

§10. Dynamic Coexistence of Micellar Shapes in Amphiphilic Solution: A Molecular Dynamics Study

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Amphiphilic molecules such as lipids and surfactants are composed of both a hydrophilic head group and a hydrophobic tail group. In aqueous solutions, these molecules spontaneously self-assemble into various structures such as micelles, bilayers and bicontinuous structures^{1)–3)}. Self-assembly of amphiphilic molecules is of great importance in many biological and industrial processes. Although several computer simulation studies have so far been done on the dynamics of amphiphilic molecules in solution, 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 perform the molecular dynamics (MD) simulations of coarse-grained semiflexible amphiphilic molecules with explicit solvent molecules and analyze the dynamical processes of micelle formation.

The computational model is the same as that used in our previous work^{4),5)}. 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 $\varepsilon_{\text{hs}}^*$ between a hydrophilic head particle and a solvent particle 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 $k_3^* = 0.0$ in solution at $T^* = 1.3$ for various values of $\varepsilon_{\text{hs}}^*$ ($1.0 \leq \varepsilon_{\text{hs}}^* \leq 3.0$). 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 ($k_3^* = 1.0, 2.0, 4.0, 8.0, 16.0$)

and MD simulations of $t^* = 5.0 \times 10^3$ (1.0×10^7 time steps) are performed for each simulation run.

Here we examine the dynamic coexistence of a cylindrical micelle and a disc micelle observed at $k_3^* = 16.0$ and $\varepsilon_{\text{hs}}^* = 2.5$. In Fig. 1, we show the time dependence of the fraction of various micellar shapes. The fractions of the micellar shapes are calculated on the basis of the orientational order parameter^{6),7)}. This figure indicates that the dominant micellar shape alternates between a cylinder and a disc. From the detailed analyses of the dynamic coexistence, it is ascertained that both the potential energy and the radius of gyration of the cylindrical micelle are larger than those of the disc micelle. This result suggests that the disc micelle is more stable and isotropic than the cylindrical one.

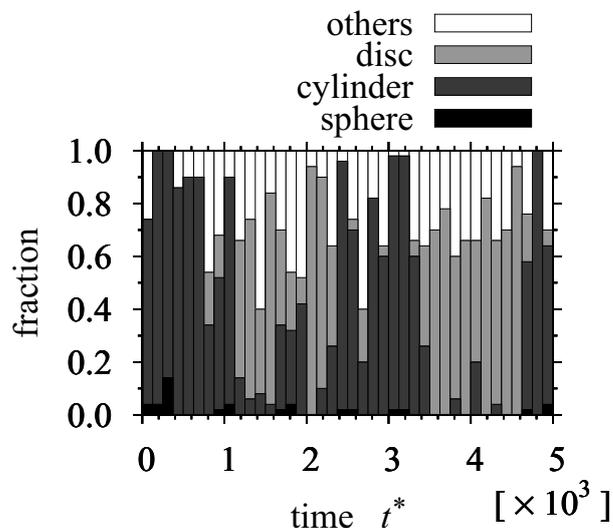


Fig. 1. The time evolution of the fraction of various micellar shapes in the case of $k_3^* = 16.0$ and $\varepsilon_{\text{hs}}^* = 2.5$.

- 1) Ben-Shaul, A. and Gelbart, W. M.: *Micelles, Membranes, Microemulsions, and Monolayers*, edited by Gelbart, W. M., Ben-Shaul, A. and Roux, D. (Springer-Verlag, New York, 1994) 1.
- 2) Israelachvili, J.N., *Intermolecular and Surface Forces* (Academic Press, London, 1992) 2nd ed.
- 3) Hamley, I.W., *Introduction to Soft Matter* (J. Wiley, Chichester, 2007) Rev. ed.
- 4) Fujiwara, S., Itoh, T., Hashimoto, M., Nakamura, H. and Tamura, Y.: *Plasma Fusion Res.* **5** (2010) S2114.
- 5) Fujiwara, S., Itoh, T., Hashimoto, M., Tamura, Y., Nakamura, H. and Horiuchi, R.: *Plasma Fusion Res.* **6** (2011) 2401040.
- 6) Fujiwara, S., Itoh, T., Hashimoto, M. and Tamura, Y.: *Mol. Simul.* **33** (2007) 115.
- 7) Fujiwara, S., Itoh, T., Hashimoto, M. and Horiuchi, R.: *J. Chem. Phys.* **130** (2009) 144901.