§17. Molecular Dynamics Simulation of Micellar Shape Change in Amphiphilic Solution: Effect of Molecular Rigidity

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

Amphiphilic molecules such as lipids and surfactants contain both a hydrophilic head group and a hydrophobic tail group. In aqueous solutions, these molecules spontaneously self-assemble into various structures such as micelles and bicontinuous structures[1]. Self-assembly of amphiphilic molecules is of great importance in many biological and industrial processes. Although several computer simulations have so far been performed on the micelle formation, few simulation studies have been done in relation to the micellar shape change. With a view to investigating the effect of molecular rigidity on micellar shape change in amphiphilic solution *at the molecular level*, we carry out the molecular dynamics (MD) simulations of coarse-grained semiflexible amphiphilic molecules with explicit solvent molecules and analyze the dynamical processes of micellar shape change.

The computational model is the same as that used in our previous work[2]. An amphiphilic molecule is modeled as a semiflexible chain which consists of one hydrophilic head particle and three hydrophobic tail particles. A solvent molecule is modeled as a hydrophilic particle. Particles interact via the non-bonded potentials and the bonded potentials. As for non-bonded potentials, 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 a Lennard-Jones potential. Here, the interaction parameter between a hydrophilic head particle and a solvent molecule represents the intensity of the hydrophilic interaction. As bonded potentials, we consider a bond-stretching potential and a bond-bending potential. The molecular rigidity is controlled by the bending modulus k_3 of the bond-bending potential. The equations of motion for all particles are solved numerically using the velocity Verlet algorithm at constant temperature with a time step of $\Delta t^* = 0.0005$ and the temperature is controlled at every 10 time steps by ad hoc velocity scaling. We apply the periodic boundary conditions and the number density is set to $\rho^* = 0.75$. Initially, we prepare an isolated micelle of 120 flexible amphiphilic molecules with a certain value of the bending modulus k_3^* in solution. The number of solvent molecules is 7520, which leads to the amphiphilic concentration of 0.06. The bending modulus k_3^* is then changed to various values suddenly and MD simulations of $t^* = 5.0 \times 10^3$ (1.0×10^7 time steps) are performed for each simulation run.

In our previous paper[2], we found that the dominant micellar shape at $k_3^* = 4.0$ is a cylinder and that at $k_3^* = 16.0$ is a disc. Here we examine the micellar shape change between a cylinder and a disc by sudden increase or decrease of the bending modulus k_3^*. We show, in Fig. 1, the time dependence of the fraction of various micellar shapes after sudden increase or decrease of k_3^*. The fractions of the micellar shapes are calculated on the basis of the orientational order parameter[3]. This figure indicates that the micellar shape starts to change immediately after sudden increase of the molecular rigidity whereas there exists an induction time to change the micellar shape after sudden decrease of the molecular rigidity. This result can be qualitatively elucidated by considering the bond-bending potential energy and the conformational entropy of the amphiphilic molecules.

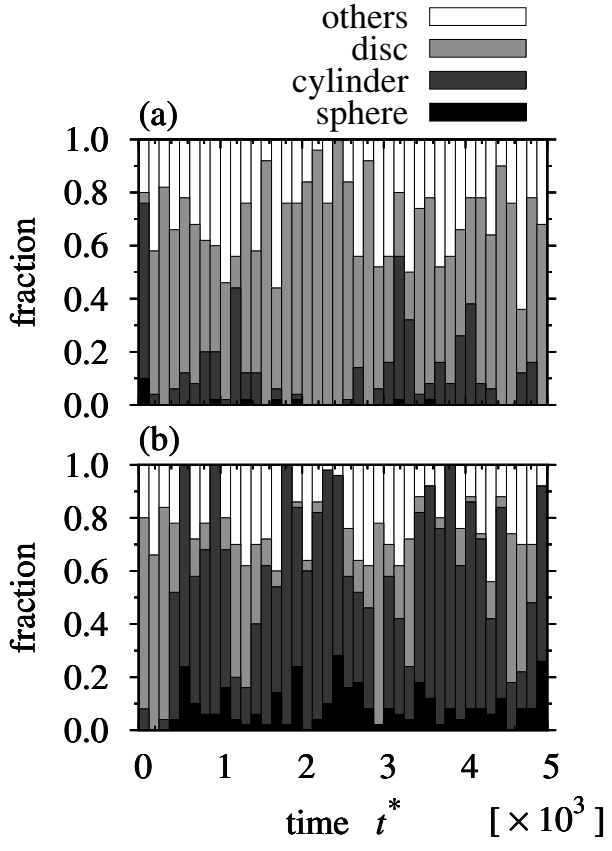

Fig. 1. The time evolution of the fraction of various micellar shapes (a) after sudden increase of k_3^* from 4.0 to 16.0 and (b) after sudden decrease of k_3^* from 16.0 to 4.0.

1) Israelachvili, J.N., *Intermolecular and Surface Forces* (Academic Press, London, 1992) 2nd 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. and Tamura, Y.: Mol. Simul. **33** (2007) 115.