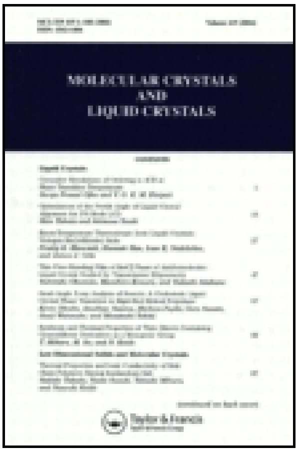

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Computer Simulation of Liquid Crystalline Molecules Composed of Spherical Interaction Elements

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COMPUTER SIMULATION OF LIQUID CRYSTALLINE MOLECULES COMPOSED OF SPHERICAL INTERACTION ELEMENTS

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Abstract Computer simulation is carried out for a system of model liquid crystalline molecules in order to understand the nature of intermolecular interactions responsible for the formation of liquid crystals. The model molecule is made up of linearly connected four spherical beads, each of which acts as a center of the Lennard-Jones interactions. The formation of a nematic phase and the subsequent nematic-isotropic phase transition are observed. It is also found that the liquid crystal formation in a high density system is predominantly driven by repulsive interactions while that in a lower density system requires additional contributions from attractive intermolecular interactions.

INTRODUCTION

Molecular dynamics simulations of real liquid crystalline molecules with full atomic details have been carried out in recent studies.[1,2,3] This approach is expected to provide useful information about the structure-property relationship in real liquid crystalline systems, however at the present stage the results may still be regarded as of only qualitative importance since computation is limited in both its size and time. Moreover, these simulations of realistic systems may fail to provide a straightforward insight into the nature of predominant intermolecular interactions responsible for the formation of liquid crystalline phases, since calculations include all possible contributions from various types of interactions.

On the other hand, the mean field theory developed for model liquid crystalline molecules (such as the Maier-Saupe theory[4]) can provide simple representation of intermolecular potential (of certain particular type) acting on liquid crystalline molecules. It is of course evident however that the mean-field theories cannot include the structural details of constituent molecules and consequently fail to discuss the effects of site-site interactions.

To fill the gap between these two approaches and understand the nature of predominant intermolecular interactions responsible for the formation of liquid crystals, we carried out in this study a computer simulation of a system of simple rod-like particles using site-site interaction potentials. The model molecule is composed of a linear array of spherical interaction elements, each of which acts as a center of atom-atom interactions. The intermolecular potential between these molecules are calculated by using the Lennard-Jones 6-12 type potential and the 12 potential, representing an attraction-repulsion interaction and a pure soft-repulsion interaction, respectively. By introducing this simple model, we can demonstrate that the formation of the liquid crystalline phase in a dense system is driven predominantly by repulsive interactions while that in a low density system requires additional contributions from attractive intermolecular interactions.

THE MODEL

The model molecule is made up of four linearly connected spheres as illustrated in Figure 1. The intermolecular pair interaction potential V_{ij} between the molecules i and j is calculated as a double sum of the Lennard-Jones site-site potential over the respective interaction sites $k \in i$ and $l \in j$ according to the following equations:

$$V_{i,j}=\sum_{k\in i}\sum_{l\in j}4\varepsilon\left\{\left(\frac{\sigma}{r_{k,l}}\right)^{12}-\left(\frac{\sigma}{r_{k,l}}\right)^{6}\right\} \qquad (1)$$

$$V_{i,j}=\sum_{k\in i}\sum_{l\in j}4\varepsilon\left(\frac{\sigma}{r_{k,l}}\right)^{12} \qquad (2)$$

where ε and σ have their conventional meaning. The Lennard-Jones 6-12 (LJ 6-12) potential defined in Eq. 1 includes both attractive and repulsive contributions and assumes a minimum value at $r_{k,l} = 1.12\sigma$, while the Lennard-Jones 12 (LJ 12) potential in Eq. 2 represents a pure soft-repulsion interaction whose strength mono-

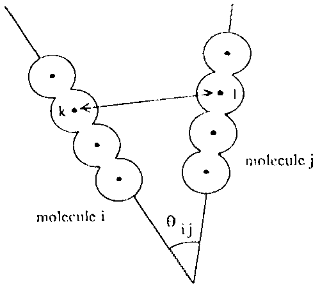

FIGURE 1 The Beads model

tonously increases with decreasing $r_{k,l}$. The orientational partition function of the whole system is then calculated by taking a sum of V_{ij} over all pairs of the molecules and over all possible configurations of the system.

In the present calculation we assume that each interaction sphere has a radius of $\sigma/3$, i.e., our model molecule has a length of $8\sigma/3$ and a diameter of $2\sigma/3$. The volume of the molecule is then calculated to be $v = 16\pi\sigma^3/81$ and this value is used to define the density of the system.

For comparison, simulations are also carried out by using the Gay-Berne potential[5] in which the collection of the LJ 6-12 potentials between multiple interaction sites of the two molecules is termed a single-site potential between their centers. The parameters assumed here for the four-site beads molecule are $\nu = 1$, $\mu = 2$, $\varepsilon_e/\varepsilon_s = 0.2$ (see ref.5 for their definition).

SIMULATION METHOD

The Monte Carlo (MC) simulations were carried out for a system of 512 molecules (4 x 512 interaction elements) in a cuboid cell of the dimension of 1:1:3. We also carried out some reference experiments for larger and smaller systems and confirmed that the calculations including more than 512 molecules reproduce the same results (i.e., free from the size effect). The simulations were performed in constant NVT ensembles according to the Metropolis scheme[6] under a periodic boundary condition.

As an initial configuration we chose a perfectly aligned nematic phase, where all molecules were placed at random positions and oriented along one direction. The density of the system is calculated to be $\rho = 512v/V$, where v is the molecular volume defined above and V is the volume of the simulation cell. In order to examine the effect of density, simulations are carried out for both high ($\rho = 0.49$) and low ($\rho = 0.31$) density systems.

All calculations were carried out on a HITAC S3800 super computer at the University of Tokyo. The program was almost fully vectorized, and the computation time for each Monte Carlo step was about 0.05 seconds. In most experiments the system was equilibrated over 10^4 steps, while the calculations in the phase transition region were extended over 3×10^4 steps.

RESULTS

In Figure 2 the variation of the intermolecular potential V_{ij} between the two beads molecules is calculated as a function of the distance between their centers of mass r_{ij} for four typical configurations; side-by-side, end-to-end, cross and T-shaped. As expected, the variation of V_{ij} depends not only on the intermolecular distance but also on the mutual orientation of the two molecules. It is particularly important to note that the cross and the T-shaped configurations, for which the Maier-Saupe theory predicts positive V_{ij} values, can assume negative (favorable) V_{ij} values in the present calculation (and the Gay-Berne model also; not shown). For example, the T-shaped configuration becomes more stable than the linear end-to-end configuration as r_{ij} is decreased to less than 3σ. Similarly, the cross configuration is significantly stabilized in the $r_{ij} < 2\sigma$ region, in contrast to the fact that the same configuration is essentially disregarded in the case of the Maier-Saupe theory. Thus, it is evident that the beads model, which takes into account the effects of site-site interactions, gives fundamentally different V_{ij} potential from that predicted by the mean-field theories.

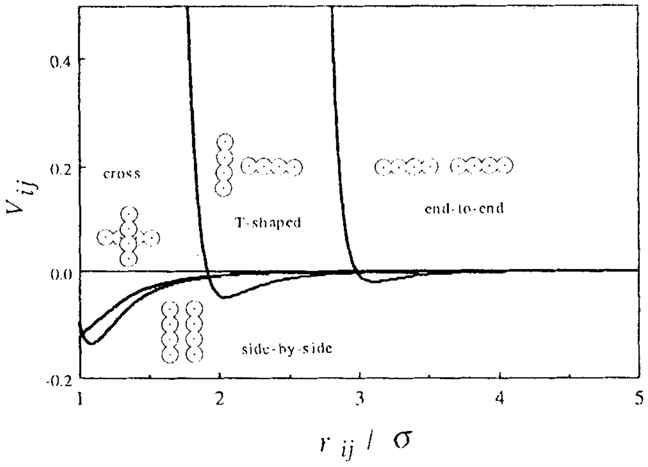

FIGURE 2 Dependence of the intermolecular potential V_{ij} on the distance r_{ij} calculated using the beads model for four typical configurations.

In Figure 3 we calculate the pair orientational order parameter $<P_2(\cos\theta_{ij})>$ as a function of the intermolecular distance r_{ij} by using three different models: the present beads model, the Gay-Berne model and the Maier-Saupe model. All these three models calculate an increase in the $<P_2(\cos\theta_{ij})>$ value with decreasing r_{ij} and thus predict the formation of an orientationally ordered liquid crystalline phase.

However the calculated profile of the $<P_2(\cos\theta_{ij})>$ curve is significantly different for these three models. The most important difference may exist between the Maier-Saupe theory and the other two theories. The former predicts a monotonous increase in $<P_2(\cos\theta_{ij})>$ with decreasing r_{ij}, however the latter two predict more complicated variations. For example, they calculate negative V_{ij} values at $2.0\sigma < r_{ij} < 2.5\sigma$, where the formation of the T-shape configuration is expected. Moreover, the beads model calculation gives a new dip at about $r_{ij} = 1.3\sigma$, which should be associated with the cross-type molecular arrangements (the lack of this local minimum in the Gay-Berne calculation is due to the fact that the set of the Gay-Berne parameters used here was optimized to reproduce the planar configurations such as side-by-side and end-to-end, rather than the cross configurations). Finally, it should be noted the position of the maximum peak calculated for the beads model is located exactly at $r_{ij} = 1.12\sigma$ which corresponds to the minimum position of the V_{ij} potential defined in Eq.1.

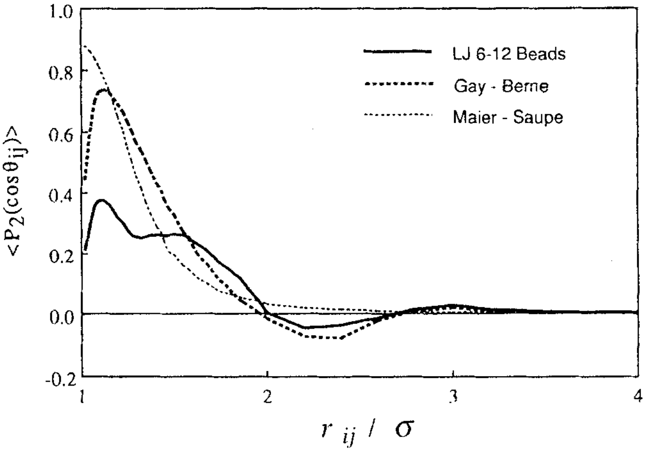

FIGURE 3 Dependences of the pair orientational order parameter $<P_2(\cos\theta_{ij})>$ on the distance r_{ij} calculated for three different models.

The result shown above indicates that simple rod-like model molecules, composed of a linear array of spherical elements and interacting with their neighbors through site-site pair potential, can form an ordered liquid crystalline phase. For more quantitative discussion we now introduce the orientational order parameter of the system $<P_2(\cos\theta_i)>$ which is determined with respect to the angle θ_i between the symmetry axis of the i-th molecule and the nematic director **n** of the system. Since the orientation of the nematic vector fluctuates during the evolution of the system, we determine the nematic director **n** at every sampling step so that the order parameter of the system becomes maximum.[7]

Figure 4 shows the temperature dependence of $<P_2(\cos\theta_i)>$ calculated for a high density system ($\rho = 0.49$). We obtain non-zero $<P_2(\cos\theta_i)>$ values with the magnitude of 0.4 - 0.7 for both LJ 6-12 (○) and LJ 12 molecules (△) at low temperatures. Examination of snap-shot pictures indicates that this phase has the nematic ordering. The calculated $<P_2(\cos\theta_i)>$ value undergoes a sharp decrease at about $k_BT/\varepsilon = 3$, indicating the presence of a nematic-isotropic transition. This temperature may be translated into T = 63°C if we can identify the critical temperature of the LJ 12-6 spheres ($k_BT/\varepsilon = 1.35$)[8,9] with the experimental critical temperature of argon (T = -122 °C). Another important observation in this figure is the fact that the nematic formation is predicted for not only the LJ 6-12 molecules but also for the LJ 12 molecules, for which the calculation includes only soft-repulsion contributions. Thus, it can be concluded that the nematic phase formation in this higher density system is essentially driven by repulsive interactions (excluded volume effect) between constituting molecules.

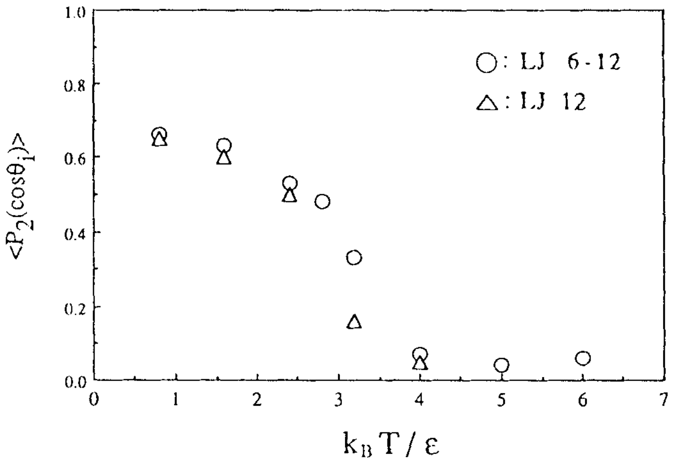

FIGURE 4 Temparature dependence of the $<P_2(\cos\theta_i)>$ value in a high density system ($\rho = 0.49$).

However, the phase behavior becomes considerably different if the system density is decreased. Figure 5 shows the temperature dependence of the orientational order parameter calculated for a system with r = 0.31. The most notable feature here is the disappearance of the nematic phase in the system of the LJ 12 molecules (△). In contrast, the LJ 6-12 molecules (○) exhibit essentially the same phase behavior as we observed for a higher density system in Figure 4. This result immediately leads to a conclusion that the role of attractive interactions becomes more important for generating the liquid crystalline order in a lower density system.

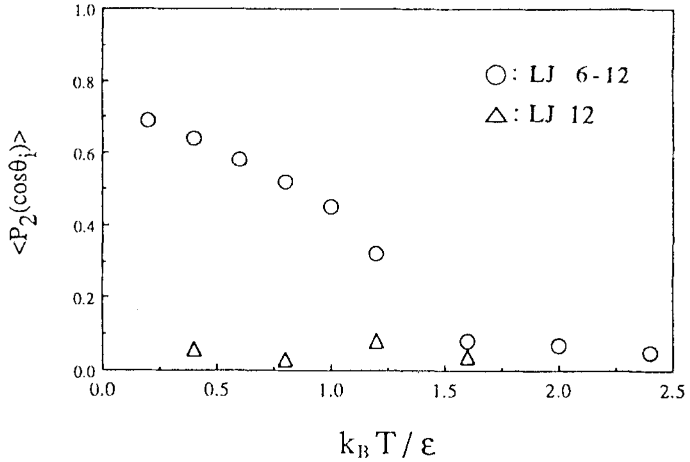

FIGURE 5 Temparature dependence of the $<P_2(\cos\theta_i)>$ value in a low density system ($\rho = 0.31$).

Finally, we compare in Figure 6 the phase transition curve calculated by using the Gay-Berne potential (□) with that obtained above for the beads model (○). The approximated, single-site Gay-Berne model can reproduce the essential feature of the beads model calculations, though the former gives slightly lower values in the transition region. This agreement supports the applicability of the Gay-Berne model, i.e., if the system is composed of linear rod-like molecules

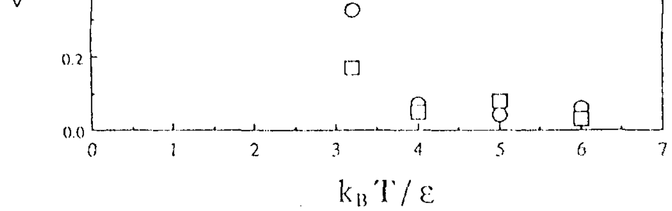

FIGURE 6 Comparison of the phase transition curves calculated by the Gay-Berne model (□) and by the LJ 6-12 beads model (○).

and the interactions between them are dominated by the Lennard-Jones type dispersion interactions, we can reduce the computation time by taking the advantage of the single-site Gay-Berne potential. In fact, the actual computation time was reduced by a factor of five in the calculation shown in Figure 6.

CONCLUSION

In the present study we have introduced a simple beads model, in which the intermolecular potential is calculated as a sum of the Lennard-Jone site-site potentials, in order to interrelate the mean field theories of model liquid crystalline molecules and the molecular dynamic simulations of real liquid crystalline molecules. The beads model, which is the simplest among the atomic models of liquid crystals, has been successful to reproduce the nematic phase formation and enabled us to understand the nature of intermolecular potential acting on liquid crystalline molecule, namely the relative importance of repulsive and attractive interactions in the formation of liquid crystals.

Another important advantage of the beads model is its expansibility. For example, the site-dependent intermolecular interactions such as the dipole-dipole interactions can easily be incorporated into this model by placing dipoles or point charges at desire sites of the molecules. Moreover, the shape anisotropy (such as biaxiallity and chirality) of the molecule can also be taken into account by simply introducing some additional interaction elements. It would also be possible to analyze the orientational behavior of liquid crystalline molecules at substrate surfaces, and the work along in this direction is now under progress.

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