§30. Molecular Dynamics Simulation of Amphiphilic Molecules in Solution: Mesophase Formation

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Amphiphilic molecules such as lipids and surfactants are composed of two different segments: a hydrophilic "head" segment and a hydrophobic "tail" segment. In aqueous solutions, these molecules spontaneously self-assemble into various structures such as micelles, mesophases and vesicles [1]. Such self-assembly of amphiphilic molecules plays an important role in many biological and industrial processes. For example, biological membranes in living cells consist of lipids and surfactants have a variety of important applications in the pharmaceutical, cosmetics and oil industries. Although numerous computer simulation studies have thus far been carried out on amphiphilic solutions, little is known about the detailed molecular mechanisms of mesophase formation in amphiphilic solution. With a view to investigating mesophase 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 mesophase 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 dimer molecule, which consists of one hydrophilic head particle and one hydrophobic tail particle. 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 $\rho^* = 0.75$. The total number of particles is 5832. Initially, we provide a randomly distributed configuration of amphiphilic molecules in solution at high temperature ($T^* = 10$) with various values of the interaction parameter ($\varepsilon^*_{\rm hs} = 1.0, 2.0, ..., 5.0$) for various amphiphilic concentrations ($c_{\rm s} = 0.1, 0.2, ..., 0.9$). The system is then quenched to $T^* = 1.3$ and MD simulations of 4.0×10^6 time steps or more are carried out for each simulation run.

Our simulations show that, in the cases of $\varepsilon^*_{\rm hs} \geq 4.0$, an isotropic micellar phase changes into a hexagonal phase, and then into a lamellar phase as the amphiphilic concentration increases (Fig. 1). No hexagonal phases emerge when the intensity of hydrophilicity ($\varepsilon^*_{\rm hs}$) is small enough ($\varepsilon^*_{\rm hs} < 4.0$). The reason for this is that structures with small curvature are more stable for small $\varepsilon^*_{\rm hs}$.

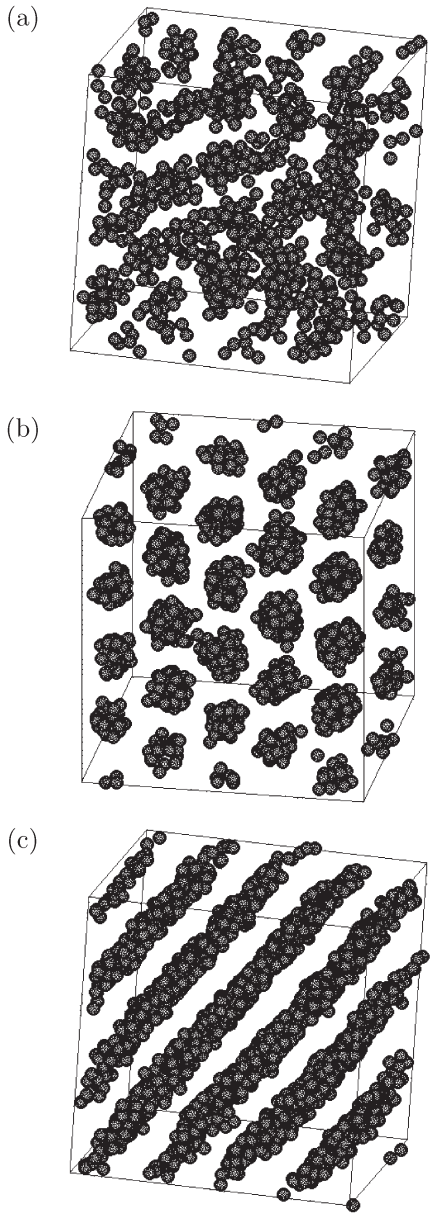

Fig. 1. Snapshots of self-assembled structure formed by amphiphilic molecules in the case of $\varepsilon^*_{\rm hs} = 4.0$: (a) isotropic micellar phase ($c_{\rm s} = 0.3$), (b) hexagonal phase ($c_{\rm s} = 0.5$) and (c) lamellar phase ($c_{\rm s} = 0.7$). Only tail particles are depicted for clarity.

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) Fujiwara, S., Hashimoto, M. and Itoh, T.: J. Plasma Phys. **72** (2006) 1011.
3) Fujiwara, S., Itoh, T., Hashimoto, M. and Tamura, Y.: Mol. Simul. **33** (2007) 115.