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Molecular dynamics simulation of self-organization in amphiphilic solution

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Abstract. The micelle formation in amphiphilic solution is investigated by means of a molecular dynamics simulation of coarse-grained amphiphilic molecules with explicit solvent molecules. A random configuration of amphiphilic molecules in solution at high temperature is quenched to a lower temperature. Our simulations show that the micellar shapes change from a cylindrical micelle to a planar bilayer as the number density increases. At higher densities, we also find the following characteristic features. (1) The potential energy relaxes in a stepwise manner. (2) The radius of gyration R_g of the largest micelles increases with time in a stepwise fashion. (3) The sharp bumps in R_g occur during coalescence of micelles.

1. Introduction

Self-organization has recently become the focus of attention in plasma physics and soft matter physics. The dominant interaction in plasmas is *long-range interaction* such as the Coulomb interaction. In contrast, one of the dominant interactions in soft matters is *short-range interaction* such as the van der Waals interaction. In this paper, we investigate the self-organization of amphiphilic molecules which are typical of soft matters. Amphiphilic molecules contain both a hydrophilic part and a hydrophobic part. In aqueous or organic solvents, these molecules form various structures such as spherical micelles and bilayer membranes [1]. Self-assembly of amphiphilic molecules plays an important role in many biological and industrial processes. Although numerous computer simulation studies have so far been carried out on amphiphilic solutions [2–4], little is known about the detailed mechanisms of micelle formation in amphiphilic solution at the molecular level. 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.

2. Simulation model and method

The computational model is based on those used by Goetz and Lipowsky [4] and by Noguchi and Takasu [5]. An amphiphilic molecule consists of one hydrophilic particle and two hydrophobic particles which are fixed on a line and spaced equally. 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: $U_{SC}(r) = 4\epsilon(\sigma_{SC}/r)^9$, and all other interactions are modeled by a

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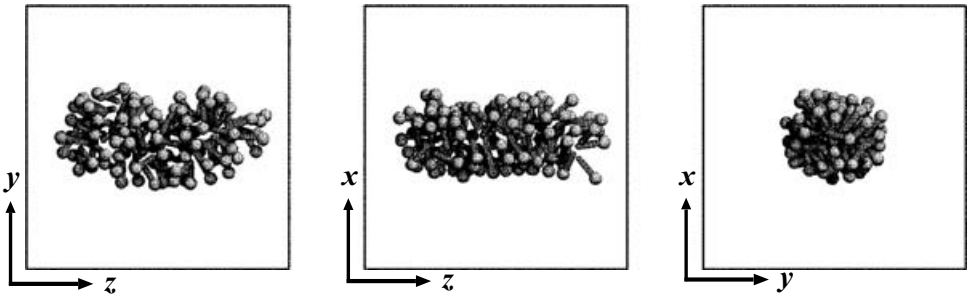


Figure 1. Snapshots of cylindrical micelle formed by amphiphilic molecules in solution at $\rho^* = 0.7$: (a) viewed along the x-axis, (b) viewed along the y-axis and (c) viewed along the z-axis. Hydrophilic and hydrophobic groups are represented by spheres and cylinders, respectively. Solvent molecules are not shown for clarity.

Lennard–Jones potential: $U_{\mathrm{LJ}}(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$, where r is the interparticle distance. The parameter σ_{SC} is set to be $\sigma_{\mathrm{SC}} = 1.05\sigma$ as in [4]. The cutoff distance for these potentials is $r_{\mathrm{c}} = 3.0\sigma$ and we use the shifted force variant of these potentials: $V(r) = U(r) - U(r_{\mathrm{c}}) - \partial U/\partial r|_{r=r_{\mathrm{c}}}(r - r_{\mathrm{c}})$, in order to avoid discontinuities both in the potential energy and in the force. In what follows, we represent dimensionless quantities by an asterisk, e.g. number density $\rho^* = \rho\sigma^3$, time $t^* = t\sqrt{\epsilon/m\sigma^2}$ and temperature $T^* = k_{\mathrm{B}}T/\epsilon$, where k_{B} is the Boltzmann constant. The equations of motion for all particles are solved numerically using the leap-frog algorithm at constant temperature with a time step of $\Delta t^* = 0.0025$ and the temperature is controlled every 10 time steps by *ad hoc* velocity scaling. We apply the periodic boundary conditions. The amphiphilic concentration is set to 0.05. Initially, we provide a randomly distributed configuration of 97 amphiphilic molecules in solution at high temperature ($T^* = 10$) for various number densities ($\rho^* = 0.6$, 0.65, 0.7, 0.75, 0.8, 0.85). The number of solvent molecules is 5541. The system is then quenched to $T^* = 1.3$ and MD simulations of $t^* = 2.0 \times 10^4$ (8.0×10^6 time steps) are carried out for each number density.

3. Simulation results

We show, in Figs 1 and 2, the snapshots of micelles formed at $\rho^* = 0.7$ and 0.75, respectively. Here, we introduce the coordinate system with three principal axes of inertia of a micelle. In this coordinate system, the origin is located at the center-of-mass position of the micelle, the x-axis is the principal axis with the largest moment of inertia and the z-axis is that with the smallest moment of inertia. Our simulations indicate that cylindrical micelles are formed at lower densities ($\rho^* \leqslant 0.7$) whereas planar bilayers are obtained at higher densities ($\rho^* \geqslant 0.75$).

The time evolution of the potential energy at $\rho^* = 0.7$ and 0.75 is shown in Fig. 3. We find, from Fig. 3, the following features: (i) the energy relaxation proceeds in a gradual manner at $\rho^* = 0.7$ (similar gradual behavior is found at $\rho^* \leqslant 0.7$); (ii) the potential energy relaxes in a stepwise manner at $\rho^* = 0.75$ (this kind of stepwise behavior is found at $\rho^* \geqslant 0.75$).

In order to investigate the micelle formation processes, we define a micelle as a collection of amphiphilic molecules whose tail particles are located close to each other. In Figs. 4 and 5, we respectively show the radius of gyration R_{g}^* of the largest micelle and the micelle sizes as a function of time at $\rho^* = 0.7$ and 0.75. At $\rho^* = 0.7$, the gradual increase of R_{g}^* is found as a whole. At $\rho^* = 0.75$, on the other hand,

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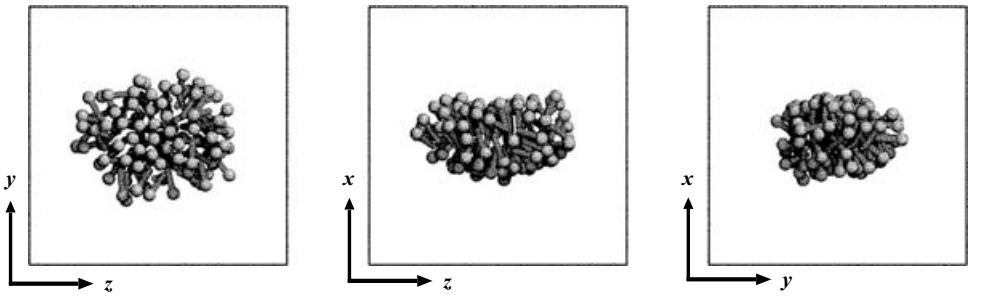


Figure 2. Snapshots of planar bilayer formed by amphiphilic molecules in solution at $\rho^* = 0.75$: (a) viewed along the x-axis, (b) viewed along the y-axis and (c) viewed along the z-axis.

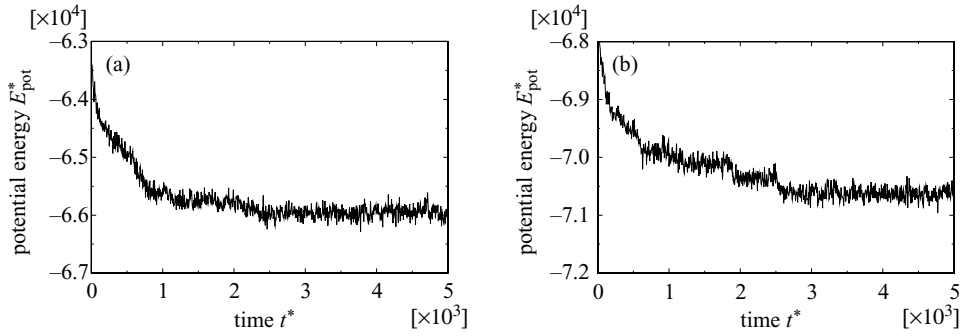


Figure 3. Time evolution of the potential energy $E^*_{\rm pot}$ (a) at $\rho^* = 0.7$ and (b) at $\rho^* = 0.75$.

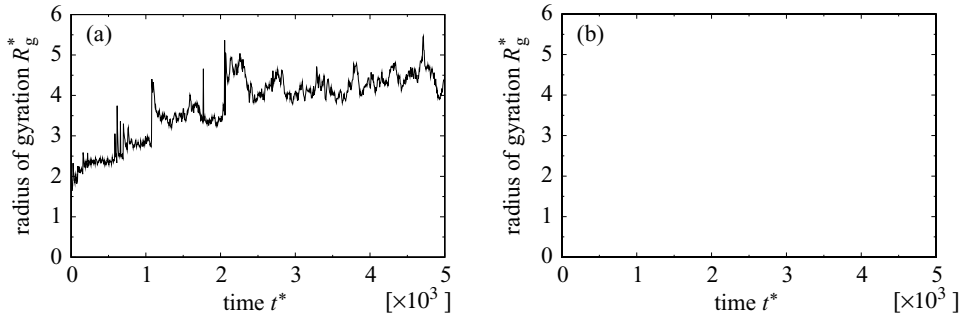


Figure 4. Time evolution of the radius of gyration $R^*_{\rm g}$ of the largest micelle (a) at $\rho^* = 0.7$ and (b) at $\rho^* = 0.75$.

$R^*_{\rm g}$ increases in a stepwise fashion as in potential energies. We can also find sharp bumps in the time evolution of $R_{\rm g}$ at both number densities. It is ascertained, from Figs 4 and 5, that the sharp bumps occur during coalescence of micelles.

4. Summary and discussion

By performing MD simulations of coarse-grained amphiphilic molecules with explicit solvent molecules, we have obtained the following new results. (1) As the

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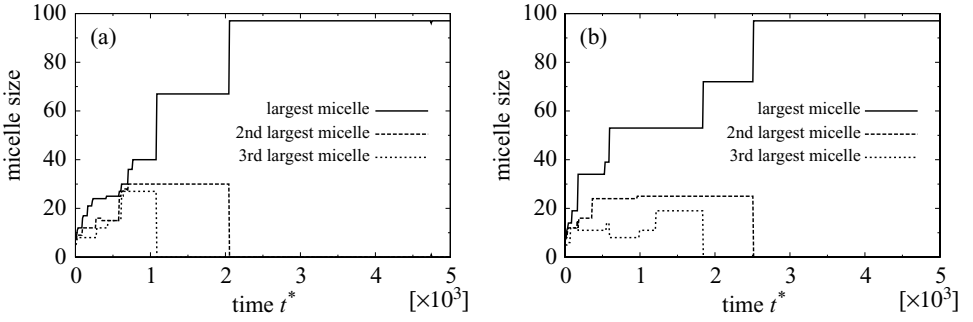


Figure 5. Time evolution of the micelle sizes (a) at $\rho^* = 0.7$ and (b) at $\rho^* = 0.75$.

number density increases, the shapes of micelles change from a cylindrical micelle to a planar bilayer. (2) At higher densities, we find the stepwise relaxation in the potential energy, the stepwise increase of the radius of gyration R_g of the largest micelles and the sharp bumps in R_g during coalescence of micelles. Our simulation results indicate that the number density has an effect not only on the micellar shape but also on the micelle formation process.

The similar stepwise energy relaxation is observed also in plasma self-organization [6]. The magnetic energy is found to relax in a stepwise fashion when a system is driven far from equilibrium.

For the future work, we will carry out MD simulation of amphiphilic solution with various amphiphilic concentrations in order to investigate the formation processes of mesophases, such as the hexagonal phase and the lamellar phase.

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