§19. Molecular Dynamics Simulation of Micelle Formation in Amphiphilic Solution: Dynamic Coexistence of Micellar Shapes

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Amphiphilic molecules such as lipids and surfactants consist of two different groups: a hydrophilic head group and a hydrophobic tail group. In aqueous solutions, these molecules spontaneously self-assemble into a wide variety of structures ranging from micelles and bilayers to bicontinuous cubic structures[1]. Such self-assembly phenomena of amphiphilic molecules are of principal importance in many biological and industrial processes. Surfactants have a wide range of important applications in the pharmaceutical, cosmetics and textile industries. Although simulation studies on the dynamics of amphiphilic molecules in solution have so far been done intensively, little is known about the detailed mechanism of micelle formation in amphiphilic solution at the molecular level. With a view to investigating the self-assembling processes of amphiphilic molecules in solution *at the molecular level*, we carry out the molecular dynamics (MD) simulations of coarse-grained amphiphilic molecules with explicit solvent molecules and analyze the dynamical processes of micelle formation systematically[2].

The computational model is the same as that used in our previous works[3),4)]. An amphiphilic molecule is modeled as a rigid rod, which consists of one hydrophilic head particle and two hydrophobic tail particles. A solvent molecule is modeled as a hydrophilic particle. 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 $\varepsilon^*_{\rm hs}$ between a hydrophilic head particle and a solvent molecule represents the intensity of the hydrophilic interaction. The equations of motion for all particles are solved numerically using the leap-frog algorithm at constant temperature with a time step of $\Delta t^* = 0.0025$. We apply the periodic boundary conditions and the number density is set to $\rho^* = 0.75$. Initially, we provide a randomly distributed configuration of 97 amphiphilic molecules in solution at high temperature ($T^* = 10$) for various values of the interaction parameter $\varepsilon^*_{\rm hs}$ ($1.0 \le \varepsilon^*_{\rm hs} \le 4.0$). The number of solvent molecules is 5541, which leads to the amphiphilic concentration of 0.05. The system is then quenched to $T^* = 1.3$ and MD simulations of $t^* = 4.0\times10^4$ (1.6×10^7 time steps) are carried out for each simulation run.

Our simulations show that the dominant micellar shape is a disc for $\varepsilon^*_{\rm hs} = 1.0$, a cylinder for $\varepsilon^*_{\rm hs} = 2.0$, and a sphere for $\varepsilon^*_{\rm hs} = 4.0$. Here, we study the micellar shapes observed in each intermediate parameter range: $1.0 < \varepsilon^*_{\rm hs} < 2.0$ or $2.0 < \varepsilon^*_{\rm hs} < 4.0$. We show, in Fig. 1, the time dependence of the fraction of micellar shapes of the largest micelle for $\varepsilon^*_{\rm hs} = 1.5$ and $\varepsilon^*_{\rm hs} = 3.0$. This figure tells us that the micellar shape becomes a disc or a cylinder as the time elapses for $\varepsilon^*_{\rm hs} = 1.5$ while it alternates between a cylinder and a sphere for $\varepsilon^*_{\rm hs} = 3.0$, which indicates that two kinds of micellar shapes coexist dynamically. From the detailed analyses of the dynamic coexistence, it is ascertained that the dynamic coexistence of a cylindrical micelle and a spherical micelle accompanies the coalescence and fragmentation of micelles whereas that of a disc micelle and a cylindrical micelle does not, but exhibits the continuous change between them.

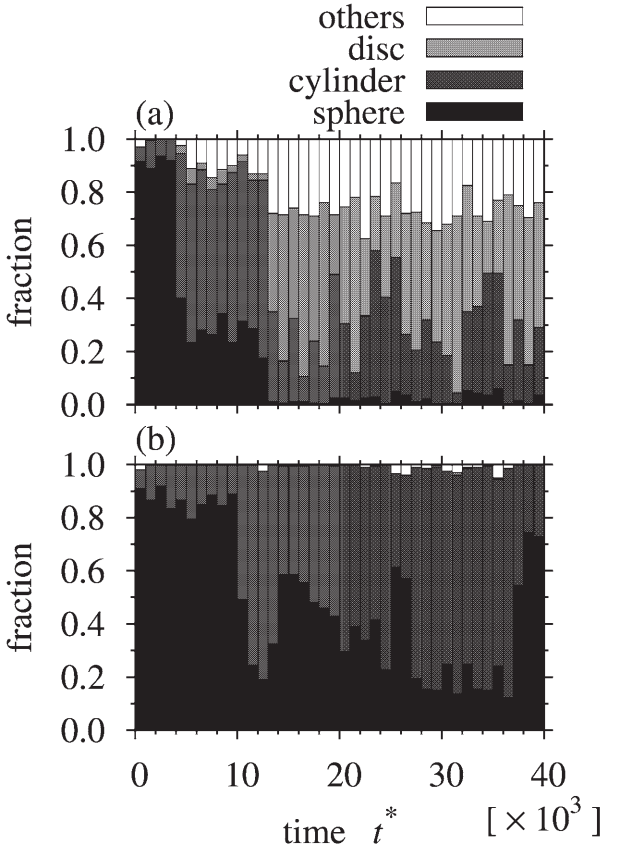

Fig. 1. The time evolution of the fraction of various micellar shapes of the largest micelle in the case of (a) $\varepsilon^*_{\rm hs} = 1.5$ and (b) $\varepsilon^*_{\rm hs} = 3.0$.

1) Israelachvili, J.N., *Intermolecular and Surface Forces* (Academic Press, London, 1992) 2nd ed.
2) Fujiwara, S., Itoh, T., Hashimoto, M. and Horiuchi, R.: J. Chem. Phys. **130** (2009) 144901.
3) Fujiwara, S., Hashimoto, M. and Itoh, T.: J. Plasma Phys. **72** (2006) 1011.
4) Fujiwara, S., Itoh, T., Hashimoto, M. and Tamura, Y.: Mol. Simul. **33** (2007) 115.