§16. Molecular Dynamics Simulation for Shape Transition of Micelles in Amphiphilic Solution

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Amphiphilic molecules such as lipids and surfactants consist of both a hydrophilic part and a hydrophobic part. In aqueous solutions, these molecules often spontaneously self-assemble into various structures such as micelles, bilayer membranes and bicontinuous structures[1]. Shape transitions of micelles play an important role in cellular physiology. Although numerous computer simulation studies have so far been carried out on micellar systems in amphiphilic solution[2], the detailed mechanisms of micellar shape transition in amphiphilic solution have not been fully understood at the molecular level. The purpose of this study is to clarify the molecular mechanism of shape transition of micelles in an amphiphilic solution. With a view to investigating the effect of the hydrophilicity on the micellar shapes in amphiphilic solution at the molecular level, we perform the MD simulations of coarse-grained rigid amphiphilic molecules with explicit solvent molecules and analyze the micellar shape transitions systematically[3].

The computational model is the same as that used in the previous work[4]. An amphiphilic molecule is a rigid rod which consists of one hydrophilic particle and two hydrophobic 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 ε_{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 by using the leap-frog algorithm at constant temperature with a time step of $\Delta t^* = 0.0025$ 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 97 amphiphilic molecules with $\varepsilon_{hs}^* = 1.0$ in solution at $T^* = 1.3$. The number of solvent particles is 5541, which leads to the amphiphilic concentration of 0.05. The intensity of the hydrophilic interaction ε_{hs}^* is then changed to various values ($\varepsilon_{hs}^* = 0.1, 0.2, ..., 4.0$) and MD simulations of $t^* = 2.0 \times 10^4$ (8.0×10^6 time steps) are carried out for each simulation run.

We show, in Fig. 1, snapshots of micelles formed by amphiphilic molecules at $\varepsilon_{hs}^* = 1.0$, 2.0 and 4.0. Isosurfaces of the density of the tail particles, which are calculated by Gaussian splatting techniques, are depicted in this figure. This figure tells us that the micellar shape changes from a disc into a cylinder, and then into a sphere as the intensity of the hydrophilic interaction ε_{hs}^* increases. It is also found that the potential energy decreases monotonically even during the shape transition of micelles as ε_{hs}^* increases.
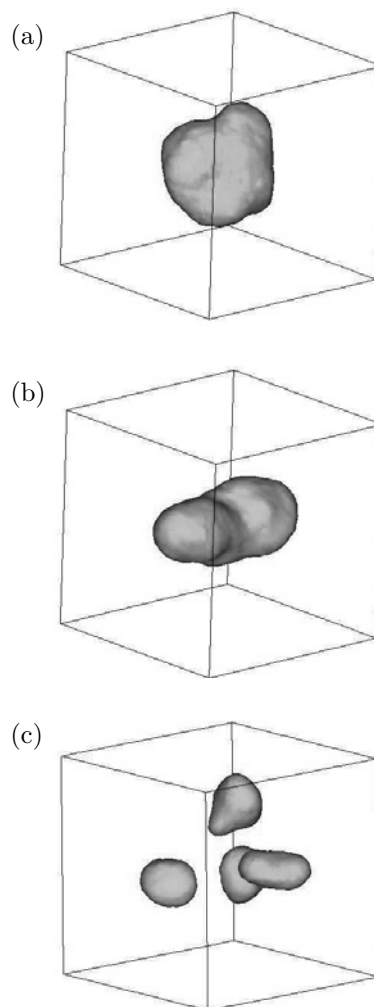

Fig. 1. Snapshots of micelles formed by amphiphilic molecules for various values of the hydrophilic interaction parameter ε_{hs}^*. (a) A disc micelle for $\varepsilon_{hs}^* = 1.0$, (b) a cylindrical micelle for $\varepsilon_{hs}^* = 2.0$ and (c) spherical micelles for $\varepsilon_{hs}^* = 4.0$. Isosurfaces of the density of the tail particles, which are calculated by Gaussian splatting techniques, are depicted to show the micellar shape clearly. Note that solvent molecules are not displayed for clarity.

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4) Fujiwara, S., Itoh, T., Hashimoto, M. and Horiuchi, R.: J. Chem. Phys. **130** (2009) 144901.