

Molecular Dynamics Simulation of Micellar Shape Change in Amphiphilic Solution^{*)}

Susumu FUJIWARA, Takashi ITOH, Masato HASHIMOTO, Yuichi TAMURA¹⁾,
Hiroaki NAKAMURA²⁾ and Ritoku HORIUCHI²⁾

Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan

¹⁾*Konan University, 8-9-1 Okamoto, Higashinada-ku, Kobe 658-8501, Japan*

²⁾*National Institute for Fusion Science, 322-6 Oroshi-cho, Toki 509-5292, Japan*

(Received 7 December 2010 / Accepted 7 March 2011)

Micellar shape change in an amphiphilic solution is investigated by a molecular dynamics simulation of coarse-grained semiflexible amphiphilic molecules with explicit solvent molecules. Our simulations show that a cylindrical micelle is obtained at small molecular rigidity while a disc-shaped micelle appears at large molecular rigidity. We find that most chains are in an extended conformation at large molecular rigidity whereas the fraction of the chains in a bent conformation becomes large at small molecular rigidity. It is also ascertained that the micellar shape starts to change immediately after sudden increase of the molecular rigidity while an induction time is needed to change the micellar shape after sudden decrease of the molecular rigidity. This result can be qualitatively explained by considering the bond-bending potential energy and the conformational entropy of the amphiphilic molecules.

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Keywords: molecular dynamics simulation, molecular rigidity, micellar shape change, chain conformation, amphiphilic solution

DOI: 10.1585/pfr.6.2401040

1. Introduction

The spontaneous structure formation, or self-organization, has recently become the focus of attention in plasma physics and soft matter physics. To explore the universal self-organizing properties in nature, we study the structure formation in soft matter systems such as the formation of the orientationally ordered structure in polymeric systems [1–5] and the self-assembly in amphiphilic systems [6–8]. Amphiphilic molecules such as lipids and surfactants contain both a hydrophilic part and a hydrophobic part. In aqueous solvents, these molecules spontaneously self-assemble into various structures such as micelles, bilayer membranes and bicontinuous structures [9–11]. Self-assembly of amphiphilic molecules plays an important role in many biological and industrial processes. Although several computer simulations have so far been carried out on the micelle formation [12–14], few simulation studies have been done on the micellar shape change.

In our previous paper [8], we have performed the molecular dynamics (MD) simulations of coarse-grained semiflexible amphiphilic molecules with explicit solvent molecules. It was found from our simulations that the micellar structure formed at small molecular rigidity is cylindrical while that formed at large molecular rigidity is disc-

shaped. The purpose of this study is to clarify the molecular mechanism of micellar shape change in an amphiphilic solution. Our particular concern is to investigate the effect of molecular rigidity on micellar shape change. With a view to investigating this in the amphiphilic solution at the molecular level, we perform MD simulations of coarse-grained semiflexible amphiphilic molecules with explicit solvent molecules and analyze the dynamical processes of micellar shape change.

2. Simulation Model and Method

The computational model is similar to that used in the previous work [6–8], which is based on the model of Goetz *et al.* [12]. An amphiphilic molecule is a semiflexible chain which consists of one hydrophilic particle and three hydrophobic particles. A solvent molecule is modeled as a hydrophilic particle. Particles interact via the nonbonded and bonded potentials.

As for nonbonded potentials, 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 the Lennard-Jones potential

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

author's e-mail: fujiwara@kit.ac.jp

^{*)} This article is based on the presentation at the 20th International Toki Conference (ITC20).

and all other interactions are modeled by the Lennard-Jones potential

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

Here, r is the interparticle distance, ϵ_{SC} is an interaction parameter representing the intensity of the hydrophobic interaction, and ϵ_{hs} represents the intensity of the hydrophilic interaction. The parameter σ_{SC} is set to $\sigma_{SC} = 1.05\sigma$, as in Ref. [12]. 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

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

where $X = SC, LJ\text{-hs},$ or LJ , and r_c is the cutoff distance, which is set to $r_c = 3.0\sigma$ here.

As bonded potentials, we consider a bond-stretching potential

$$U_2(d_i) = k_2(d_i - \sigma)^2, \quad (5)$$

where k_2 is the bond-stretching modulus and d_i is the bond length between two neighboring particles along the amphiphilic molecule and a bond-bending potential

$$U_3(\theta_i) = k_3(1 - \cos \theta_i), \quad (6)$$

where k_3 is the bending modulus of the semiflexible amphiphiles and θ_i is the bond angle between two neighboring bonds. The parameter k_2 is set to $k_2 = 5000\epsilon\sigma^{-2}$, as in Ref. [12]. The molecular rigidity is controlled by the bending modulus k_3 . In the following sections, we represent dimensionless quantities by an asterisk, e.g., time $t^* = t\sqrt{\epsilon/m\sigma^2}$ and temperature $T^* = k_B T/\epsilon$, where k_B is the Boltzmann constant.

The equations of motion for all particles are solved numerically by using the velocity Verlet algorithm at constant temperature with a time step of $\Delta t^* = 0.0005$, and the temperature is controlled at every 10 time steps by ad hoc velocity scaling [18]. We apply periodic boundary conditions, and the number density is set to $\rho^* = 0.75$.

Initially, we provide an isolated micelle of 120 semiflexible amphiphilic molecules with a certain value of the bending modulus k_3^* in solution at $T^* = 1.3$ for various values of the interaction parameters ϵ_{SC}^* and ϵ_{hs}^* ($1.0 \leq \epsilon_{SC}^*, \epsilon_{hs}^* \leq 3.0$). The number of solvent molecules is 7520, which yields an amphiphilic concentration of 0.06. We then change the value of the bending modulus k_3^* to various values suddenly, i.e., during 1 time step and MD simulations of $t^* = 5.0 \times 10^3$ (1.0×10^7 time steps) are carried out for each simulation run. In this paper, we focus on the results for $(\epsilon_{SC}^*, \epsilon_{hs}^*) = (1.0, 2.0)$.

3. Simulation Results

3.1 Micellar shape change

In our previous paper [8], it was found that the micellar structure formed at $k_3^* = 4.0$ is cylindrical and that at

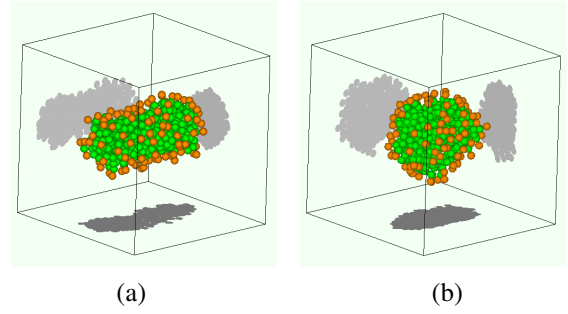


Fig. 1 Snapshots of micelles formed by amphiphilic molecules after sudden increase of k_3^* from 4.0 to 16.0 (a) at $t^* = 0$ and (b) at $t^* = 200$. Orange and green particles denote hydrophilic head particles and hydrophobic tail particles, respectively. Gray shadows of the micelle projected on three planes are also depicted to illustrate its shape. Note that, for clarity, solvent molecules are not displayed.

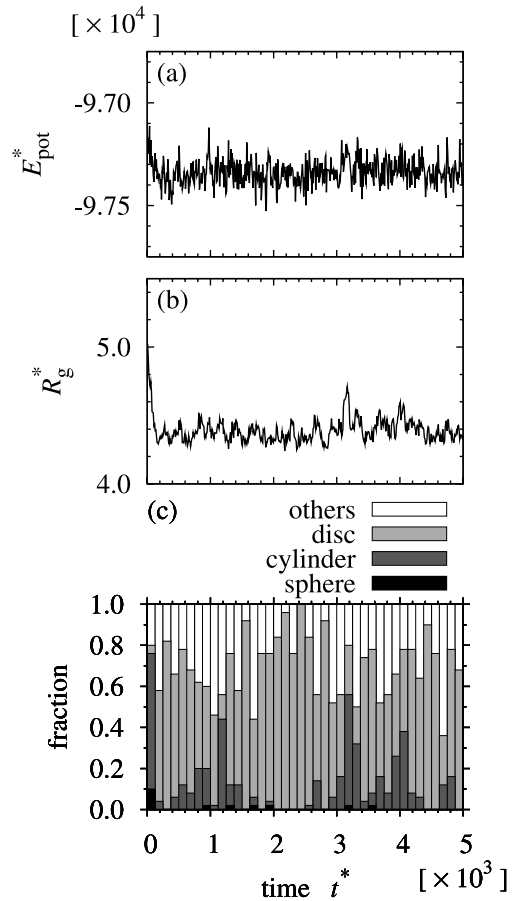


Fig. 2 Time evolution of (a) the total potential energy E_{pot}^* , (b) the radius of gyration of the micelle R_g^* , and (c) the fraction of various micellar shapes after sudden increase of k_3^* from 4.0 to 16.0.

$k_3^* = 16.0$ is disc-shaped. In this subsection, we examine the micellar shape change between a cylinder and a disc by sudden increase or decrease of the bending modulus k_3^* .

Simulation results in the case of sudden increase of k_3^* from 4.0 to 16.0 are shown in Figs. 1 and 2. We show,

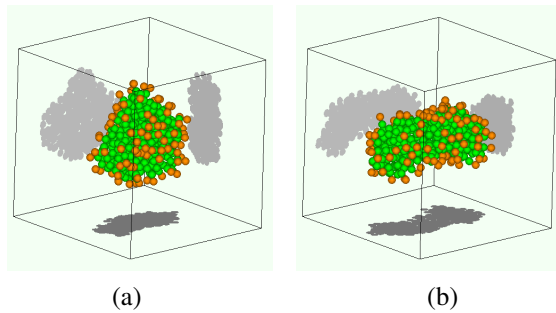


Fig. 3 Snapshots of micelles formed by amphiphilic molecules after sudden decrease of k_3^* from 16.0 to 4.0 (a) at $t^* = 300$ and (b) at $t^* = 500$. Orange and green particles denote hydrophilic head particles and hydrophobic tail particles, respectively. Gray shadows of the micelle projected on three planes are also depicted to illustrate its shape. Note that, for clarity, solvent molecules are not displayed.

in Fig. 1, snapshots of micelles formed by amphiphilic molecules at $t^* = 0$ and 200. Gray shadows of the amphiphilic molecules projected on three planes are also depicted in this figure to show the micellar shape clearly. This figure indicates that the micellar shape changes from a cylinder to a disc as the intensity of the molecular rigidity, k_3^* , increases from 4.0 to 16.0. Figure 2 shows the time dependence of the total potential energy E_{pot}^* , the radius of gyration of the micelle R_g^* , and the fraction of various micellar shapes after sudden increase of k_3^* from 4.0 to 16.0. As in our previous papers [6–8], we calculate the fractions of the micellar shapes on the basis of the orientational order parameters. The following characteristic features are identified from Fig. 2. (1) The potential energy starts to decrease immediately after sudden increase of k_3^* and reaches an equilibrium value at $t^* \approx 200$ (Fig. 2 (a)). (2) The radius of gyration starts to decrease immediately after sudden increase of k_3^* and reaches an almost constant value at $t^* \approx 200$ (Fig. 2 (b)) in accordance with the time evolution of the potential energy (Fig. 2 (a)). (3) The dominant micellar shape is a cylinder in the initial time region ($t^* < 200$) whereas that is a disc afterward (Fig. 2 (c)). These results indicate that the micellar shape starts to change immediately after sudden increase of the molecular rigidity. The same kind of behavior is also found for different initial configurations.

Simulation results in the case of sudden decrease of k_3^* from 16.0 to 4.0 are shown in Figs. 3 and 4. We show, in Fig. 3, snapshots of micelles formed by amphiphilic molecules at $t^* = 300$ and 500. This figure tells us that the micellar shape changes from a disc to a cylinder as the intensity of the molecular rigidity, k_3^* , decreases from 16.0 to 4.0. Figure 4 shows the time dependence of the total potential energy E_{pot}^* , the radius of gyration of the micelle R_g^* , and the fraction of various micellar shapes after sudden decrease of k_3^* from 16.0 to 4.0. We find the following fea-

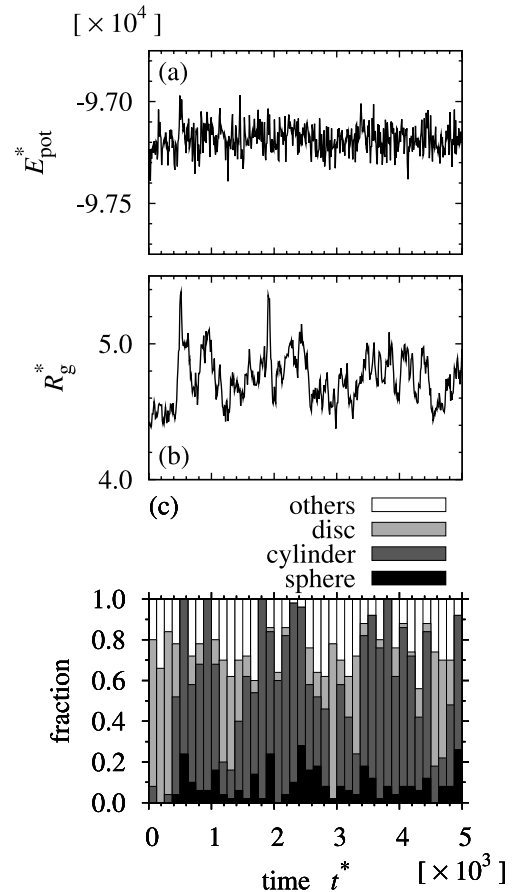


Fig. 4 Time evolution of (a) the total potential energy E_{pot}^* , (b) the radius of gyration of the micelle R_g^* , and (c) the fraction of various micellar shapes after sudden decrease of k_3^* from 16.0 to 4.0.

tures from Fig. 4. (1) The potential energy remains almost constant although a sharp increase is found at $t^* \approx 400$ (Fig. 4 (a)). (2) The radius of gyration is found to increase sharply at $t^* \approx 400$ (Fig. 4 (b)), which corresponds to the transition from a disc to a cylinder. (3) The dominant micellar shape is a cylinder after the transition from a disc to a cylinder at $t^* \approx 400$ (Fig. 4 (c)). These results show that there exists an induction time to change the micellar shape after sudden decrease of the molecular rigidity. The similar behavior is also found for different initial configurations.

3.2 Chain conformation

In this subsection, we examine the chain conformation in order to clarify the internal structures of cylindrical and disc-shaped micelles. In Fig. 5, we show the distribution of the bond angle $P(\theta)$ for $k_3^* = 16.0$ and 4.0. At $k_3^* = 16.0$, $P(\theta)$ has a peak around $\theta = \pi/10$, which means that most chains are in an extended conformation. At $k_3^* = 4.0$, on the other hand, $P(\theta)$ has a peak around $\theta = \pi/6$ and the tail of $P(\theta)$ extends to $\theta \approx 2\pi/3$, which implies that the fraction of the chains in a bent conformation becomes large as the intensity of the molecular rigidity decreases.

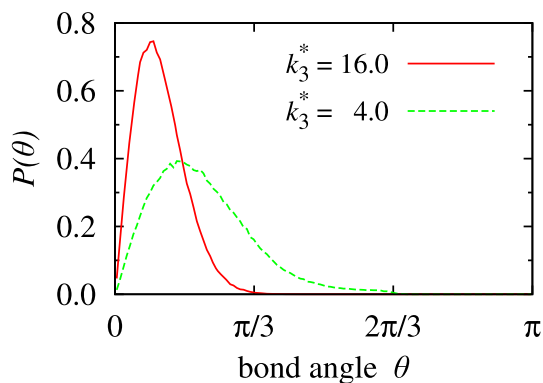


Fig. 5 Distribution of the bond angle $P(\theta)$ for $k_3^* = 16.0$ and 4.0 .

4. Summary and Discussion

We have obtained the following new results by performing MD simulations of coarse-grained semiflexible amphiphilic molecules with explicit solvent molecules. (1) A cylindrical micelle is obtained at small molecular rigidity whereas a disc-shaped micelle is formed at large molecular rigidity. (2) Most chains are in an extended conformation at large molecular rigidity whereas the fraction of the chains in a bent conformation becomes large at small molecular rigidity. (3) The micellar shape starts to change immediately after sudden increase of the molecular rigidity while there exists an induction time to change the micellar shape after sudden decrease of the molecular rigidity.

The second result suggests that the classification method of the micellar shapes based on the orientational order parameters, which is originally proposed for the rigid molecules, is not adequate for the semiflexible molecules with small k_3^* because the orientational correlation becomes weak due to the bent conformation.

Here we perform energy and entropy consideration of the semiflexible chains to elucidate the third result. We consider the bond-bending potential energy E_{bend} and the conformational entropy S_c on the basis of the conformation of the molecules. In the case of sudden increase of k_3^* from 4.0 to 16.0, E_{bend} increases and the region of available bond angles decreases (Fig. 5), which indicates a decrease in S_c , just after sudden increase of k_3^* . Therefore, the cylindrical micelle starts to change its shape immediately after sudden increase of k_3^* because the cylindrical micelle becomes energetically and entropically unstable just after sudden increase of k_3^* . In the case of sudden decrease of k_3^*

from 16.0 to 4.0, on the other hand, E_{bend} decreases and the region of available bond angles increases (Fig. 5), which indicates an increase in S_c , just after sudden decrease of k_3^* . Therefore, the disc-shaped micelle needs an induction time to change its shape after sudden decrease of k_3^* because the disc-shaped micelle becomes energetically and entropically metastable just after sudden decrease of k_3^* .

Acknowledgment

This study was partially supported by a Grants-in-Aid (No. 22540419) from the Ministry of Education, Culture, Sports, Science and Technology, Japan and was partially performed with the support and under the auspices of the NIFS Collaborative Research Program (NIFS10KDAS001). The authors thank the Supercomputer Center, Institute for Solid State Physics, University of Tokyo for the use of the facilities.

- [1] S. Fujiwara and T. Sato, *J. Chem. Phys.* **107**, 613 (1997).
- [2] S. Fujiwara and T. Sato, *J. Chem. Phys.* **114**, 6455 (2001).
- [3] S. Fujiwara and T. Sato, *Phys. Rev. Lett.* **80**, 991 (1998).
- [4] S. Fujiwara and T. Sato, *J. Chem. Phys.* **110**, 9757 (1999).
- [5] S. Fujiwara, M. Hashimoto, T. Itoh and H. Nakamura, *J. Phys. Soc. Jpn.* **75**, 024605 (2006).
- [6] S. Fujiwara, T. Itoh, M. Hashimoto and Y. Tamura, *Mol. Simul.* **33**, 115 (2007).
- [7] S. Fujiwara, T. Itoh, M. Hashimoto and R. Horiuchi, *J. Chem. Phys.* **130**, 144901 (2009).
- [8] S. Fujiwara, T. Itoh, M. Hashimoto, H. Nakamura and Y. Tamura, *Plasma Fusion Res.* **5**, S2114 (2010).
- [9] J.N. Israelachvili, *Intermolecular and Surface Forces* (Academic Press, London, 1992) 2nd ed.
- [10] *Micelles, Membranes, Microemulsions, and Monolayers*, edited by W.M. Gelbart, A. Ben-Shaul and D. Roux (Springer-Verlag, New York, 1994), p.1–104.
- [11] I.W. Hamley, *Introduction to Soft Matter* (J. Wiley, Chichester, 2007) Rev. ed.
- [12] R. Goetz and R. Lipowsky, *J. Chem. Phys.* **108**, 7397 (1998).
- [13] R. Goetz, G. Gompper and R. Lipowsky, *Phys. Rev. Lett.* **82**, 221 (1998).
- [14] S.J. Marrink, D.P. Tieleman and A.E. Mark, *J. Phys. Chem. B* **104**, 12165 (2000).
- [15] T. Miura, R. Kishi, M. Mikami and Y. Tanabe, *Phys. Rev. E* **63**, 061807 (2001).
- [16] T. Sakaue and K. Yoshikawa, *J. Chem. Phys.* **117**, 6323 (2002).
- [17] N. Yoshinaga and K. Yoshikawa, *J. Chem. Phys.* **127**, 044902 (2007).
- [18] M.P. Allen and D.J. Tildesley, *Computer Simulation of Liquids* (Clarendon, Oxford, 1987).