§25. Molecular Dynamics Simulation of Self-Assembly in Bolaamphiphilic Solutions

Fujiwara, S., Hashimoto, M. (Kyoto Inst. Tech.), Nakamura, H., Horiuchi, R., Tamura, Y. (Konan Univ.)

The spontaneous formation of structures is a universal characteristic of nonequilibrium and nonlinear systems such as plasma systems and soft matter systems. We here investigate structure formation in amphiphilic systems in order to explore the universal selforganizing properties of nature. Amphiphilic molecules such as lipids and surfactants are composed of both hydrophilic and hydrophobic parts. In aqueous solvents, amphiphilic molecules often self-assemble into various structures such as micelles, hexagonal structures, and bicontinuous structures¹⁾. Although numerous computer simulation studies have so far been conducted on selfassembly of amphiphilic molecules, each of which consists of a hydrophilic head group and a hydrophobic tail group, there have been few theoretical and simulation studies on self-assembly of bolaamphiphilic molecules, each of which contains a hydrophobic stalk and two hydrophilic ends. The purpose of this study is to clarify the effect of hydrophilicity on self-assembly in bolaamphiphilic solutions. With a view to investigating the self-assembly processes in bolaamphiphilic solutions at the molecular level, we carry out the molecular dynamics (MD) simulations of coarse-grained bolaamphiphilic molecules with explicit solvent molecules and analyze the self-assembly processes.

The computational model is the same as the one used in our previous work $^{2)}$. A bolaamphiphilic molecule is modeled as a semiflexible chain that is composed of a hydrophobic stalk with three particles (denoted by B) and two hydrophilic ends (denoted by A and C), each of which consists of one particle. A solvent molecule is modeled as a hydrophilic particle (denoted by S). As bonded potentials, we consider the bond-stretching potential and the bond-bending potential. The interaction between a hydrophilic particle and a hydrophobic particle is modeled by a repulsive soft core potential and all other interactions are modeled by the Lennard-Jones (LJ) potential. Numerical integrations of the equations of motion for all particles are carried out using the velocity Verlet algorithm at constant temperature with a time step of 0.0005. We apply the periodic boundary conditions and the number density is set to 0.75. The total number of particles is 5832. Initially, we provide homogeneous bolaamphiphilic solutions with the amphiphilic concentration of $c_{\rm s} = 0.5$ at high temperature $(T^* = 10)$ for various values of the hydrophilic interaction parameter $\varepsilon_{\rm CS}^*$ between a hydrophilic end particle C and a solvent particle S ($0.5 \le \varepsilon_{\rm CS}^* \le 5.0$). The system is then quenched at $T^* = 1.3$ and MD simulations of $t^* = 2.5 \times 10^4 (5.0 \times 10^7)$

time steps) are performed for each simulation run.

In Fig. 1, we show the snapshots of self-assembled structures formed by bolaamphiphilic molecules for $\varepsilon_{\rm CS}^*=1.0$, 3.0 and 5.0 at $c_{\rm s}=0.5$. In this figure, isosurfaces of the density of the hydrophobic particles, which are calculated by Gaussian splatting techniques, are depicted. This figure shows that the lamellar structure changes to the bicontinuous structure, and then to the hexagonal structures at $c_{\rm s}=0.5$ as the hydrophilic interaction parameter $\varepsilon_{\rm CS}^*$ increases.



Fig. 1. Snapshots of self-assembled structures formed by bolaamphiphilic molecules at $c_{\rm s} = 0.5$: (a) the lamellar structure ($\varepsilon_{\rm CS}^* = 1.0$), (b) the bicontinuous structure ($\varepsilon_{\rm CS}^* = 3.0$) and (c) the hexagonal structure ($\varepsilon_{\rm CS}^* = 5.0$). Isosurfaces of the density of the hydrophobic particles, which are calculated by Gaussian splatting techniques, are depicted to show the structures clearly.

- Hamley, I.W., Introduction to Soft Matter (J. Wiley, Chichester, 2007) Rev. ed.
- Fujiwara, S., Miyata, T., Hashimoto, M., Tamura, Y., Nakamura, H. and Horiuchi, R.: Plasma Fusion Res. 10 (2015) 3401029.