Dissipative Particle Dynamics Simulation of Phase Behavior in Bolaamphiphilic Solution

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We study the phase behavior of bolaamphiphilic solution performing the dissipative particle dynamics simulations of coarse-grained bolaamphiphilic molecules with explicit solvent molecules. Our simulations show that there are six kinds of phases: isotropic micellar, micellar, rod-shaped micellar, hexagonal, network-structure and lamellar. The network-structure and the lamellar phases disappear when the restoring potential against the bending of bolaamphiphilic molecules in our simulation model is excluded; and the isotropic micellar and the hexagonal phases disappear when the restoring potential is included. This suggests that the bending potential is important in the formation of the higher-ordered structures by the bolaamphiphilic molecules.

Keywords: bolaamphiphilic solution, dissipative particle dynamics simulation, phase diagram, micellar phase, hexagonal phase, lamellar phase

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1. Introduction

Investigation of self-organization in nonequilibrium and nonlinear systems is very important to improve plasma confinement. To gain insights into the universal self-organizing properties in nature, we study the self-organization in model systems such as amphiphilic molecules. Amphiphilic molecules such as lipids and surfactants contain hydrophobic and hydrophilic parts. In aqueous solvents, amphiphilic molecules often self-assemble spontaneously into various structures such as micelles, mesophases, and bicontinuous cubic structures [1]. The phase behavior of coarse-grained amphiphilic dimers in solution has been investigated by molecular dynamics simulations [2] and by dissipative particle dynamics (DPD) simulations [3, 4]. Although several experimental studies on the supramolecular architectures based on bolaamphiphilic molecules, containing a hydrophobic stalk and two hydrophilic ends, have been done [5], there have only been a few theoretical and simulation studies on the phase behavior of bolaamphiphilic solutions. The purpose of this study is to clarify the phase behavior of bolaamphiphilic solutions. With a view to investigating the phase behavior of bolaamphiphilic solutions at the molecular level, we perform DPD simulations on coarse-grained bolaamphiphilic molecules with explicit solvent molecules and analyze the formation processes of micelles and mesophases.

2. Simulation Method

2.1 DPD algorithm

First, we express the DPD model and algorithm [3, 6]. According to ordinary DPD model, all atoms are coarse-grained to particles whose masses are the same. We define the total number of particles as $N$. The position and velocity vectors of particle $i$ (1 ≤ $i$ ≤ $N$) are indicated by $\vec{r}_i$ and $\vec{v}_i$, respectively. Particle $i$ moves according to the following equations of motion, where all physical quantities are made dimensionless.

$$\frac{d\vec{r}_i}{dt} = \vec{v}_i, \quad m \frac{d\vec{v}_i}{dt} = \sum_{j\neq i}^{N} \vec{F}_{ij} + \sum_{(j,k) \neq i}^{N} \vec{F}_{ij,k}, \quad (1)$$

where $m$ is the mass of each particle and $\langle j,k \rangle$ denotes the summation over combinations of $j$ and $k$. $\vec{F}_{ij}$ is the total force between two particles which acts on particle $i$ from particle $j$. $\vec{F}_{ij,k}$ is a force from a three-body interaction which acts on particle $i$ from a combination of particles $j$ and $k$. $\vec{F}_{ij}$ is written as follows:

$$\vec{F}_{ij} = \vec{F}^c_{ij} + \vec{F}^b_{ijk} + \vec{F}^d_{ij} + \vec{F}^l_{ij} \quad (2)$$

In Eq. 2, $\vec{F}^c_{ij}$ is a conservative force deriving from a potential exerted on particle $i$ by particle $j$, $\vec{F}^d_{ij}$ and $\vec{F}^b_{ijk}$ are the...
dissipative and random forces between particles $i$ and $j$, respectively, and $F_{ij}^B$ is the bond-stretching force between neighboring particles.

The conservative force $F^C$ has the following form:

$$F^C_{ij} = -\nabla \phi_{ij},$$  \hspace{1cm} (3)

where $\nabla = \partial / \partial \vec{r}_i$. For computational convenience, we adopted the cut-off length as the unit of length. It is assumed that the conservative force $F^C$ are truncated at a radius of this length. Following this assumption, the two-point potential $\phi_{ij}$ in Eq. 3 is defined as follows:

$$\phi_{ij} \equiv \phi(r_{ij}) = \frac{1}{2} a_{ij} (r_{ij} - 1)^2 H(1 - r_{ij}),$$  \hspace{1cm} (4)

where $r_{ij} = |\vec{r}_{ij}|$, $\vec{n}_{ij} \equiv \vec{r}_{ij} / r_{ij}$ is the unit vector between particles $i$ and $j$. The step function $H$ in Eq. 4 is defined by

$$H(x) \equiv \begin{cases} 0 & \text{for } x < 0, \\ 1 & \text{for } x \geq 0. \end{cases}$$  \hspace{1cm} (5)

Español and Warren proposed the following simple forms for the random and dissipative forces [7]:

$$F^R_{ij} = \sigma \omega_R(r_{ij}) \vec{n}_{ij} \frac{\zeta_{ij}}{\sqrt{\Delta t}},$$  \hspace{1cm} (6)

$$F^D_{ij} = -\gamma \omega_D(r_{ij}) \left( \vec{v}_{ij} \cdot \vec{n}_{ij} \right) \vec{n}_{ij},$$  \hspace{1cm} (7)

where $\omega_R$ and $\omega_D$ are introduced as the weight functions of random and dissipative forces, respectively. $\zeta_{ij}$ is a Gaussian random variable with zero mean and unit variance, chosen independently for each pair $(i, j)$ of interacting particles at each time step, and $\vec{n}_{ij} = \vec{r}_{ij} / r_{ij}$ is the unit vector between particles $i$ and $j$. The strength of the dissipative and random forces is determined by the dimensionless parameters $\sigma$ and $\gamma$, respectively. The parameter $\Delta t$ is a dimensionless time interval of integrating the equation of motion.

Now we consider the fluctuation-dissipation theorem of the DPD method. The time evolution of the distribution function of the DPD system is governed by the Fokker-Planck equation [7]. The system evolves to the same steady state as the Hamiltonian system, that is, the Gibbs-Boltzmann canonical ensemble, if the coefficients of the dissipative and random force terms have the following relations:

$$\omega_D = (\omega_R)^2, \hspace{1cm} \sigma^2 = 2T \gamma,$$  \hspace{1cm} (8)

where $T$ is the dimensionless equilibrium temperature. The forms of the weight functions $\omega_D$ and $\omega_R$ are not specified in the original DPD algorithm. We adopted a simple form of the weighting function $\omega_R(r) = \omega_R^{\text{naive}}(r) = \omega(r)$, where the function $\omega$ is defined by $\omega(x) \equiv (1 - x) H(1 - x)$. [6, 7]

Finally, we introduce the dimensionless potential energies $\phi_{ij}^B$ and $\phi_{ij}^{BM}$. $\phi_{ij}^B$ corresponds to the bond-stretching force $F_{ij}^B$. If particle $i$ is connected to particle $j$, $\phi_{ij}^B$ is given by $\phi_{ij}^B = \phi^B(r_{ij}) = a_B r_{ij}^2 / 2$, otherwise $\phi_{ij}^B = 0$, where $a_B$ is the potential energy coefficient. $\phi_{ij}^{BM}$ is the potential energy that causes $F_{ij}^{BM}$. For ABA molecules, $F_{ij}^{BM}$ is the restoring force against bending of the ABA axis. If particle $i$ is 'A' and is connected to a combination of particle $j$ ('B') and particle $k$ ('C'), $\phi_{ijk}^{BM}$ is given by $\phi_{ijk}^{BM} = \phi_{ijk}^{BM}(\vec{r}_{ij}, \vec{r}_{jk}) = a_{BM} \cos^{-1}\left(|\vec{r}_{ij} \cdot \vec{r}_{jk}| / (r_{ij}r_{jk})\right)^2 / 2$ otherwise $\phi_{ijk}^{BM} = 0$, where $a_{BM}$ is the potential energy coefficient.

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Table 1: Coefficients $a_{ij}$, which depend on kinds of particles $i$ and $j$.

NOTE: W is a “water” particle, A is a “hydrophilic” particle and B is a “hydrophobic” particle. $\alpha$ is varied from 50 to 90 in simulations.

2.2 Simulation model and parameters

In our simulation, we use modified Jury model molecule that is composed of a hydrophilic particle (A) and a hydrophobic particle (B) [3]. Water molecules are modeled as particles W. The mass of all particles are assumed to be unity. The number density of particles $\rho$ is set to $\rho = 5$. Total number of particles $N \equiv 3N_{ABA} + N_W$ is fixed to $N = 5000$, where $N_{ABA}$ is the number of modeled bolaamphiphilic molecules ABA and $N_W$ is the number of water particles.

The simulation box is set to cubic. The dimensionless length of the box $L$ is $L = (N/\rho)^{1/3} = 10.0$. We use periodic boundary conditions in simulation. The interaction coefficients $a_{ij}$ in Eq. 4 are presented in Table 1. The coefficient of the interaction between A and B is written by a variable $\alpha$ which is varied from 50 to 90 in our simulation. The strength of the interaction between W and B is set to be equal to that of the interaction between A and B. The coefficient of the bond-stretching potential $a_B$ is adopted as $a_B = 100$. We use the dimensionless time-interval as $\Delta t = 0.06$. The dimensionless strength of the random and dissipative forces are $\sigma = 3.0$ and $\gamma = 9.0/(2T)$, respectively.

In the initial configuration, all molecules and water particles are located randomly and the velocity of each particle is set under Maxwell distributions with dimensionless temperature $T$. We prepare ABA solutions of various concentrations ($0.1 \leq c = 3N_{ABA}/N \leq 0.9$) and DPD simulations of $1.0 \times 10^7$ time intervals are carried out for each run.

3. Simulation Results and Discussion

3.1 Self-assembled structures for $a_{BM} = 0$

First, we set the interaction parameter $a_{BM}$ to $a_{BM} = 0$. 

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Fig. 1 Self-assembled structures of the bolaamphiphilic molecules in the case of $T = 1.0$ and $\alpha = 70$ for various concentrations $c$. The interaction parameter $a_{BM}$ of the bending potential is set to $a_{BM} = 0$. The isosurfaces of density of the hydrophobic particles (i.e., B particles) are shown. a) The isotropic micellar phase ($c = 0.2$), b) the micellar phase ($c = 0.3$), c) the rod-shaped micellar phase ($c = 0.6$), and d) the hexagonal phase ($c = 0.8$).

Fig. 2 (Color online) Phase diagrams. The interaction parameter $a_{BM}$ is set to $a_{BM} = 0$. a) Dimensionless temperature $T$ vs. concentration phase diagram of ABA solution. b) Intensity of the interaction coefficient $\alpha$ vs. concentration phase diagram of ABA solution. In these figures, the abscissa represents the concentration $c$. Symbol $\times$, blue triangles, brown squares, and red circles represent the isotropic micellar phase, the micellar phase, the rod-shaped micellar phase, and the hexagonal phase, respectively.

This excludes the effect of the bending potential energy. The dimensionless temperature $T$ and the parameter $\alpha$ are selected to be 1.0 and 70, respectively. Figure 1 shows the self-assembled structures of molecules at various concentrations $c = 0.2, 0.3, 0.6, \text{ and } 0.8$. The isosurfaces of the densities of the hydrophobic particles (i.e., B particles) are shown. An isotropic micellar phase (i.e., the phase in which the globe-shaped micelles mainly appear) is observed at low concentration ($c = 0.2$), whereas a hexagonal phase is observed at high concentration ($c = 0.8$). These figures tell us that, as the concentration $c$ increases, the self-assembled structures of the molecules grow and they form higher-ordered structures.

3.2 Phase diagram for $a_{BM} = 0$

We simulated the other cases of $(\alpha, c, T)$ to obtain the phase diagram of ABA molecule in W monomers. (see Fig. 2) In Fig. 2a), the ordinate denotes the dimensionless temperature $T$ and the interaction coefficient $\alpha$ is selected to be 70. In Fig. 2b), the ordinate denotes the intensity of the interaction coefficient $\alpha$. The dimensionless temperature $T$ is set to $T = 1.0$. The abscissas of these figures represent the concentration $c$. The obtained molecular configurations are classified into four phases: the isotropic micellar, the micellar, the rod-shaped micellar, and the
Fig. 3 The self-assembled structure of the bolaamphiphilic molecules when $a_{BM} = 10.0$, $c = 0.5$, and $T = 1.0$. Isosurfaces of densities of the hydrophobic particles are shown. a) The network-structure phase ($\alpha = 50$). b) The lamellar phase ($\alpha = 70$).

3.3 Self-assembled structures and phase diagrams for $a_{BM} \neq 0$

Figure 3 shows the self-assembled structures obtained when $a_{BM} = 10.0$, and the dimensionless temperature $T$ and the concentration $c$ are selected to be 1.0 and 0.5, respectively. A network-structure phase and a lamellar phase are formed at $\alpha = 50$ and 70, respectively.

We simulated the other cases of $(\alpha, c)$ to obtain phase diagram in which $a_{BM}$ and $T$ are set to $a_{BM} = 10.0$ and $T = 1.0$, respectively. The obtained molecular configurations are classified into four phases: the micellar, the rod-shaped micellar, the network-structure, and lamellar. In Fig. 4, the simulated phase diagram is shown. The ordinate denotes the intensity of the interaction coefficient $\alpha$ and the abscissa represents the concentration $c$. Blue triangles, brown squares, open squares, and green rhombuses represent the micellar phase, the rod-shaped micellar phase, the network-structure phase, and the lamellar phase, respectively.

4. Conclusions

We have performed DPD simulations of bolaamphiphilic solutions. We found that four kinds of phases (isotropic micellar, micellar, rod-shaped micellar, and hexagonal phase) were formed when $a_{BM} = 0$. When $T \geq 1.0$, the isotropic micellar phase is observed at lower concentrations, whereas the hexagonal phase is observed at high concentrations. In the case of $a_{BM} = 10.0$, two new phases appear, namely, the network-structure phase and the lamellar phase. The isotropic micellar phase and the hexagonal phase disappear. The phase behavior of the bolaamphiphilic solutions is obtained for $a_{BM} = 0$ and $a_{BM} = 10.0$ in Figs. 2 and 4, respectively. It would be very interesting to know if these phase behaviors can be observed experimentally. A detailed examination is future problem.

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