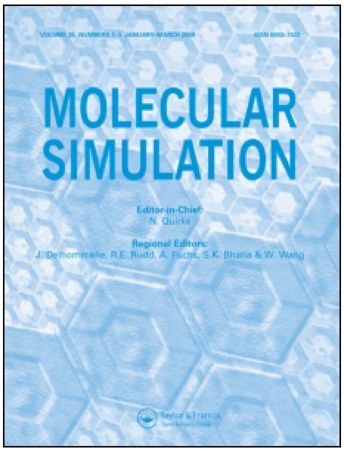

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MONTE CARLO SIMULATION ON NEMATIC ORDER OF CHAIN MODEL USING MEAN FIELD POTENTIAL – ORDER PARAMETER IN BINARY MIXTURE

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Monte Carlo simulations for the linear chain model composed of four successive atoms have been performed using the method of Vacatello and lovino based on the Flory-Ronca-Irvine mean field theory. We assumed three kinds of molecules having different ordering parameters and calculated each pure system and the binary systems of these molecules. The ordering properties for each component have been determined as a function of temperature and composition. In the binary system consisting of substances exhibiting the nematic phase with different order parameters, there is an approximately linear relationship between the order parameter and the composition. When the isotropic molecules are mixed with the nematic substance, the order parameter decreases with increasing mole fraction of the isotropic molecule, and the nematic phase changes into the isotropic phase at a certain composition.

Keywords: Liquid crystal; binary system; nematic phase; isotropic phase; Monte Carlo; mean field

INTRODUCTION

Liquid-crystalline nematic order can be understood on the basis of the anisotropy of either molecular shape [1] or intermolecular force [2]. Consequently, in computer simulation studies of liquid-crystalline orders, the essential factor can be the anisotropy of either molecular shape [3] or intermolecular force [4] or both [5]. Recently, Vacatello and Iovino [6] have

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proposed an interesting computer-simulation model in which anisotropy of both factors is taken into account, with the molecular-force-anisotropy incorporated through a mean-field-type potential. Their model is, in a sense, a computer-simulation model hybridized with the mean field theory that has been widely applied to the study of liquid-crystalline orders and expanded to real molecular systems with extremely high precision in the evaluation of ordering properties [7]. Vacatello and Iovino's model is particularly attractive for its flexibility and computationally less demanding nature.

Computer simulations have recently been applied to complicated systems such as a system of a liquid crystal mixture [8] and a system including a solid surface [9], *etc.* It is very interesting to investigate ordering properties in detail for such complex systems. It is also important in industrial applications such as those involved in the development of liquid crystal displays. However, it is necessary to treat a large simulation system in order to evaluate the physical properties of mixtures. Also, many parameters are required to describe mixtures compared to pure systems. Therefore, the use of a mean-field type potential is a favorable choice from the point of view of computational load and clarity of correspondence between the simulation parameters and physical properties. In the present paper, we apply Vacatello and Iovino's model to binary systems. The simulation method used and the results of the order for pure and binary systems are described.

METHOD

The Monte Carlo simulation was carried out using the method of Vacatello and Iovino [6] based on the Flory-Ronca-Irvine (FRI) theory [10]. The energy of molecule i is given by

$$E_i = E(\theta_i) + \frac{1}{2}\sum_{j\neq i} E_{ij}. \tag{1}$$

An order potential function in the mean field, $E(\theta_i)$, is given by

$$E(\theta_i) = -\frac{kx_i\tau_i}{V_r} S \frac{3\cos^2\theta_i - 1}{2}, \tag{2}$$

as a function of angle θ_i between molecule i and the director (z axis), where k is the Boltzmann constant. The order parameter for the whole system is calculated by

$$S = \frac{3\langle\cos^2\theta_i\rangle - 1}{2}. \tag{3}$$

Although θ_i and S are variables in the simulation, reduced volume, $V_r = V/Nx_i\sigma^3$, characteristic temperature, τ_i, and the number of atoms in one molecule, x_i, are used as constants. The interatomic distance in the molecule is fixed to the length of σ, and the flexibility of the molecule is ignored. The energy E_{ij} is the term from anisotropy of the molecular shape.

$$\begin{aligned}
&E_{ij} = \textstyle\sum_{k=1}^{x_i}\sum_{l=1}^{x_j} E(r_{kl}) && \\
&E(r_{kl}) = \infty && r_{kl} < 0.75\sigma \\
&E(r_{kl}) = \varepsilon\left\{\left(\frac{\sigma}{r_{kl}}\right)^{12} - 2\left(\frac{\sigma}{r_{kl}}\right)^{6} + 1\right\} && 0.75\sigma \le r_{kl} \le \sigma \\
&E(r_{kl}) = 0 && \sigma < r_{kl}
\end{aligned} \tag{4}$$

The reported value of 6.91×10^{-22} J was used for the softness parameter of an atom, ε [6]. The number of molecules, N, was determined to be 5760, on the basis of reliable information on a system size for $N = 3125$ or smaller systems [6].

A completely ordered nematic state was used for the initial configuration of the simulation. The same result was obtained by the simulation started from the initial configuration with a lower orientational state ($S = 0.29$). A physical quantity was obtained by the average of the final 10^8 steps (attempted translations and rotations) after 2×10^8 to 8×10^8 equilibration steps. The ratio of acceptance was kept at 50 percent, but the value of the rotating angle was not higher than 10 degrees [6]. Calculations were performed in a cell with 3-dimensional periodic boundary conditions under an NVT ensemble.

In the simulation for binary systems, we regard the parameters x_i and τ_i as peculiar constants of the molecule. The parameter x_i is the measure of the shape anisotropy. The parameter τ_i is also introduced for the ordering ability of molecules because many examples are experimentally known in which substances can differ in the ordering ability even when they have a similar shape. In other words, the τ_i parameter expresses the ordering ability caused by the chemical structure. We took the τ_i values of 250 K [6], 350 K and 150 K for the three molecules I, II and III, respectively. The value of 4 for x_i and the value of 1.25 for V_r were used for each molecule [6].

RESULTS AND DISCUSSION

Pure Systems I, II and III

Figure 1 shows the dependence of the order parameter S upon temperature T for pure systems. In the system I, which has already been studied by Vacatello and Iovino [6], the order parameter shows a relatively large value at 240 K and decreases with increasing temperature. The value of S is reduced sharply around temperatures of 290 K – 300 K, and the system exhibits a disordered state at temperatures higher than 300 K. Figure 2A and 2B show the distributions of the center of molecules along the z axis at 310 K and 280 K, respectively. These distributions are uniform, indicating no layer structure. Figure 3 shows the plots of an angle correlation function within the intermolecular distance of 3σ.

$$A(|\cos\phi|) = n(|\cos\phi|)/N'\Delta\cos\phi \tag{5}$$

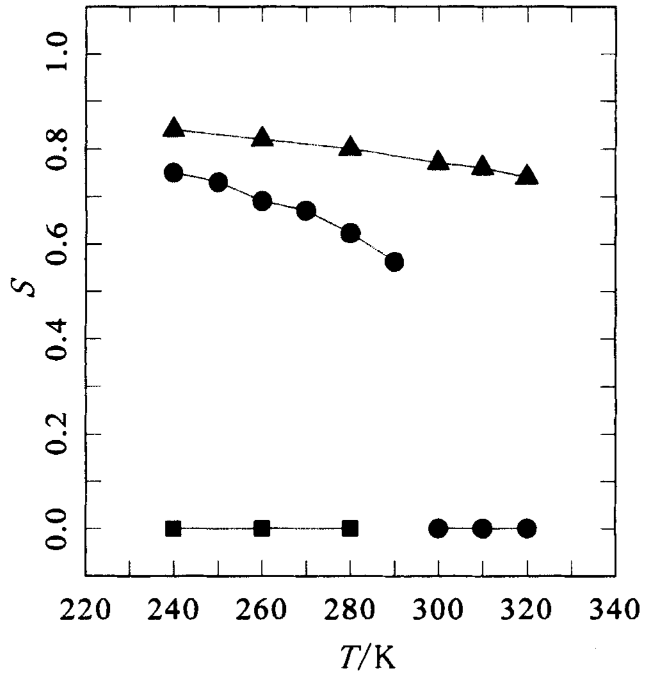

FIGURE 1 Temperature dependence of the order parameter S for the pure system I (circles), II (triangles) and III (squares).

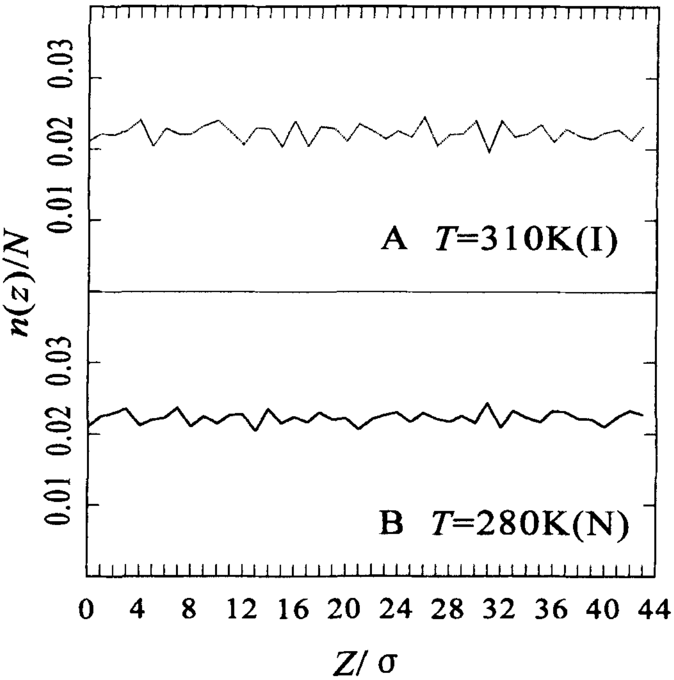

FIGURE 2 Plots of the distributions of the center of molecules for the direction of the z axis at 310 K (A) and 280 K (B) in system I.

where ϕ is the angle between the axes of two molecules, $n(|\cos\phi|)$ is the number of molecules in the range of $|\cos\phi| - \Delta\cos\phi/2$ to $|\cos\phi| + \Delta\cos\phi/2$, and N' is a normalization constant. As shown in Figure 3, no angle correlation appears at 310 K, although a high correlation is observed at 280 K. Therefore, the system at a temperature below 290 K is reasonably identified as the nematic phase because it has only an orientational order in the long and short ranges and has no layer structure. On the other hand, the system exhibits the isotropic phase above 300 K. These results concerning the transitional behavior are in good agreement with those reported by Vacatello and Iovino [6]. In the same manner, system II and system III in the temperature range calculated are identified as the nematic phase and the isotropic phase, respectively.

Binary System I + II

The pure systems I and II exhibit the nematic phase at 240 K – 280 K as described above. The order parameter of system II is higher than that of

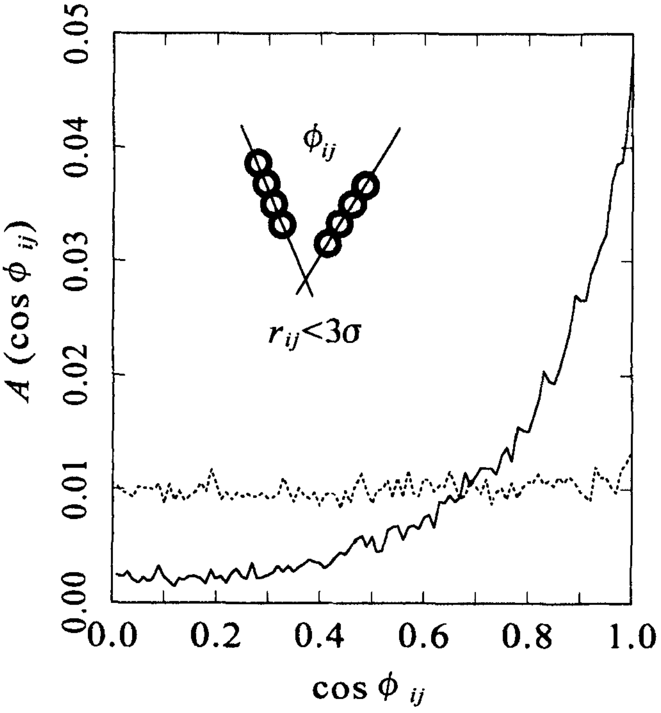

FIGURE 3 Plots of angle correlation functions $A(|\cos\phi_{ij}|)$ within the intermolecular distance of 3σ at 280 K (solid line) and 310 K (dotted line) in system I.

system I. The molecules I and II are reasonably assumed to have high miscibility in the mixture because their intermolecular interactions are identical. In the simulation for the binary system I + II, the molecules of I and II were mixed homogeneously using a randomizing routine as an initial configuration. Figure 4 shows the composition dependence of the order parameter S (open circles) of overall particles at 280 K (A), 260 K (B) and 240 K (C). The mole fraction of molecule II is expressed as

$$C_{\mathrm{II}} = \frac{N_{\mathrm{II}}}{N_{\mathrm{I}} + N_{\mathrm{II}}}, \tag{6}$$

where N_{I} and N_{II} are the numbers of molecules I and II, respectively. The nematic phase is confirmed in the entire range of compositions at the temperatures of 240 K to 280 K. The value of S (open circles in Fig. 4) in the mixture increases with an increase in mole fraction C_{II}. The broken lines indicate the results calculated by a mean field (MF) approximation. The MF approximation is based on FRI's procedure [6, 10] except for the treatment

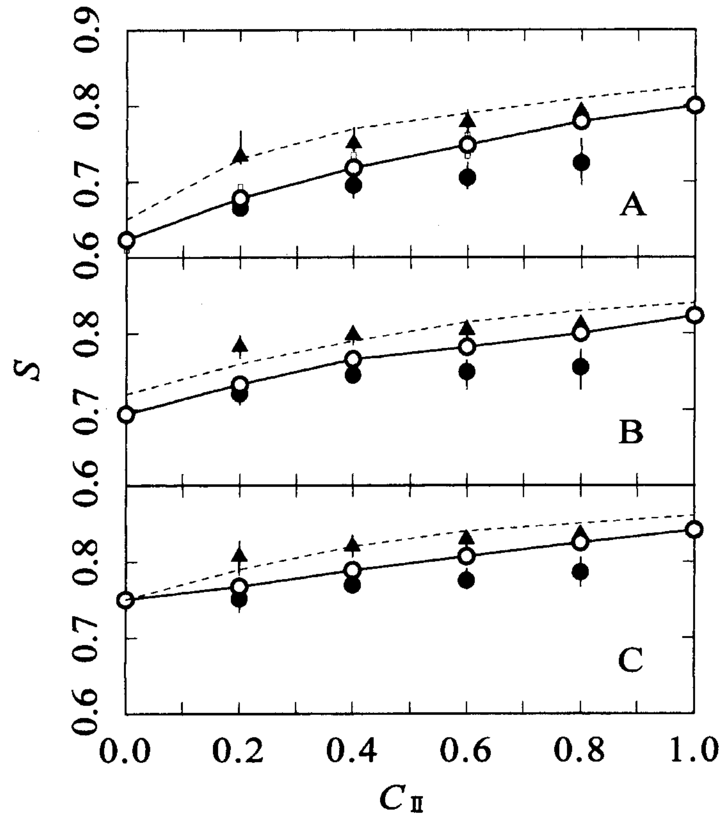

FIGURE 4 Plots of the composition dependence of the order parameters for overall molecules (open circles), molecule I (closed circles) and molecule II (triangles) in the binary system I + II at 280 K (A), 260 K (B) and 240 K (C). The broken lines correspond to the theoretical results using the MF approximation.

of the parameter T^*. In the FRI theory, the parameter T^* expresses the strength of the mean interaction and is a characteristic parameter for the system. On the other hand, the parameter τ in our simulation is regarded as the ability to follow the surrounding orientation and is a characteristic parameter of each molecule. To obtain the order parameter for the binary systems by the MF approximation, the parameter T^* is treated as a function of the composition,

$$T^* = C_{\rm I}\tau_{\rm I} + C_{\rm II}\tau_{\rm II}. \tag{7}$$

As shown in Figure 4, the order parameters of our simulation are smaller than those of the MF approximation, but the upward convex nature of the

MF curve is slightly reproduced in our simulation at 280 K. The order parameter of molecule I, S_{I} (closed circles in Fig. 4), in the binary system is smaller than that of the overall particles, S, whereas the value of S_{II} (squares in Fig. 4) is higher than the value of S. The ordering ability in molecule II ($\tau_i = 350\,\mathrm{K}$) is larger than that in molecule I ($\tau_i = 250\,\mathrm{K}$). Therefore, the value of S_{II} is higher than that of S_{I} in the mixtures. The values of S_{I} and S_{II} are, however, different from the corresponding values in the pure systems. We are unable to compare the result with that of an experiment in which it is difficult to evaluate separately the order parameter for each component in a mixture.

The interaction between molecule I and molecule II is not considered in Eq. (2). If the interaction term between molecules I and II is added, it is expected to expand the method to more complicated systems.

Binary System I + III

At 240 K – 280 K, the nematic and the isotropic phases are stable for the pure systems I and III, respectively. Figure 5 shows the composition dependence of the order parameter S at 280 K (A), 260 K (B) and 240 K (C), in the binary system I + III. The composition dependence of S is different from that in the binary system I + II. In the binary system I + II, large values of S remain in all compositions, whereas S in the binary system I + III decreases with increasing C_{III} in the region below 0.20 at 280 K. In this region, the nematic phase is stable for the binary system. However, S decreases sharply at $C_{\mathrm{III}} = 0.25$ and the system exhibits the isotropic phase in $C_{\mathrm{III}} \geq 0.25$. These analyses indicate the presence of a transition from the nematic to the isotropic phase around $C_{\mathrm{III}} = 0.20-0.25$. The transition is shifted toward higher C_{III} composition with decreasing temperature ($C_{\mathrm{III}} = 0.20-0.25$ at 280 K, $C_{\mathrm{III}} = 0.35-0.40$ at 260 K and $C_{\mathrm{III}} = 0.50-0.55$ at 260 K). The asterisks in Figure 5 indicate the total energy,

$$E_{\mathrm{total}} = \frac{\sum E_i}{N_{\mathrm{I}} + N_{\mathrm{III}}}. \tag{8}$$

Clear transitions are also observed in the values of E_{total}. The value of E_{total} increases with C_{III} in the nematic phase and remains constant in the isotropic phase at each temperature. The latter behavior is attributable to the same interaction parameters except τ for the molecules I and III. Compared with the result of the MF approximation, the order parameter is

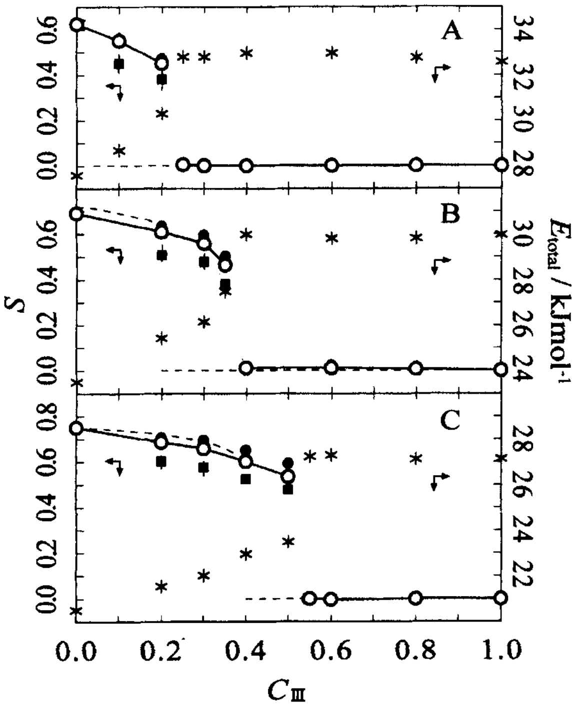

FIGURE 5 Plots of the concentration dependence of the order parameters for overall molecules (open circles), molecule I (closed circles) and molecule III (squares), and of the total energy E_{total} (asterisks) in the binary system I + III at 280 K (A), 260 K (B) and 240 K (C). The broken lines correspond to the theoretical results using the MF approximation.

underestimated in the nematic phase, but the C_{III} composition at the transition point in the simulation is larger than that in the MF approximation.

It is well-known experimentally that the nematic phase disappears on mixing a non-liquid-crystalline molecule with a liquid-crystalline substance. The calculated results agree qualitatively with the experiment.

Figure 6(A) shows a snapshot at 280 K for the system with a composition of $C_{III} = 0.20$. The molecule illustrated with the dark tone is molecule I, and that with the bright tone is molecule III. The nematic phase with an order parameter of 0.45 is found to be stable; the ordering of molecule III is consequently induced at this composition as shown in Figure 5(A, squares). The induction of ordering for molecule III is obtained, but the value of S_{III} is smaller than that of S_I or S at each temperature. On the other hand, the

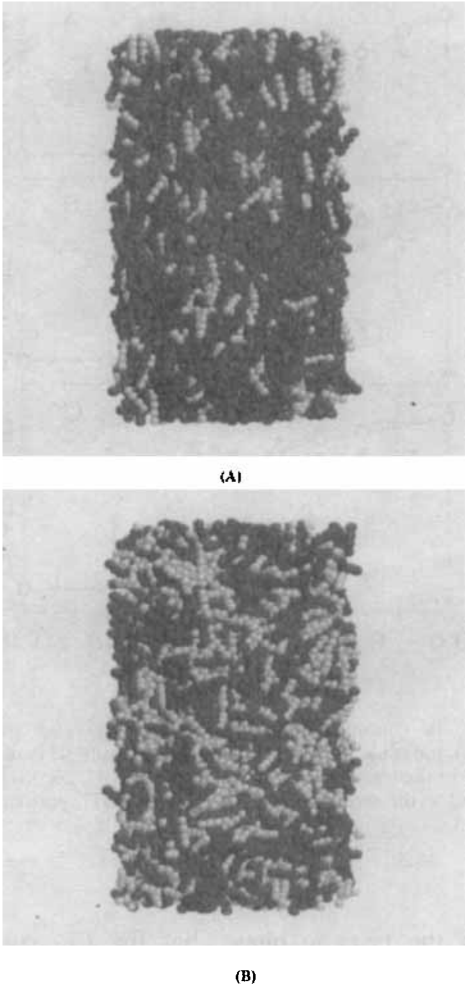

FIGURE 6 Snapshots of the binary system I + III in $C_{III} = 0.20$ (A) and $C_{III} = 0.30$ (B) at 280 K.

order is completely lost at $C_{III} = 0.30$ and $T = 280$ K as shown in Figure 6(B). In this case, the value of the order parameter is actually zero not only for molecule III but also for molecule I. For each case, phase separation is not observed. Based on these results, this method has made it possible to discuss the phenomena of phase transition caused by the temperature and the composition.

CONCLUSIONS

The Monte Carlo simulation for the linear chain model was performed using the method of Vacatello and Iovino based on the Flory-Ronca-Irvine theory. The ordering properties were determined for each pure system and the binary systems of three kinds of molecules with different values of τ_i. The binary system consisting of substances exhibiting the nematic phase in the pure systems shows the nematic phase. On the other hand, a nematic-isotropic transition is observed for the binary system consisting of substances exhibiting the nematic phase or the isotropic phase in their pure systems.

The molecular simulation by adopting the mean field potential has the advantage of reduction of computing time and simplification of a parameter. In this molecular simulation, some parameters are conveniently assumed to be constant for a molecule. However, a modification of the model is necessary for expansion of this method to more complicated systems. We are studying these subjects for applying this method to a complex system of liquid crystals.

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