§21. Self-Assembly in Bolaamphiphilic Solutions: A Molecular Dynamics Study

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

Amphiphilic molecules such as lipids and surfactants are composed of hydrophilic and hydrophobic parts. In aqueous solutions, amphiphilic molecules often self-assemble into various structures such as micelles, mesophases, and bicontinuous structures[1]. The self-assembly of amphiphilic molecules plays an important role in many biological and industrial processes. Although numerous computer simulation studies have so far been done on self-assembly of amphiphilic molecules, each of which consists of a hydrophilic head group and a hydrophobic tail group, there have been few theoretical and simulational 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 molecular mechanism of self-assembly in bolaamphiphilic solution. With a view to investigating the self-assembly process in bolaamphiphilic solution at the molecular level, we perform the molecular dynamics (MD) simulations of coarse-grained bolaamphiphilic molecules with explicit solvent molecules and analyze the self-assembly process.

The computational model is similar to that used in our previous works[2),3)]. A bolaamphiphilic molecule is modeled as a semiflexible chain that is composed of a hydrophobic stalk with three particles and two hydrophilic ends (H1 and H2), each of which consists of one particle. A solvent molecule is modeled as a hydrophilic particle. 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 the repulsive soft core potential and all other interactions are modeled by the Lennard-Jones (LJ) potential. It is noteworthy that the LJ interaction parameter $\varepsilon^*_{\rm hs2}$ between a hydrophilic end particle (H2) and a solvent particle can be varied. The 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 at 0.75. The total number of particles is 5832. Initially, we provide homogeneous bolaamphiphilic solutions with the amphiphilic concentration of $c_{\rm s} = 0.4$ at high temperature ($T^* = 10$) for various values of the interaction parameter $\varepsilon^*_{\rm hs2}$ ($0.5 \leq \varepsilon^*_{\rm hs2} \leq 5.0$). The system is then quenched at $T^* = 1.3$ and MD simulations of $t^* = 2.5 \times 10^4$ (5.0×10^7 time steps) are performed for each simulation run.

In Fig. 1, we show the snapshots of self-assembled structures formed by bolaamphiphilic molecules for $\varepsilon^*_{\rm hs}$=1.0, 2.0 and 4.0 at $c_{\rm s} = 0.4$. In this figure, isosurfaces of the density of the hydrophobic particles, which are calculated by Gaussian splatting techniques, are depicted. This figure indicates that the lamellar structure changes to the bicontinuous structure, and then to the wormlike micelles at $c_{\rm s} = 0.4$ as the interaction parameter $\varepsilon^*_{\rm hs2}$ increases.

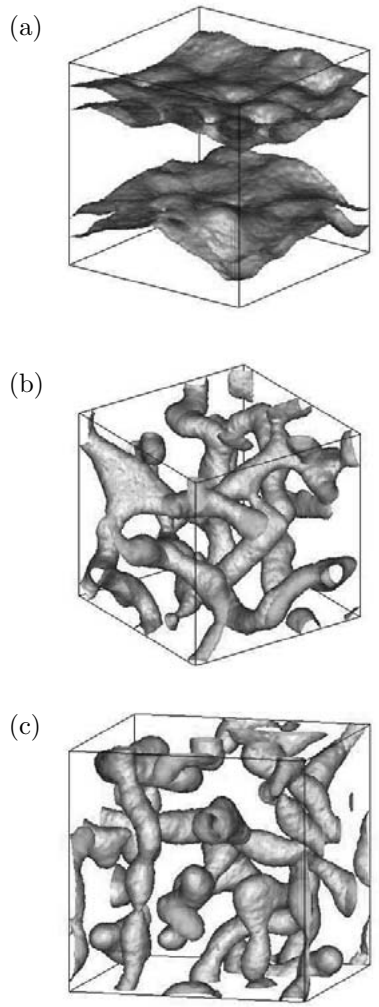

Fig. 1. Snapshots of self-assembled structures formed by bolaamphiphilic molecules at $c_{\rm s} = 0.4$: (a) the lamellar structure ($\varepsilon^*_{\rm hs2} = 1.0$), (b) the bicontinuous structure ($\varepsilon^*_{\rm hs2} = 3.0$) and (c) the wormlike micelles ($\varepsilon^*_{\rm hs2} = 5.0$). Isosurfaces of the density of the hydrophobic particles, which are calculated by Gaussian splatting techniques, are depicted to show the micellar shape clearly. Note that solvent molecules are not displayed for clarity.

1) Hamley, I.W., *Introduction to Soft Matter* (J. Wiley, Chichester, 2007) Rev. ed.
2) Fujiwara, S., Itoh, T., Hashimoto, M., Nakamura, H. and Tamura, Y.: Plasma Fusion Res. **5** (2010) S2114.
3) Fujiwara, S., Itoh, T., Hashimoto, M., Tamura, Y., Nakamura, H. and Horiuchi, R.: Plasma Fusion Res. **6** (2011) 2401040.