

DEFORMATION OF COPOLYMER MICELLES INDUCED BY AMPHIPHILIC DIMER PARTICLES*

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Abstract Combining self-consistent-field theory and density-functional theory, we systematically study the deformation of copolymer micelles induced by the presence of amphiphilic dimer particles. Due to the amphiphilic nature, dimer particles tend to accumulate onto the interface of the copolymer micelle. With increasing concentration of the symmetric dimer particles, which are made of two identical spherical particles, the micelle deforms from the initial sphere to ellipse, dumbbell, and finally separates into two micelles. Furthermore, asymmetric dimer particles, composed by two particles with different sizes, are considered to investigate the influence of geometry of dimer particles on the deformation of the micelle. It is found that the micelle inclines to deform into dumbbell due to the additional curvature originating in the gathering of asymmetric dimer particles onto the interface of the micelle. The present study on the deformation of micelles is useful to understand the possible shape variation in the course of cell division/fusion.

Keywords: Dimer particle; Copolymer micelle; Deformation; Self consistent field theory; Density function theory.

INTRODUCTION

Surfactant is known to modify the interfacial properties greatly, particularly to influence the shape and stability of interfaces/surfaces. A typical surfactant is composed of amphiphilic molecules. For example, studies, including experiments^[1, 2] and theories^[3, 4], have shown that the morphological change of vesicles or membrane tubes was induced by adsorbing amphiphilic polymers on their interfaces. Budding and pearling occur in vesicles or membrane tubes due to the introduction of amphiphilic polymers. Amphiphilic particle is another widely used surfactant. Experiments have shown the formation of nonspherical shapes of bubbles or liquid droplets with the presence of amphiphilic particles^[5]. In the recent experiment, Studart *et al.* found that the particle-coated bubbles and droplets can retain nonspherical shape (such as dumbbell) after deformation, where particles were wetted by both liquids^[6]. They also studied the amphiphilic dimer particles which coated on the surface of the emulsions, and found the ellipsoidal as well as cylindrical droplets were present together with spherical drops^[7]. Moreover, the kinetics of vesicle formation of the copolymers from an initially homogeneous state was theoretically and experimentally investigated by adding particles into the system. The pathway of spontaneous vesicle deformation was verified largely depending on the particles addition rate^[8]. Furthermore, janus particles, characterized by two different chemical compositions, were taken as surfactant in experiments^[9–11]. Nowadays, all kinds of surfactant have been used to the modification of interfaces/surfaces.

Copolymer micelles, as models of real cell, are applied widely. One of the interesting issues is controlling the deformation of micelles according to the different environment conditions, such as by chemical

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modification^[12], kinetic controlling^[13], photo inducing^[14] and the introduction of surfactant. Although the deformation of cells/micelles has been observed in many experiments^[15–18], the theoretical studies are still limited. In this paper, we try to systematically investigate the influence on the deformation of copolymer micelles induced by the addition of amphiphilic dimer particles, and explain the impact of the geometry of dimer particles.

We use the self-consistent field theory (SCFT) for the copolymer micelle and density functional theory (DFT) for the dimer particles. SCFT is widely used in polymer systems, which well reflects the conformation of flexible chains^[19, 20]. DFT is good for hard sphere systems, which reflects the steric interaction resulting from the specific geometry of the hard sphere^[21–26]. Since we consider the amphiphilic dimer particles, we follow works of Christopher *et al.*^[27, 28] and Thompson^[29, 30] where they considered cases of symmetric dimer particles, which are composed of two identical spheres. On the contrary, asymmetric dimer particles are made up of two spheres with different sizes.

MODEL AND METHODS

The interesting system consists of copolymer micelles, the polymer solvent and the dimer particles. The copolymer micelle has N_c AB diblock copolymers. There are N_s polymer solvent molecules and N_p amphiphilic dimer particles in the system. The partition function for the system can be written as:

$$Z = \frac{1}{n_c!n_s!n_p!} \int \prod_{\alpha=1}^{n_c} \hat{D}r_{\alpha}(s) \prod_{\gamma=1}^{n_p} \hat{D}r_{\gamma}(r) \prod_{\beta=1}^{n_p} \hat{D}R_{\beta a} d\hat{\mu} \delta(R_{\beta a} - R_{\beta b} - l\hat{\mu}) \delta(1.0 - \sum_i^{a,b,h,t,s} \hat{\Phi}_i) \exp\{-\rho_0 \int dr \chi \hat{\Phi}_h(r) [\hat{\Phi}_t(r) + \hat{\Phi}_s(r) + \hat{\Phi}_b(r)] + \chi \hat{\Phi}_a(r) [\hat{\Phi}_t(r) + \hat{\Phi}_s(r)]\} \quad (1)$$

where the first δ function reflects the fact that two spheres are together to form a dimer amphiphilic particles^[29, 30] and the second δ function enforces incompressibility. The weighting factor $\hat{D}r_{\alpha}(s)$ incorporates the Gaussian nature of the chains. Taking the steric interaction between spheres into account, through a transformation^[23, 31], the mean-field free energy of the system can be written as follows:

$$\begin{aligned} \frac{NF}{\rho_0 k_B T} = & -\phi_s \ln\left(\frac{Q_s}{V\phi_s}\right) - \frac{\phi_p}{\alpha_p} \ln\left(\frac{Q_p \alpha_p}{V\phi_p}\right) - \phi_c \ln\left(\frac{Q_c}{V\phi_c}\right) - \frac{1}{V} \int dr \{W_s(r) \varphi_s(r)\} \\ & - \frac{1}{V} \int dr \{W_h(r) \varphi_h(r) + W_t(r) \varphi_t(r)\} - \frac{1}{V} \int dr \{W_a(r) \rho_a(r) + W_b(r) \rho_b(r)\} \\ & + \frac{1}{V} \int \{\chi N \varphi_h(r) [\varphi_t(r) + \varphi_s(r) + \varphi_b(r)] + \chi N \varphi_a(r) [\varphi_t(r) + \varphi_s(r)]\} \\ & + \sum_i^{a,b} \rho_i \Psi(\zeta_i, \eta_1, \eta_2, \eta_3) \end{aligned} \quad (2)$$

The self-consistent calculations are carried out in two-dimensional boxes for convenience with $N_x \times N_y$ lattices ($N_x = 100$, $N_y = 100$). The boundary conditions in x and y directions are periodic. We give the two-dimensional schematic illustration of the system as Fig. 1 shows, in which we consider the dimer particle as the fused colloidal disks. V is the volume of the system. Each copolymer and polymer solvent is composed of N total segments. $W_i(r)$ ($i = h, t, a, b, s$) are self-consistent fields acting on different components of the system, which take the place of the many-body interactions in the system. Q_c , Q_p and Q_s are the single-molecule partition function of copolymers, dimer particles and solvents. ϕ_s , ϕ_c , ϕ_p are overall volume fractions of the solvents, copolymers and dimer particles. We fix the overall volume fraction of copolymers as $\phi_c = 0.18$, which satisfies the incompressible constraint $\phi_s + \phi_c + \phi_p = 1.0$. The Flory-Huggins interaction parameter, between the hydrophilic components (solvents, T block of the copolymers, B-disk of the dimer particles) and the hydrophobic components (H block of the copolymers, A-disk of the dimer particles), is fixed to be $\chi N = 30.0$.

$\varphi_h(r)$ and $\varphi_t(r)$ are the local volume fractions of two blocks of the copolymers. The number of the copolymer segments is taken as $N = 400$. f is the fraction of the diblock and the hydrophilic chemical species of copolymers and is chosen as $f = 0.65$. Different parts of the amphiphilic dimer particles center distribution are expressed as $\rho_a(r)$ and $\rho_b(r)$, the local volume fractions of the amphiphilic dimer particles are given by:

$$\varphi_i(r) = \frac{\alpha_i}{V_{r_i}} \int_{|r'| \leq r_i} \rho_i(r+r') \, d\mathbf{r}', \quad (i = a, b) \quad (3)$$

where V_{r_i} denotes the volume of a sphere of radius r_a and r_b are the radius of the two disks for the dimer particles. In Eq. (3), $\alpha_i = v_i \rho_0 / N$ ($i = a, b$) is the volume ratio of i -type disk in the dimer particles to the copolymers chain, where v_i denotes the volume of the i -type disk. All of the sizes and volumes involved in the present system are measured in units of a and ρ_0^{-1} . For convenience, we set $a = 1.0$, $\rho_0^{-1} = 1.0$ and $k_B T = 1.0$. $\alpha_p = \alpha_a + \alpha_b$ is the volume ratio of the dimer particles to the copolymers chain. Polymer solvent is given by $\varphi_s(r)$, the solvents only offer a hydrophilic background to maintain the copolymer micelle, so we can use the homopolymer solvents instead of small molecules for convenience^[32, 33]. The seventh term in Eq. (2) is the enthalpic free energy (U), implying the interactions between different components. The last term in Eq. (2) is the nonideal steric term including the excluded volume interactions between different spheres in the amphiphilic dimer particles (F_{st}). We follow the expression of Mansoori *et al.*^[34], which is given by:

$$\Psi(\zeta_i, \eta_1, \eta_2, \eta_3) = (\zeta_i - 1)(\zeta_i + 3) - \frac{3}{2}(\zeta_i^2 - 1)\eta_1 - \frac{3}{2}(\zeta_i - 1)^2\eta_2 + \left[\frac{1}{2}(\zeta_i - 1)(\zeta_i - 3) + \ln \zeta_i\right](1 - \eta_3) \quad (4)$$

where $\zeta_i = 1/(1 - \bar{\varphi}_i)$, and the weighted densities are in the Tarazona form^[35],

$\bar{\varphi}_i(r) = \sum_j^{a,b} \frac{\alpha_j}{V_{(r_i+r_j)}} \int_{|r'| \leq r_i+r_j} \rho_i(r+r') \, d\mathbf{r}'$. In Eq. (4), η_1, η_2, η_3 are functions of the diameter of the particles. If

the diameter of two type disks in the dimer particles are the same, then $\eta_1 = 0$, $\eta_2 = 0$, $\eta_3 = 1.0$, which simplifies Eq. (6) to the Carnahan-Starling equation for the case of monodisperse spheres.

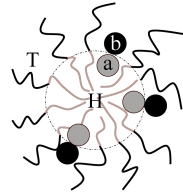


Fig. 1 The schematic illustration of the system
Two disks fused together to form a dimer particle adsorbing on the interface of the copolymer micelle in the environment of polymer solvents.

By minimizing the free energy F , we obtain the mean-field equations that describe equilibrium morphologies as follows:

$$W_h(r) = \chi N [\varphi_t(r) + \varphi_b(r) + \varphi_s(r)] + \varepsilon(r) \quad (5)$$

$$W_s(r) = \chi N [\varphi_h(r) + \varphi_a(r)] + \varepsilon(r) \quad (6)$$

$$W_t(r) = \chi N [\varphi_h(r) + \varphi_a(r)] + \varepsilon(r) \quad (7)$$

$$W_a(r) = \Psi(\bar{\varphi}_a, \eta_1, \eta_2, \eta_3) + \frac{\alpha_a}{V_{r_a}} \int_{|r'| \leq r_a} dr' \{ \chi N [\varphi_t(r) + \varphi_s(r)] + \varepsilon(r) \} \\ + \sum_i^{a,b} \frac{\alpha_a}{V_{r_a+r_i}} \int_{|r'| \leq r_a+r_i} dr' \rho_i(r+r') \Psi'(\bar{\varphi}_i, \eta_1, \eta_2, \eta_3) \quad (8)$$

$$W_b(r) = \Psi(\bar{\varphi}_b, \eta_1, \eta_2, \eta_3) + \frac{\alpha_b}{V_{r_b}} \int_{|r'| \leq r_b} dr' \{ \chi N \varphi_h(r) + \varepsilon(r) \} \\ + \sum_i^{a,b} \frac{\alpha_b}{V_{r_b+r_i}} \int_{|r'| \leq r_b+r_i} dr' \rho_i(r+r') \Psi'(\bar{\varphi}_i, \eta_1, \eta_2, \eta_3) \quad (9)$$

$$\varphi_s(r) = \frac{V\phi_s}{Q_s} \int_0^1 ds q(r, s) q^+(r, s) \quad (10)$$

$$\varphi_h(r) = \frac{V\phi_c}{Q_c} \int_f^1 ds q(r, s) q^+(r, s) \quad (11)$$

$$\varphi_t(r) = \frac{V\phi_c}{Q_c} \int_0^f ds q(r, s) q^+(r, s) \quad (12)$$

$$\rho_a(r) = \frac{V\phi_p}{Q_p \alpha_p} \int d\mu \exp \{ W_a(r) + W_b(r+l\mu) \} \quad (13)$$

$$\rho_b(r) = \frac{V\phi_p}{Q_p \alpha_p} \int d\mu \exp \{ W_b(r) + W_a(r+l\mu) \} \quad (14)$$

$\alpha(r)$ is the incompressibility field. In Eq. (8) and Eq. (9), $\Psi'(\zeta_i, \eta_1, \eta_2, \eta_3) = \partial \Psi(\zeta_i, \eta_1, \eta_2, \eta_3) / \partial \varphi$. In Eq. (11) and Eq. (12), Q_c is the partition function of a single copolymer molecule,

$$Q_c = \int dr q(r, s) q^+(r, s) \quad (15)$$

where, the propagator $q(r, s)$ represents the probability of finding segment s at position r , which satisfies the diffusion equation,

$$\frac{\partial q(r, s)}{\partial s} = \frac{Na^2}{6} \frac{\partial^2 q(r, s)}{\partial r^2} - W(r) q(r, s) \quad (16)$$

subject to the initial condition $q(r, 0) = 1.0$. Here $W(r) = W_t(r)$ when $0 < s < f$, and $W(r) = W_b(r)$ when $f < s < 1$. The contour length s increases continuously from 0 to 1 as the block changes from one end to the other. In Eq. (13) and Eq. (14), the partition function of dimer particles subject to the field $W_a(r)$ and $W_b(r)$ given by $Q_p = \int dr d\mu \exp \{ W_a(r) + W_b(r+l\mu) \}$, where μ means the orientation of the dimer particles in the system, l means the center distance between the two particles.

The numerical simulation is carried out until the relative free energy changes at each iteration are smaller than 10^{-5} and the incompressibility condition is achieved. The simulations starting with a different initial random states are repeated for 5–8 times to ensure that the observed phenomena are not accidental^[36, 37]. We found that these results show very similar morphologies, while the free energy for each case has a subtle difference. The results shown in this paper have the minimum free energy, which are stable under the frame of SCFT/DFT method^[21]. For the case of asymmetric dimer particles, we choose $d_a = 4a$ and $d_b = 6a$. So the particle has a small

hydrophobic part and a large hydrophilic part as the previous experiment done by Kim^[7]. Finally, we discuss the case with the addition of asymmetric dimer particles with $d_a = 6a$ and $d_b = 4a$ in order to compare with conditions of symmetric ($d_a = 4a$, $d_b = 4a$) and asymmetric particles ($d_a = 4a$ and $d_b = 6a$).

RESULTS AND DISCUSSION

In Fig. 2 we give a morphology of the pure copolymer micelle. For the amphiphilic character of copolymers in the solvents, they can form a spherical morphology with the hydrophobic part inside to reduce the interfacial energy of the system.

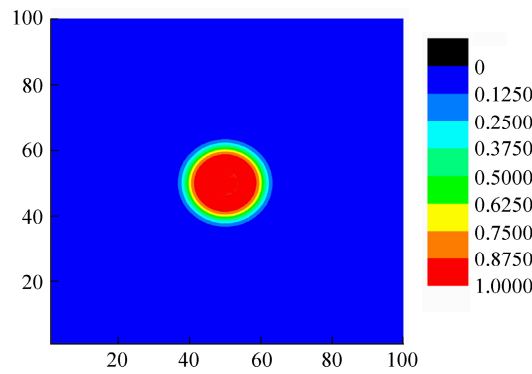


Fig. 2 The micelle structure of copolymers with the hydrophobic part
The right scale represents the volume fraction of hydrophobic part.

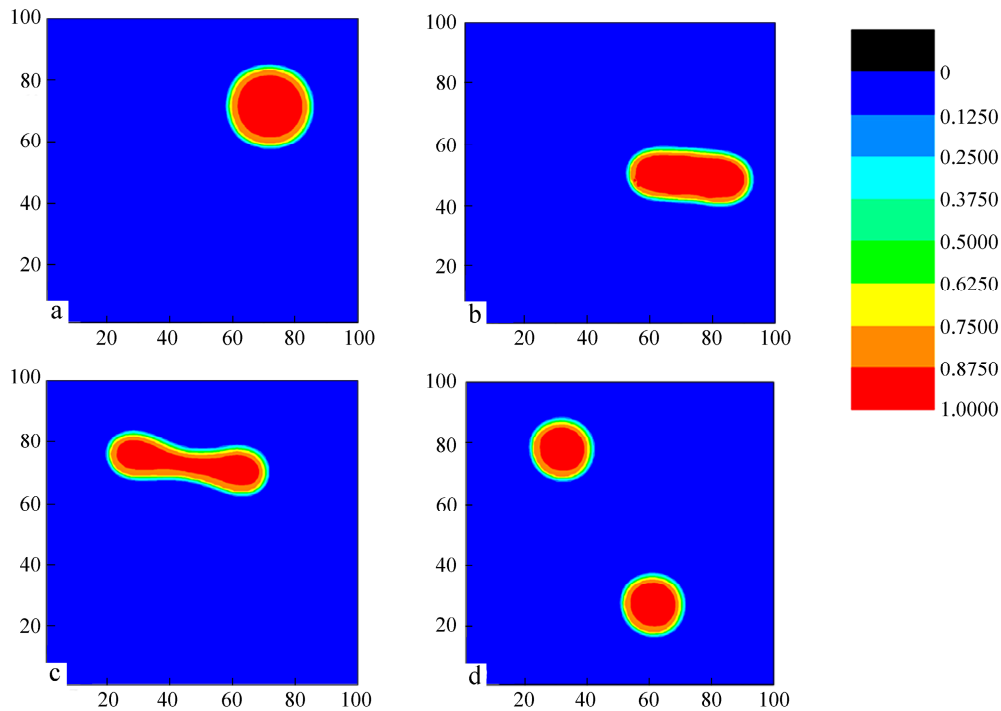


Fig. 3 The spherical or nonspherical morphologies of copolymer micelles with different concentrations of the symmetric dimer particles ($d_a = 4a$, $d_b = 4a$): (a) $\phi_p = 0.12$, (b) $\phi_p = 0.16$, (c) $\phi_p = 0.19$ and (d) $\phi_p = 0.20$

By increasing the volume fraction of the symmetric dimer particles ($d_a = 4a$, $d_b = 4a$), we get series of morphologies for copolymer micelle in Fig. 3. We find that the copolymer micelle is nonspherical when the concentration of the dimer particles is increased. The shape of the copolymer micelle emerges into ellipse at $\phi_p = 0.16$ and dumbbell at $\phi_p = 0.19$. When the concentration of dimer particles added to $\phi_p = 0.20$, the copolymer micelle undergoes fission into two micelles. With more and more particles gather onto the interface of micelle, steric repulsions among particles begin to play important roles, which lead to the deformation and fission of the micelle. Therefore controlling the deformation of micelle can be achieved by changing the number of dimer particles in the system.

In order to explore the influence of geometry of amphiphilic dimer particles on the deformation of micelle, we study the case of asymmetric dimer particle, which includes two particles with different diameters ($d_a = 4a$, $d_b = 6a$). Figure 4 provides the morphology changes of a micelle as the concentration of asymmetric dimer particles increases. Comparing with the symmetric dimer particle, asymmetric dimer particle also can lead to the deformation and fission for copolymer micelle. However, comparing with Fig. 3, we find that there is no ellipse, instead by dumbbell at $\phi_p = 0.18$ and long dumbbell at $\phi_p = 0.25$. When $\phi_p = 0.28$, the long dumbbell separates into two dumbbells. Clearly, the deformation of micelle inclines to be dumbbell under the influence of asymmetric dimer particles. This is because of the additional curvature caused by the presence of asymmetric dimer particles. Thus, it can be concluded that changing the geometry of surfactant is an effective way to modify the morphology of micelles.

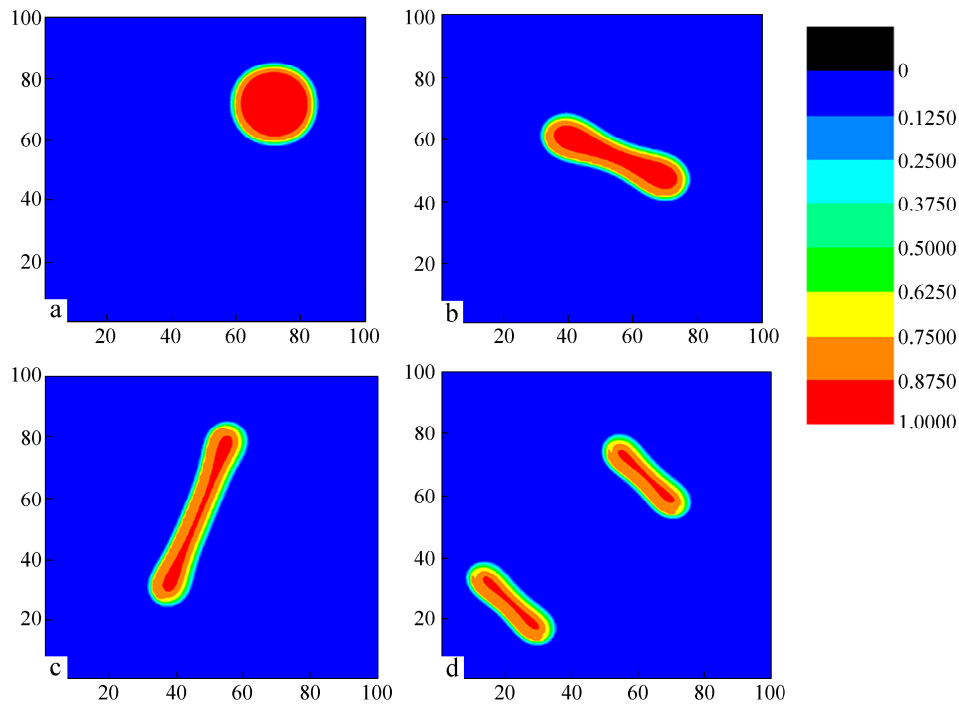


Fig. 4 The spherical or nonspherical morphologies of copolymer micelles with different concentrations of the asymmetric dimer particles ($d_a = 4a$, $d_b = 6a$): (a) $\phi_p = 0.16$, (b) $\phi_p = 0.18$, (c) $\phi_p = 0.25$ and (d) $\phi_p = 0.28$

To further disclose the differences induced by symmetric and asymmetric dimer particles on the deformation of micelles, we compare morphologies of the micelle with the same number of symmetric and asymmetric particles. Figures 5(a)–5(c) are different morphologies with the addition of symmetric particles, while 5(d)–5(f) are asymmetric cases. The number of dimer particles are the same in Figs. 5(a)/5(d), as well as in Figs. 5(b)/5(e) and Figs. 5(c)/5(f). We also give the volume fraction of the dimer particles for the above cases. Comparing each case with the same number of particles, we find that morphologies of the micelle are different

under the influence of different dimer particles. Because of the symmetric character of particles, the arrangement of the particles at the interface of the micelle prefers to flat and thus emerge a flat ellipse of the micelle. However, for the asymmetric dimer particles, there is no flat ellipse but dumbbell and long dumbbell. The reason is that the asymmetric dimer particles have spontaneous curvature and feel uncomfortable be absorbed on the flat ellipse. Therefore, the asymmetric dimer particles will make the shape of micelle become dumbbell. For the asymmetric dimer particle, the hydrophilic part is bigger than the hydrophobic, so it will pull the dumbbell into long dumbbell when the concentration of the particles is further increased. Moreover, to make the copolymer micelle become deformed, it needs less number of asymmetric particles due to the large steric repulsions of the asymmetric particle. This is also the reason why the asymmetric dimer particles can more easily make the copolymer micelle fission into two micelles than the symmetric dimer particles.

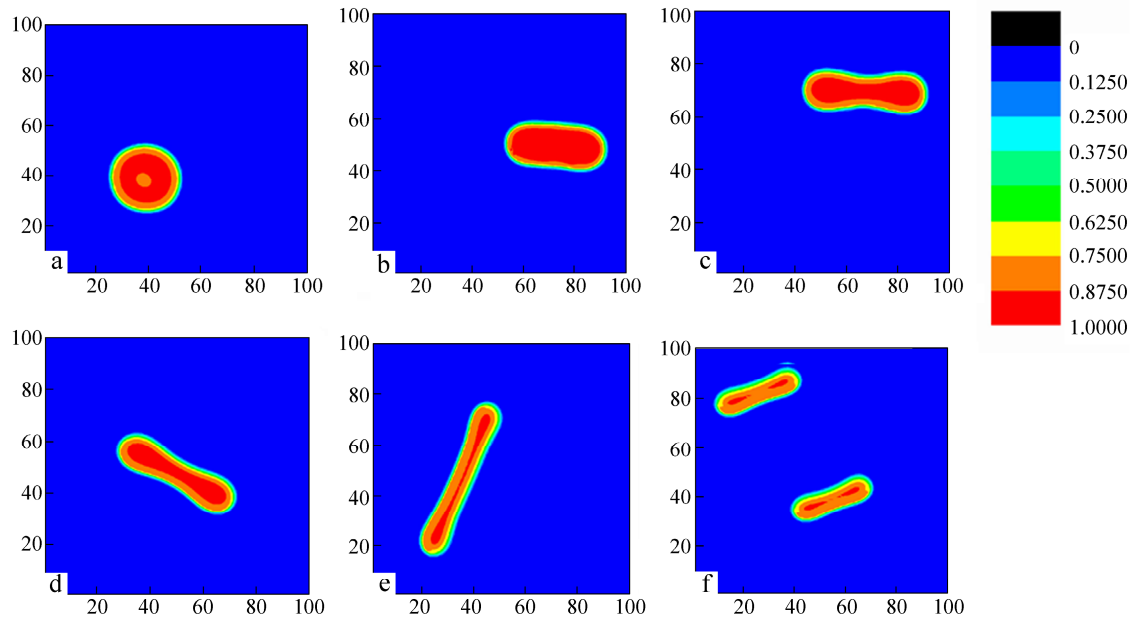


Fig. 5 The spherical or nonspherical morphologies of copolymer micelles at the same number concentration for the symmetric dimer particles (the first row) and asymmetric dimer particles (the second row): (a)/(d) = 48, (b)/(e) = 64, (c)/(f) = 72

The volume fractions of the dimer particles at the same number concentration between the symmetric and asymmetric dimer particles are different: (a) $\phi_p = 0.12$, (b) $\phi_p = 0.16$, (c) $\phi_p = 0.18$, (d) $\phi_p = 0.20$, (e) $\phi_p = 0.26$, (f) $\phi_p = 0.29$

In Fig. 6 we give the interfacial energy of the micelle (ΔU) and the steric interaction energy (F_{st}) varying with the number of particles for the symmetric and asymmetric cases. It can be seen that both of them increase when the number of particles increases. Comparing the symmetric and asymmetric cases, we find that the increased interfacial energy caused by asymmetric particles is smaller than that of symmetric particles at the same number of particles. We also find the steric repulsions induced by asymmetric particles are larger. This is because the gathering of asymmetric particles with the bigger volume decreases the concentration of copolymer micelle's segments on the interface. Therefore, the changes of interfacial energy in the case of asymmetric particle are not so large as in the case of symmetric particle. Under the influence of the higher interfacial energy, micelles with the addition of symmetric particles prefer to keep small interface, while the shape of micelles with the asymmetric particles tends to be dumbbell due to the extra curvature. Furthermore, for the same number of particles, the steric interactions of asymmetric dimer particles are stronger than those of the symmetric particles, which leads to the distinct deformation in the case of asymmetric particle. Here we verify that size and geometry are two important factors for surfactants, which directly affect the deformation of the micelle. That is to say, we can control the shape of the micelle by choosing amphiphilic particles with proper size and geometry.

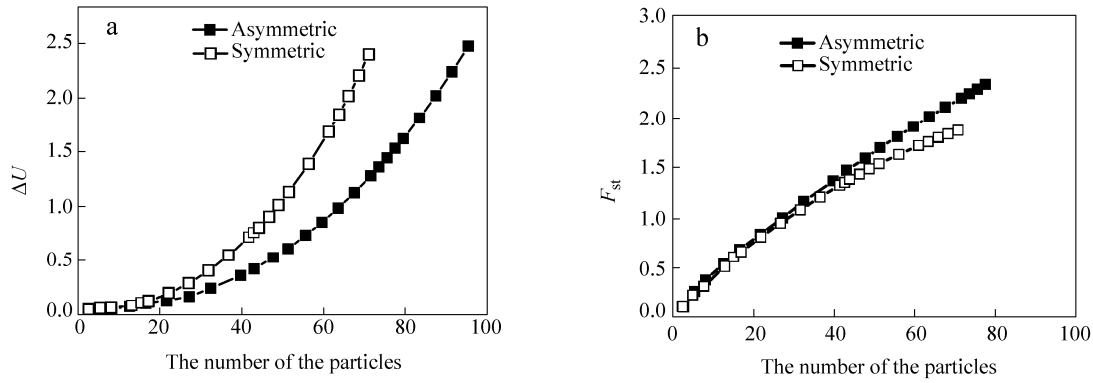


Fig. 6 The interfacial energy ΔU (a) and the steric energy F_{st} (b) verses the number concentration of the dimer particles

For the interfacial energy, ΔU means the interaction energy of the system between the real system and the reference system, which we regard the system without particles as the zero energy reference system ($\Delta U = U_{\text{real}} - U_{\text{reference}}$).

Figure 7 shows the influence of the asymmetric dimer particles with a large hydrophobic part and a small hydrophilic part, $d_a = 6a$ and $d_b = 4a$. With increasing concentration of the dimer particles, the micelle splits into two at $\phi_p = 0.07$ and becomes three micelles at $\phi_p = 0.10$. Comparing Fig. 7 with Fig. 3 and Fig. 4, we find the micelle can split into multi micelles very easily with the presence of asymmetric particles having large hydrophobic part. The reason can be attributed to the large hydrophobic part of the dimer particle which tends to act as a nucleus for the self assembly of copolymers.

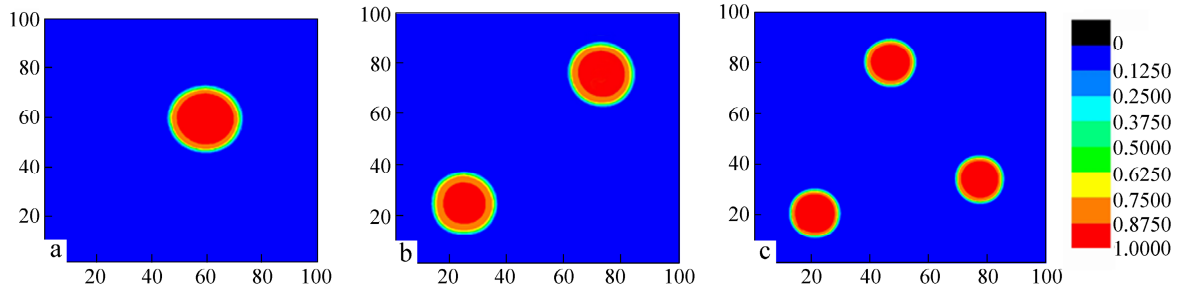


Fig. 7 The spherical morphologies of copolymer micelle for system with different concentrations of the asymmetric dimer particles ($d_a = 6a$, $d_b = 4a$): (a) $\phi_p = 0.04$, (b) $\phi_p = 0.07$, (c) $\phi_p = 0.10$

CONCLUSIONS

In a summary, we have carried out the study of the shape deformation and fission of the copolymer micelle induced by the addition of amphiphilic dimer particles. The influence of different particles on the deformation of copolymer micelles is different. The spherical or nonspherical morphologies of micelles are obtained by adding different amphiphilic dimer particles. We conclude that the interfacial energy of the micelle and the steric repulsion are two important factors determining the deformation/fission of the micelle, which relates to the size and geometry of the particle. Our work verifies that it is an effective way to control the morphology of micelles by using different surfactants. It helps us to understand the possible deformation of cells, micelles and liquid droplets under the influence of surfactants observed in experiments. Actually, there are many other phenomena observed in experiments induced by the surfactants, such as the formation of domain structures in cell membranes. Those systems usually include the subtle interplay between different molecules. In our future work, we plan to do more theoretical modelings to explore the mechanism of these complex systems.

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