the rigid limit. As the Landau point is essentially split into a line of first order phase transitions, this means that the large region of biaxial nematic is forced to low temperature. However, where this line joins the transition lines to the isotropic phase, a biaxial nematic phase is

observed, albeit in a very narrow region of phase space, below which a uniaxial nematic phase is observed.

Flexibility clearly has an influence on the phase behavior of bent core molecules. The larger the flexibility, the larger the change in the phase diagram. Flexibility appears to destabilize the biaxial nematic phase with respect to the N^+ uniaxial phase, dominated by rodlike conformations. This leads to interesting behavior in the vicinity of the Landau point, which is split into a line of first order phase transitions between two types of uniaxial nematic. While the low temperature biaxial region may be too low to access for a real molecule, the narrow biaxial nematic region that occurs where this first order line approaches the isotropic transition may be accessible.

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