§32. Molecular Dynamics Simulation of Micelle Formation in Amphiphilic Solution: Identication of Micellar Shape

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Amphiphilic molecules such as lipid molecules and surfactant molecules are composed of two parts: one is a hydrophilic part and the other is a hydrophobic part. In aqueous or organic solvents, these molecules often spontaneously self-assemble into various structures such as micelles, mesophases and bilayer membranes[1]. Self-assembly of amphiphilic molecules plays an important role in many biological and industrial processes. For example, surfactant layers have been successfully used in the fabrication of new optical and electronic devices. Although numerous computer simulation studies have so far been carried out on amphiphilic solutions, little is known about the detailed molecular mechanisms of micelle formation in amphiphilic solution. With a view to investigating micelle formation in amphiphilic solution at the molecular level, we perform the molecular dynamics (MD) simulations of coarse-grained amphiphilic molecules with explicit solvent molecules and analyze the micelle formation process.

The computational model is the same as that used in our previous works[2),3)]. An amphiphilic molecule is modeled as a rigid linear molecule, 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 parameters. 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 8.0×10^6 time steps are carried out for each simulation run.

We focus on the orientational order of amphiphilic molecules in order to characterize the three types of micellar shapes: disc (bilayer), cylindrical and spherical micelles. The orientational order parameters p_x, p_y and p_z are defined by $p_i = \left\langle (3\cos^2\theta_i - 1)/2 \right\rangle$, where θ_i is the angle between the vector along the molecular axis of an amphiphile and the i-axis ($i = x, y, z$) in the coordinate system with three principal axes of inertia of the micelle, and $\langle \cdots \rangle$ denotes the average over all amphiphilic molecules. Note that the average is taken for the amphiphilic molecules in the proximity of the center-of-mass position of the largest micelle. Ideally, the orientational order parameters take the following values: $(p_x, p_y, p_z) = (0, 0, -0.5)$ for a disc (bilayer), $(p_x, p_y, p_z) = (1, -0.5, -0.5)$ for a cylinder and $(p_x, p_y, p_z) = (0, 0, 0)$ for a sphere. We show, in Fig. 1, the distribution functions $P(p_x)$, $P(p_y)$ and $P(p_z)$ for the three types of micelles. We find from this figure that three types of micellar shapes are clearly distinguishable by the orientational order parameters: $0.5 < p_x < 1.0$ and $-0.5 < p_y, p_z < -0.25$ for a disc micelle, $-0.25 < p_x, p_y < 0.5$ and $-0.5 < p_z < -0.25$ for a cylindrical micelle, and $-0.25 < p_x, p_y, p_z < 0.5$ for a spherical micelle.

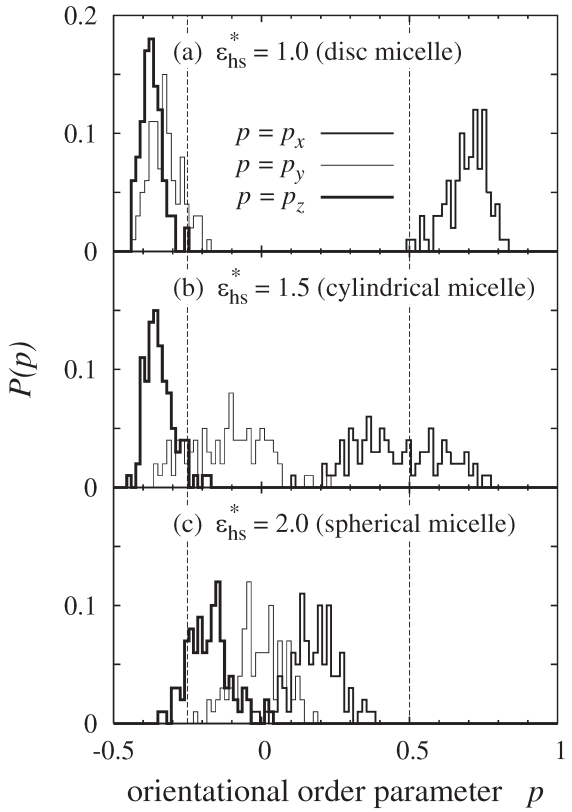

Fig. 1. Distribution functions of orientational order parameter $P(p_x)$, $P(p_y)$ and $P(p_z)$ in the vicinity of the centerer-of-mass of the largest micelle: (a) disc micelle, (b) cylindrical micelle and (c) spherical micelle.

References

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2) Fujiwara, S., Hashimoto, M. and Itoh, T., J. Plasma Phys. **72**, (2006) 1011.
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