

Shape transition of micelles in amphiphilic solution: A molecular dynamics study

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Abstract. The shape transition of micelles in an amphiphilic solution is studied by a molecular dynamics simulation of coarse-grained rigid amphiphilic molecules with explicit solvent molecules. Our simulations show that the micellar shape changes from a disc into a cylinder, and then into a sphere as the hydrophilic interaction increases. We find that the potential energy decreases monotonically even during the micellar shape transition as the hydrophilic interaction increases. In contrast, it is ascertained that there exists a wide coexistence region in the intensity of the hydrophilic interaction between a cylinder and a sphere.

1. Introduction

Amphiphilic molecules such as lipids and surfactants contain both a hydrophilic part and a hydrophobic part. In aqueous or organic solvents, these molecules often spontaneously self-assemble into various structures such as micelles, bilayer membranes and bicontinuous structures [1, 2, 3]. Shape transitions of micelles play an important role in cellular physiology. The sphere-to-rod transitions of surfactant micelles in aqueous solution have recently been investigated by coarse-grained molecular dynamics (MD) simulations [4, 5]. Although numerous computer simulation studies have so far been carried out on micellar systems in amphiphilic solution [6], 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.

2. Simulation model and method

The computational model is the same as that used in the previous work [7, 8, 9, 10]. 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

$$U_{\text{SC}}(r) = 4\varepsilon_{\text{SC}} \left(\frac{\sigma_{\text{SC}}}{r} \right)^9, \quad (1)$$

the interaction between a hydrophilic head particle and a solvent particle is modeled by a Lennard-Jones (LJ) potential

$$U_{\text{LJ-hs}}(r) = 4\varepsilon_{\text{hs}} \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (2)$$

and all other interactions are modeled by an LJ potential

$$U_{\text{LJ}}(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]. \quad (3)$$

Here, r is the interparticle distance, ε_{SC} is an interaction parameter for the intensity of the hydrophobic interaction and ε_{hs} is that for the intensity of the hydrophilic interaction. The parameter σ_{SC} is set to $\sigma_{\text{SC}} = 1.05\sigma$ as in [11]. To avoid discontinuities in both the potential energy and the force due to the potential energy cutoff, we use the shifted force variant of these nonbonded potentials

$$V_X(r) = U_X(r) - U_X(r_c) - \left. \frac{\partial U_X}{\partial r} \right|_{r=r_c} (r - r_c), \quad (4)$$

where $X = \text{SC, LJ-hs or LJ}$, and r_c is the cutoff distance, which is set to $r_c = 3.0\sigma$ here. In what follows, we represent dimensionless quantities by an asterisk, e.g., number density $\rho^* = \rho\sigma^3$, time $t^* = t\sqrt{\varepsilon/m\sigma^2}$ and temperature $T^* = k_{\text{B}}T/\varepsilon$, where k_{B} is the Boltzmann constant.

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 [12]. 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 $(\varepsilon_{\text{SC}}^*, \varepsilon_{\text{hs}}^*) = (1.0, 1.0)$ 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 $\varepsilon_{\text{hs}}^*$ is then changed to various values ($\varepsilon_{\text{hs}}^* = 1.2, 1.4, \dots, 4.0$) and MD simulations of $t^* = 2.0 \times 10^4$ (8.0×10^6 time steps) are carried out for each simulation run.

3. Simulation results and discussion

3.1. Micellar shape

We show, in figure 1, snapshots of micelles formed by amphiphilic molecules at $\varepsilon_{\text{hs}}^* = 1.0, 2.0$ and 4.0 . Isosurfaces of the density of the tail particles, which are calculated by Gaussian splatting techniques, are depicted in this figure. Figure 1 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 $\varepsilon_{\text{hs}}^*$ increases.

3.2. Potential energy

In figure 2, the total potential energy E_{pot}^* is shown as a function of the intensity of the hydrophilic interaction $\varepsilon_{\text{hs}}^*$. This figure indicates that the total potential energy changes monotonically with the intensity of the hydrophilic interaction even during the micellar shape transition.

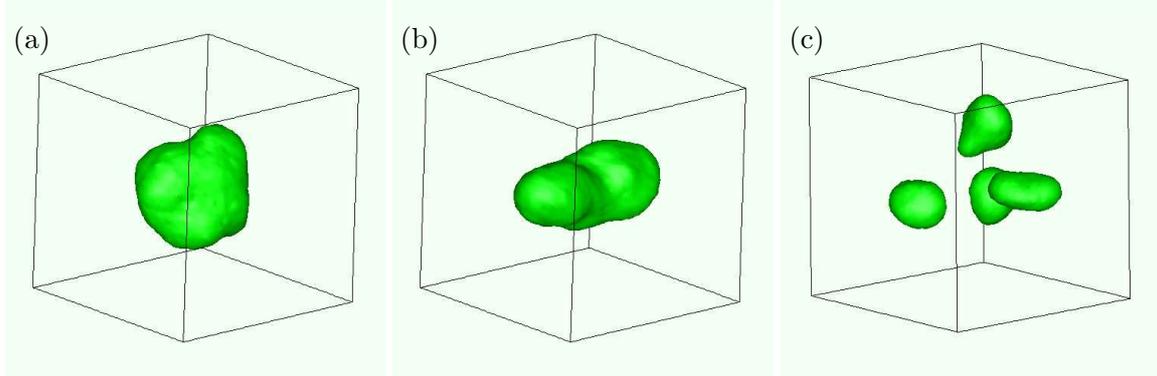


Figure 1. Snapshots of micelles formed by amphiphilic molecules for various values of the hydrophilic interaction parameter $\varepsilon_{\text{hs}}^*$. (a) A disc micelle for $\varepsilon_{\text{hs}}^* = 1.0$, (b) a cylindrical micelle for $\varepsilon_{\text{hs}}^* = 2.0$ and (c) spherical micelles for $\varepsilon_{\text{hs}}^* = 4.0$. 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.

3.3. Fraction of micellar shapes

Here, we examine the micellar shape distribution in order to quantitatively investigate how the micellar shape changes with the hydrophilicity. As in our previous papers [8, 9, 10], we use the orientational order parameters as indices to characterize the micellar shape. We introduce a coordinate system that uses the three principal axes of inertia of the micelle. 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 the principal axis with the smallest moment of inertia. The orientational order parameters p_x , p_y and p_z are defined by

$$p_i = \left\langle \frac{3 \cos^2 \theta_i - 1}{2} \right\rangle \quad (i = x, y, z), \quad (5)$$

where θ_i is the angle between the end-to-end vector of an amphiphilic molecule and the i -axis ($i = x, y, z$), and $\langle \dots \rangle$ denotes the average over of all amphiphilic molecules. Note that the average is taken for the amphiphilic molecules in the vicinity of the center-of-mass position of the micelle, that is, those in the region $-\Delta r < x, y, z < \Delta r$. We set $\Delta r = 2.5\sigma$ in the calculation of p_i . Ideally, the orientational order parameters take the following values: $(p_x, p_y, p_z) = (1, -0.5, -0.5)$ for a disc, $(p_x, p_y, p_z) = (0, 0, -0.5)$ for a cylinder and $(p_x, p_y, p_z) = (0, 0, 0)$ for a sphere. Detailed analysis of the distribution functions of these orientational order parameters showed that, in practice, 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 [8, 9, 10]. We calculate the fractions of the micellar shapes on the basis of these orientational order parameters.

Figure 3 shows the fraction of various micellar shapes as a function of the intensity of the hydrophilic interaction $\varepsilon_{\text{hs}}^*$. We find from this figure that the dominant micellar shape is a disc for $\varepsilon_{\text{hs}}^* \leq 1.2$, a cylinder for $\varepsilon_{\text{hs}}^* = 2.0$ and 2.2 , and a sphere for $\varepsilon_{\text{hs}}^* \geq 3.6$. It is also found that there exists a wide coexistence region in the intensity of the hydrophilic interaction between a cylinder and a sphere for $2.4 \leq \varepsilon_{\text{hs}}^* \leq 3.4$. The micellar shapes are visibly distinguishable even in the coexistence region, that is, a cylinder and a sphere coexist dynamically.

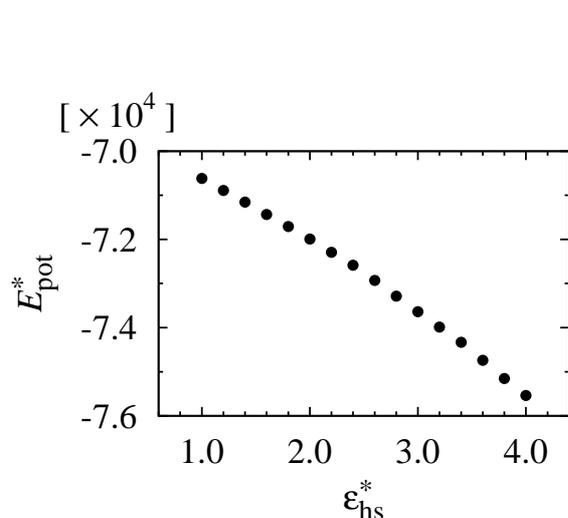


Figure 2. The total potential energy E_{pot}^* versus the hydrophilic interaction parameter ϵ_{hs}^* .

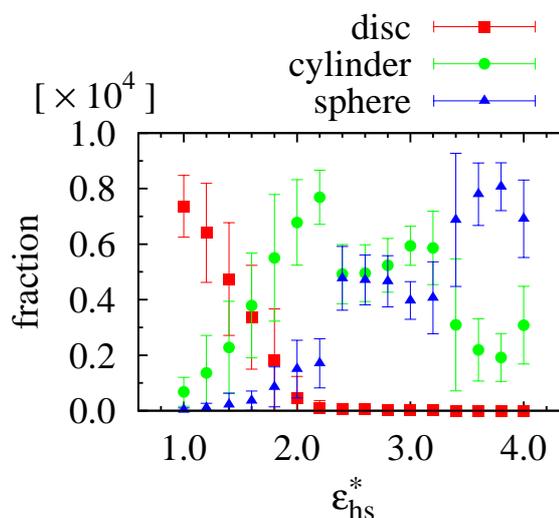


Figure 3. The fraction of various micellar shapes versus the hydrophilic interaction parameter ϵ_{hs}^* .

4. Conclusions

We have obtained the following new results by performing MD simulations of coarse-grained rigid amphiphilic molecules with explicit solvent molecules. (1) As the intensity of the hydrophilic interaction, ϵ_{hs}^* , increases, the micellar shape changes from a disc into a cylinder, and then into a sphere. (2) The potential energy decreases monotonically even during the shape transition of micelles as ϵ_{hs}^* increases. (3) There exists a wide coexistence region in the intensity of the hydrophilic interaction between a cylinder and a sphere.

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