

Computer simulations of dipolar model molecules

K. Satoh, S. Mita and S. Kondo

Department of Chemistry, Faculty of Science, Science University of Tokyo,
1-3 Kagurazaka, Shinjuku-ku, Tokyo 162, Japan

Monte Carlo simulations of the dipolar prolate/oblate Gay-Berne molecules have been performed using the reaction field in a treatment of long-range dipolar interaction. In the case of prolate molecules with $L/D=3$, the temperature dependence of the orientational and positional orders has been investigated at a fixed density of 0.30. It is shown that the dipole at the end of a molecule causes a shift of nematic-isotropic transition toward higher temperature. Furthermore, the formation of liquid crystalline phases has been discussed for the system composed of the oblate molecules with $L/D=0.345$. The molecules in condensed system are apt to form the edge-to-edge configuration rather than the face-to-face configuration.

1. INTRODUCTION

Successful applications of liquid crystals have been developed in the area of electrooptical displays, it is then necessary to require the information in the molecular level for materials science. A detail knowledge of liquid crystalline molecules by a modeling of simple particles would provide the important information on mechanism of the formations of various liquid crystalline phases and on the thermal behavior.

In fact, a modeling of simple particles such as hard ellipsoids, spherocylinders, has been undertaken on the formation in liquid crystal phases [1-5]. It is known that anisotropic repulsive and attractive interactions play a role in the stabilization of liquid crystalline order. A system of prolate/oblate molecules interacting via the Gay-Berne potential [6] composed of anisotropic repulsive and attractive terms forms a variety of liquid crystalline phases depending on the number density and temperature [7-11]. Although there are many liquid crystal compounds with polar substituent groups, the effect of polar forces on liquid crystalline formations and thermal behavior are still far from being completely clarified. In the present paper we discuss the results of the liquid crystalline formations for the system of the prolate/oblate Gay-Berne molecules with Monte Carlo simulations.

2. METHOD

Monte Carlo calculations were performed with 256 molecules using the Metropolis scheme [12]. The total pair potential used can be expressed in the form

$$U_{\text{total}} = U_{\text{GB}} + U_{\text{Dipole}} \quad (1)$$

where U_{GB} is the Gay-Berne potential and U_{Dipole} is the dipole-dipole interaction. The results of the simulation for this model are given in the length and energy units of σ_0 and ε_0 . For the system composed of the prolate molecules with L/D of 3.0, we set the same parameters in previous papers [13, 14]. For the system composed of the oblate molecules, we used the parameters for the Gay-Berne potential with $(\sigma_o/\sigma_s, \varepsilon_o/\varepsilon_s)=(0.345, 5.0)$, and the same parameters for exponents in our previous. The longitudinal dipole, μ was positioned at the center of a molecule. We used a cubic cell as the simulation box with usual periodic boundary conditions. A series of simulations were performed with the reduced dipole moment of 0.0 and 0.5 in the range of 1.0 to 15.0 for the reduced temperature, T^* ($\equiv kT/\varepsilon_0$), and reduced number density, ρ^* of 2.4 to 3.0. In all calculations the cutoff radius, r_c , beyond which the short-range interaction potential was set equal to zero, was set at $2.1\sigma_0$. The long-range dipolar interaction was treated by the re-

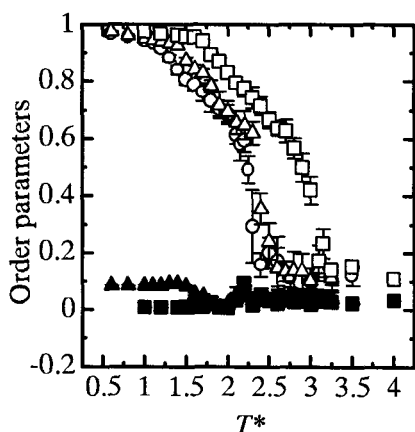


Fig. 1. Temperature dependence of the orientational order parameters for the system composed of the prolate molecules with $\mu^*=0.0, 2.0$. Closed and opened symbols denote the $\langle P_1 \rangle$ and $\langle P_2 \rangle$, respectively. Circles; $\mu^*=0.0$, triangles; central dipole, $\mu^*=2.0$, squares; terminal dipole, $\mu^*=2.0$.

action field method as the same in our previous calculations [13, 14]. Initial configurations were set to be an isotropic state and the results of spontaneous phase formation obtained by cooling process were examined. At each temperature the system was equilibrated in 4.0×10^5 to 2.0×10^6 MC steps and then additional 2.0×10^5 MC steps were generated. The preceding configuration in a series of calculations was used for a subsequent calculation by reducing the temperature.

3. RESULTS AND DISCUSSION

3.1. rod-like molecules

Fig.1 shows the temperature dependence of the orientational order parameters for the system composed of the prolate molecules with $\mu^*=0.0-2.0$. No difference is found in the behavior of the orientational order in between the central dipolar and non-polar systems. On the other hand, it is appeared that the temperature in the nematic-isotropic transition for the terminal dipolar system shifts toward higher temperature. The results are qualitatively in accord with the transition behavior of real compounds such as phenylpyrimidine series. The positional order has been analyzed by the pair

correlation functions and the instantaneous snapshots. The phase transition from the isotropic to nematic phase is found on cooling. By further cooling the smectic and crystalline phases are formed through the nematic phase independent of the strength and position of dipole, and the temperature of the smectic-nematic transition is not appreciably influenced by the position of dipole [14]. The terminal dipole plays thus a role in stabilization of a nematic phase. The values of $\langle P_1 \rangle$ denoted as the magnitude of the polarization in the system are almost zero, no ferroelectric order is formed for the systems in the present study. The theoretical investigation of the system composed of the ellipsoidal particles has predicted the similar results [15]. In addition, the molecules in the nearest neighbor within a layer form antiparallel pairs as described below.

In order to analyze the short-range order, the dipole-dipole correlation functions as a function of

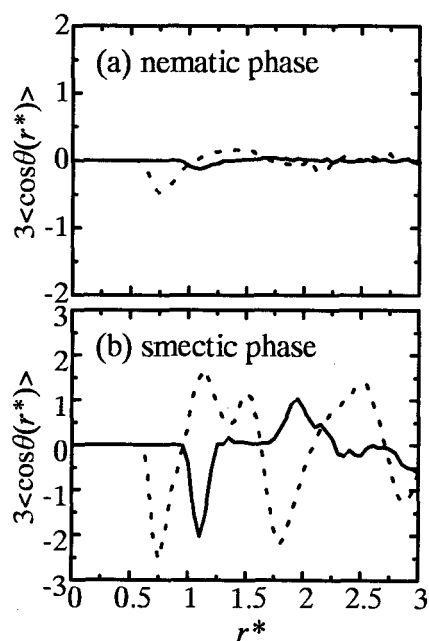


Fig. 2. Dipole-dipole correlations as a function of the separation between the point dipoles (broken lines) and between the centers of mass (solid lines) for the dipolar system with $\mu^*=2.00$ in nematic (a) and smectic (b) phases.

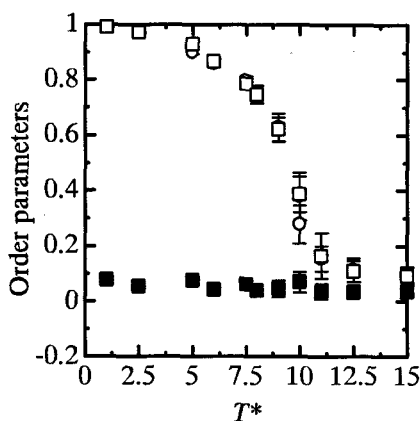


Fig. 3. Temperature dependence of the orientational order parameters for the non-polar system (circles) and dipolar system (squares) composed of the oblate molecules at $\rho^*=2.8$. Closed and opened symbols denote the $\langle P_1 \rangle$ and $\langle P_2 \rangle$, respectively.

the separation between the point dipoles are shown in Fig. 2. The orientational pair correlation function is defined as

$$h(r) = 3 \langle \cos \theta_{ij}(r) \rangle \quad (2)$$

where θ_{ij} is the angle between the axes of two particles separated by r . In the nematic phase, the negative peak at around 0.7 denotes the antiparallel pairs in the nearest neighbor for the terminal dipolar system. On the other hand, no apparent peak is shown for the central dipolar system. The terminal dipolar system in comparison with the central dipolar system is thus liable to form the short-range order in the nematic phase. For the smectic phase, long-range orientational order appears in the both systems. It is shown that the dipole located at the end of a molecule therefore affects the microstructure of layer.

3.2. disc-like molecules

Fig.3 shows the temperature dependence of the orientational order parameters for the systems of the oblate molecules with $\mu^*=0.0, 0.5$ at $\rho^*=2.8$. The magnitude of dipole is set by considering adequate motions of translation and rotation. The system is found to form the ordered states spontaneously from an isotropic state on cooling process as well as the

system composed of the prolate molecules. The ordered phase is assigned to the discotic nematic phase from the positional correlation functions as described below. There is no difference in the thermal behavior of $\langle P_2 \rangle$ for the dipolar and non-polar systems. The similar behavior is obtained at the different densities. No ferroelectricity is confirmed from $\langle P_1 \rangle$ value which is close to zero.

Fig. 4 shows the longitudinal and transverse

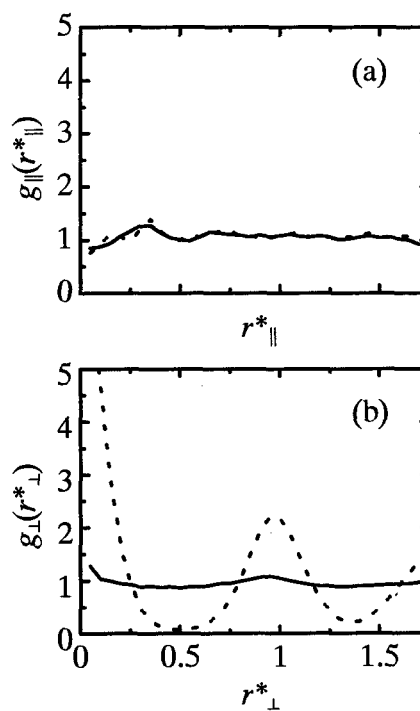


Fig. 4. The longitudinal (a) and transverse (b) pair correlation functions for the system of the oblate molecules at $\mu^*=0.0$ (solid lines) and 0.5 (broken lines) at $T^*=5.0$ and $\rho^*=2.8$.

positional pair correlation functions for the systems of the oblate molecules with $\mu^*=0.0, 0.5$ at $T^*=5.0$ and $\rho^*=2.8$. There is no correlations for the face-to-face configuration in (a). It is clearly shown in (b) that the correlations for the system with $\mu^*=0.5$ indicate the formation of the edge-to-edge configurations. On the other hand, no apparent peak is shown for the non-polar system even if in the highly ordered state. The discotic nematic phase is

thus formed from an isotropic phase in both systems. It is found that the dipole causes a shift to the higher temperature in the formation of the edge-to-edge configurations at the all densities used in the present study.

Fig. 5 shows the longitudinal pair correlation functions at $T^*=2.5$. Both correlations indicate the formation of the columnar phase. The dipole in a oblate molecule thus has no effect on the formation of the columnar phase. The molecules in condensed system are apt to form the edge-to-edge configurations rather than the face-to-face configurations

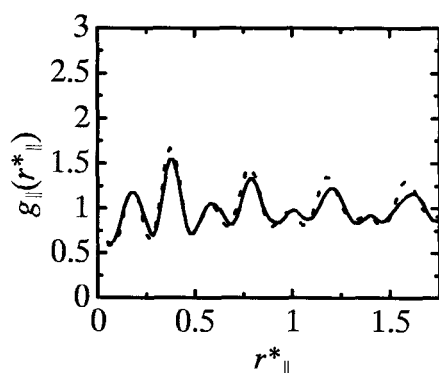


Fig. 5. The longitudinal pair correlation functions for the system of the oblate molecules at $\mu^*=0.0$ (solid lines) and 0.5 (broken lines) at $T^*=2.5$ and $\rho^*=2.8$.

(parallel stacking) being energetically favorable for the oblate molecules. In the lower temperature at the low densities, we have confirmed the formation of some clusters. The parallel pairs are formed in the first and second nearest neighbors in the dipole-dipole correlations for the columnar phase. The longitudinal dipole of 0.5 in an oblate molecule has thus no influence on the temperatures in the discotic nematic-columnar phase transition.

4. CONCLUSIONS

The effects of dipole on the phase formation of liquid crystals and on the transition behavior are discussed for the system composed of the prolate or oblate molecules using Monte Carlo simulations.

For the prolate molecular system, the dipole located at the end of a molecule is found to increase the nematic-isotropic transition temperature and to stabilize the nematic phase. For the oblate molecular system, no effect of dipole on the transition temperatures are found at various densities. However, the dipole is sensitive to the formation of the edge-to-edge configurations in comparison with that of the stacked configuration aligned in parallel.

REFERENCES

1. A.W. Stroobants, H.N. Lekkerkerker and D. Frenkel, *Phys. Rev. A*, 36 (1987) 2929.
2. D. Frenkel, B.M. Mulder and J.P. McTague, *Mol. Cryst. Liq. Cryst.*, 123 (1985) 119.
3. J.J. Weis, D. Levesque and G.J. Zarragoicoechea, *Phys. Rev. Lett.*, 69 (1992) 913.
4. D. Levesque, J.J. Weis and G.J. Zarragoicoechea, *Phys. Rev. E*, 47 (1993) 496.
5. G.J. Zarragoicoechea, D. Levesque and J.J. Weis, *Mol. Phys.*, 74 (1991) 629; *ibid*, 75 (1992) 989.
6. J.G. Gay and B.J. Berne, *J. Chem. Phys.*, 74 (1981) 3316.
7. G.R. Luckhurst, R.A. Stephens and R.W. Phippen, *Liq. Cryst.*, 8 (1990) 451.
8. E. De Miguel, L.F. Rull, M.K. Chalam and K.E. Gubbins, *Mol. Phys.*, 74 (1991) 405.
9. G.J. Zarragoicoechea, D. Levesque and J.J. Weis, *Mol. Phys.*, 78 (1993) 1475.
10. A.P.J. Emerson, G.R. Luckhurst and S. G. Whatling, *Mol. Phys.*, 82 (1994) 113.
11. M.A. Bates and G.R. Luckhurst, *J. Chem. Phys.*, 104 (1996) 6696.
12. N. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth, A.H. Teller and E. Teller, *J. Chem. Phys.*, 21 (1953) 1087.
13. K. Satoh, S. Mita and S. Kondo, *Liq. Cryst.*, 20 (1996) in press.
14. K. Satoh, S. Mita and S. Kondo, *Chem. Phys. Lett.*, (1996) in press.
15. A. Perera and G.N. Patey, *J. Chem. Phys.*, 91 (1989) 3045.