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Self-Assembly of Two-Dimensional Patchy Colloidal Dumbbells

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We study the self-assembly of two-dimensional patchy colloidal dumbbells, which are composed of attractive and repulsive circles. The shape of a colloidal dumbbell is characterized by the ratio of the diameters of the two circles forming it, q , and the dimensionless distance between the centers of mass of the two circles, l . We carry out Monte Carlo simulations and show that various self-assembled structures, micelles, elongated micelles, straight string, a meshlike structure, and large clusters with voids, are formed by changing the combination of q and l . q represents the steric effect of the repulsive part of colloidal dumbbells. l represents the anisotropy of the particle shape and increasing the periphery of attractive part. From our simulations, we find that the shapes of self-assembled structures are more sensitive to q than to l .

1. Introduction

Recently, colloidal particles with site-specific directional interactions have been formed by the development of synthesis methods for patchy particles.^{1–10)} Patchy particles are promising materials for forming self-assemblies with complex structures, for example the kagome structure can be formed by particles with two patches.⁴⁾ In theoretical studies and simulations,^{11–21)} the self-assembled structures formed by patchy spherical particles have been well studied. Patchy particles are characterized by the attractive area, attractive length, patch position, patch number, and patch shape. In the case of one-patch particles with a low particle density,^{12,13,16,19,20)} micelles, tubes, and disks are formed by controlling both the attractive area and attractive length. When the particle density is high and the patchy particle is a Janus particle,²¹⁾ in which its hemisphere is the attractive area, the face-centered-cubic (fcc) structure, hexagonal-close-packed (hcp) structure, which have various orientational orders of the patch direction,

and wrinkled bilayer sheets are formed for a short attractive length. The variety of stable crystal structures increases when the attractive length increases¹⁸⁾ and the ratio of attractive area is changed.^{16,19)}

In experiments,^{1,3,6,9,10)} not only spherical patchy particles but also nonspherical patchy particles have been synthesized. In a computational simulation,²²⁾ Avvisati and co-workers studied the self-assembly of patchy colloidal dumbbells comprising of an attractive sphere and a repulsive sphere. They carried out Monte Carlo simulations and showed that micelles, elongated micelles, vesicles, bilayers, liquid droplets, and polyhedra are formed by changing the form of the patchy colloidal dumbbell. In their study,²²⁾ the volume fractions of colloidal dumbbells were set to be low. The authors only studied the change in the shape of small clusters. The effects of the ratio of the diameters of the two spherical parts on self-assembled structures have not been studied in detail.

In this paper, we study the effects of the shape of patchy colloidal dumbbells on self-assembled structures by carrying out Monte Carlo simulations. In Ref. 22, the volume fraction was so small that the authors studied only small self-assembled clusters. In our paper, we use a sufficiently high particle density to form self-assembled structures whose size is comparable to the system size. We should carry out the simulations in a three-dimensional system with a high particle density or by controlling the pressure. In previous simulations of spherical patchy colloids, however, various structures were predicted to be formed by controlling the patch size¹⁹⁾ and interaction length.²¹⁾ Thus, we consider that various structures will probably be formed in a three-dimensional system in the case of patchy colloidal dumbbells. To determine the effects of the dumbbell-like shape, we carry out two-dimensional simulations as a first step. Thus, a patchy colloidal dumbbell is expressed as composite of an attractive circle and repulsive circle. We study the effects of both the dimensionless distance between the centers of the two circles, l , and the ratio of the diameters of the two circular parts, q . Here, we study how self-assembled structures change with l and q . In Sect. 2, we introduce our model, where we use the attractive potential based on the Kern–Frenkel potential.²³⁾ In Sect. 3, we show our results. First, we show typical snapshots of self-assembled structures. Then, we show how the self-assembled structures depend on q and l . In Sect. 4, we summarize our results and give a brief discussion.

2. Model and Method

In our simulation, patchy colloidal dumbbells are composed of attractive and repulsive circles as shown in Fig. 1. Their diameters are σ_a and σ_r , respectively. As the

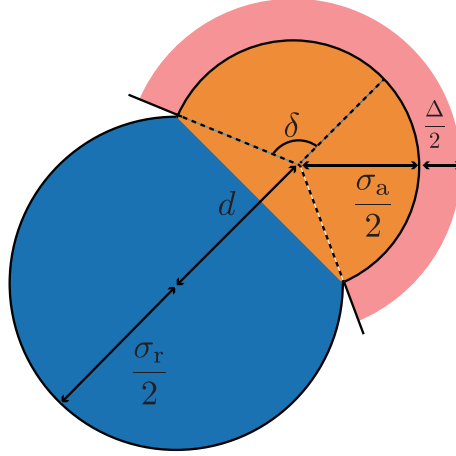


Fig. 1. (color online) Shape of patchy colloidal dumbbell composed of two circles. The diameters of the attractive and repulsive circles are σ_a and σ_r , respectively. The attractive length for each particle is $\Delta/2$.

interaction potential between two patchy colloidal dumbbells, we use a modified Kern–Frenkel potential, in which the noncircular shape of patchy colloidal dumbbells is taken into account.^{22,23)} The interaction potential between the i th and j th particles, U_{ij} , is given by

$$U_{ij} = U^{\text{SW}}(r_{ij}^{\text{aa}})f(\hat{r}_{ij}^{\text{aa}}, \hat{n}_i, \hat{n}_j) + U^{\text{rep}}, \quad (1)$$

where the first and second terms represent attractive and repulsive parts, respectively. In the first term in Eq. (1), r_{ij}^{aa} represents the distance between the centers of the attractive circles of the i th and j th dumbbells. $\hat{r}_{ij}^{\text{aa}}$ is the unit vector from the center of the i th dumbbell to that of the j th dumbbell. $\hat{n}_i$ is the unit vector from the center of the repulsive circle to that of the attractive circle in the i th dumbbell. $U^{\text{SW}}(r_{ij}^{\text{aa}})$ is the square-well potential defined as

$$U^{\text{SW}}(r_{ij}^{\text{aa}}) = \begin{cases} \epsilon & \text{for } \sigma_a \leq r_{ij}^{\text{aa}} \leq \sigma_a + \Delta, \\ 0 & \text{for } \sigma_a + \Delta \leq r_{ij}^{\text{aa}} \end{cases}, \quad (2)$$

where $\epsilon < 0$ and Δ is constant. $f(\hat{r}_{ij}^{aa}, \hat{n}_i, \hat{n}_j)$ is expressed as

$$f(\hat{r}_{ij}^{aa}, \hat{n}_i, \hat{n}_j) = \begin{cases} 1 & \text{for } \hat{n}_i \cdot \hat{r}_{ij}^{aa} \geq \cos \delta \text{ and } \hat{n}_j \cdot \hat{r}_{ji}^{aa} \geq \cos \delta \\ 0 & \text{otherwise} \end{cases}, \quad (3)$$

where 2δ is the angle formed by the center of the attractive circle and the two intersection points between the attractive circle and repulsive circle. Thus, $\cos \delta$ is given by

$$\cos \delta = \frac{1}{4\sigma_r d} (\sigma_r^2 - \sigma_a^2 - 4d^2), \quad (4)$$

where d is the distance between the centers of the attractive and repulsive circles in a dumbbell. The repulsive part in Eq. (1), U^{rep} , is a hard-core-type repulsive potential, which prevents the overlap of the two colloidal dumbbells. The form of the patchy colloidal dumbbell is characterized by two parameters, l and q , which are defined as $q = \sigma_r/\sigma_a$ and $l = 2d/(\sigma_r + \sigma_a)$. They represent the ratio of the diameter of the repulsive circle to that of the attractive circle and the dimensionless distance between the centers of the two circles, respectively. We carry out simulations with various values of l and q , and study the change in the self-assembled structures formed by the patchy colloidal dumbbells.

3. Results of Simulations

We carry out Monte Carlo simulations in an NVT system. We consider a square system whose size is given by $L \times L$ and use the periodic boundary condition. The number of patchy colloidal dumbbells, N , is 512, and the area fraction ϕ is set to 0.5. The volume density is small in Ref. 22: thus, the so that self-assembled structures that formed in the simulations were much smaller than the system size. In our simulation, the area fraction is large: thus, the formation of structures whose size is comparable to the system size is possible. Since the area of a patchy colloidal dumbbell changes with l and q , L is tuned to satisfy $\phi = 0.5$. The length and depth of the attractive potential, Δ and $\epsilon/k_B T$, are set to $0.5\sigma_a$ and 8, respectively, where k_B is the Boltzmann constant and T is temperature. Initially, the patchy colloidal dumbbells are located randomly. We choose one dumbbell and perform a translational trial. After the trial, we carry out a rotational trial on the dumbbell. The maxima of the translational distance and rotational angle during a trial are tuned, so that the acceptance ratios of the trials is about 0.4. When the interaction energy is saturated after repeating many trials, we

regard the system as the equilibrated system.

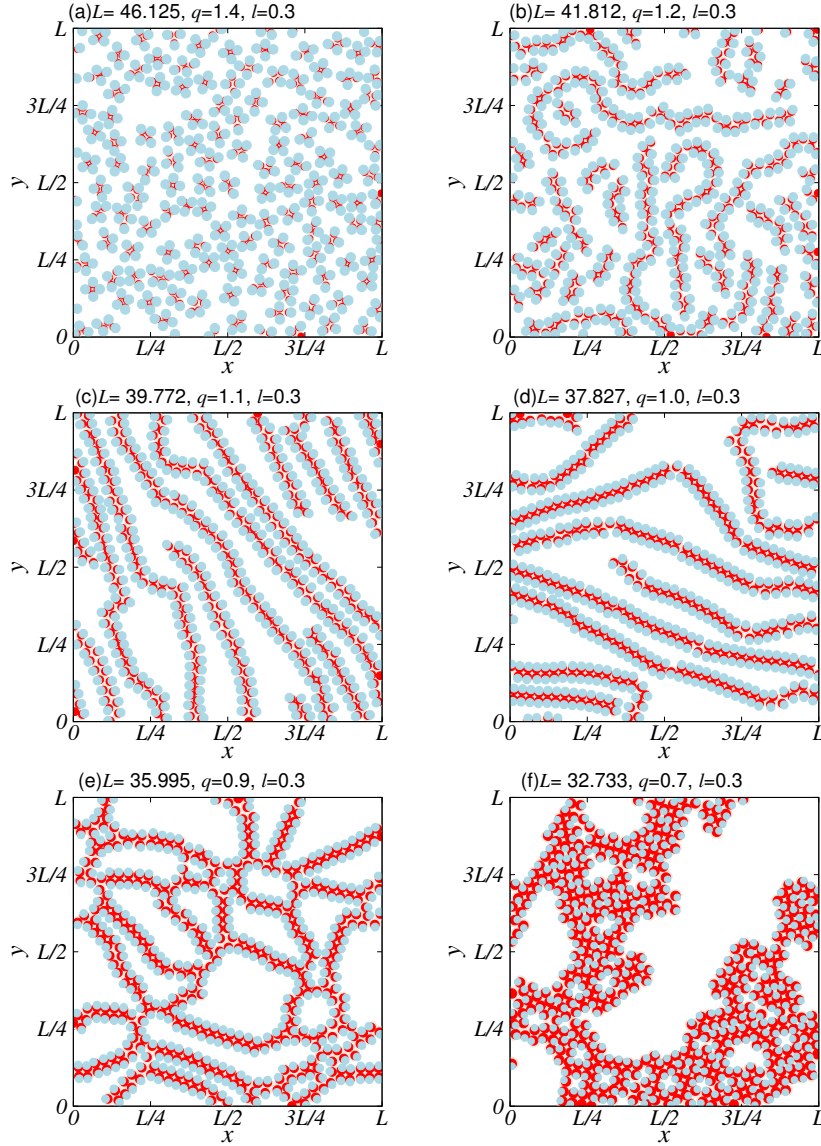


Fig. 2. (color online) Snapshots formed by patchy colloidal dumbbells. Blue and red areas represent repulsive and attractive parts, respectively. $\sigma_a = 1$ and $l = 0.3$. In each figure, L and q are (a) 46.125 and 1.4, (b) 41.812 and 1.2, (c) 39.772 and 1.1, (d) 37.827 and 1.0, (e) 35.995 and 0.9, and (f) 32.733 and 0.7, respectively.

We show typical snapshots in Fig. 2, in which l is set to 0.3. Since the distance between the centers of the two circles in a colloidal dumbbell is not so large, the form of the colloidal dumbbell is close to that of a one-patch circle. Figure 2(a) shows a snapshot in the case of $q = 1.4$. Since σ_r is larger than σ_a , the ratio of the attractive periphery to the non-interaction periphery is small. In this case, the patchy colloidal

dumbbells form small micelles, which consist of four dumbbells. Figure 2(b) shows a snapshot in the case of $q = 1.2$. The difference between σ_r and σ_a is smaller than that in Fig. 2(a). Owing to the increase in the attractive area, the form of the self-assemblies is changed from isotropic micelles to curved long ones. When $q = 1.1$ [Figs. 2(c) and 2(d)], strong attraction prevents the curved long micelles from being torn off, and the elongated micelles are changed to long straight strings, which are formed by double rows of patchy dumbbells. The attractive periphery of the colloidal dumbbells is inside the strings. The elongated micelles are curved smoothly in Fig. 2(b), but the straight strings bend abruptly in Figs. 2(c) and 2(d). When $q < 1$, the attractive area is larger than the repulsive area. The attractive periphery protrudes from bent parts of the strings. In Fig. 2(e), the subdivision of straight strings occurs at the bent parts, and a meshlike structure consisting of double rows of patchy dumbbells is formed. When $q = 0.7$ [Fig. 2(f)], most of the periphery of a colloidal dumbbell is attractive. Thus, the colloidal dumbbells aggregate and form large clusters with voids.

To study the dependence of the self-assembled structures on q and l in more detail, we calculate the average number of colloidal dumbbells in a self-assembled structure, N_c , and introduce order parameters, B_c and B_n .²²⁾ The order parameters are defined as follows:

$$N_c = \frac{1}{N} \sum_m N_m, \quad (5)$$

$$B_c = \sum_m \frac{2}{N_m(N_m - 1)} \sum_{(i,j)_m} (\hat{n}_i \cdot \hat{n}_j)^2, \quad (6)$$

$$B_n = \sum_i \frac{1}{N_i} \sum_j (\hat{n}_i \cdot \hat{n}_j)^2, \quad (7)$$

where N , N_m , and N_i are the number of self-assembled clusters, the number of colloidal dumbbells in the m th self-assembled cluster, and the number of attractive dumbbells neighboring the i th particle, respectively. In Eq. (6), $\sum_{(i,j)_m}$ means the summation over all the pairs of attracting dumbbells in the m th self-assembled cluster, and $\sum_j$ in Eq. (7) represents the summation over all the attractive neighbors of the i th dumbbell. B_c represents the average order of the dumbbell direction in a self-assembled cluster and B_n represents the local order of the dumbbell direction. In our estimation, B_c and B_n are averaged 1000 times every 1000 Monte Carlo steps in a run after equilibration.

Figure 3 shows the dependence of B_c and B_n on q at $l = 0.3$. Both B_c and B_n are small at large q , where the small micelles are formed. When the elongated micelles are

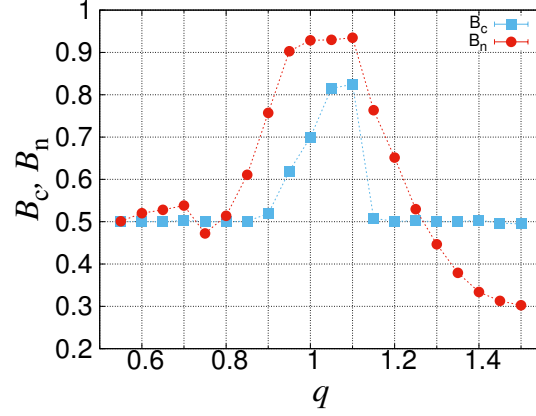


Fig. 3. (color online) Dependence of B_c and B_n on q at $l = 0.3$.

Table I. Criteria for distinguishing the types of structures. To calculate B_c , N_c , and N_n , data are averaged 1000 times every 1000 Monte Carlo steps in a run after equilibration.

type of structure	B_c	B_n	N_c
small micelles	< 0.6	< 0.6	< 100
long micelles	< 0.6	> 0.6	< 100
straight strings	> 0.6	> 0.6	> 400
meshlike structure	< 0.6	> 0.6	> 400
clusters with voids	< 0.6	< 0.6	> 400

formed, B_n becomes larger than that for the small micelles. However, since the elongated micelles are curved, as shown in Fig. 2(b), B_c is as large as that for the small micelles. Both order parameters, B_n and B_c , are large when long straight strings composed of two rows of colloidal dumbbells are formed. In the meshlike structure, the direction of colloidal dumbbells is ordered locally but different by places. Thus, B_n is large but B_c becomes small in the case of the meshlike structure. When large clusters with voids are formed, both B_c and B_n are small. Thus, to distinguish the self-assembled structures, we use the criteria listed in Table I, in which we also give the criterion on N_c . If it is difficult to classify a self-assembled structure by the criteria, we observe a snapshot and visually distinguish the type of structure.

Figure 4 shows the dependence of the self-assembled structure on q and l . With increasing q , the clusters with voids sequentially changes to the meshlike structure, the straight strings, the elongated micelles, and the micelles. The value of l has a strong effect on the self-assembled structure in two regions. One region is the parameter region

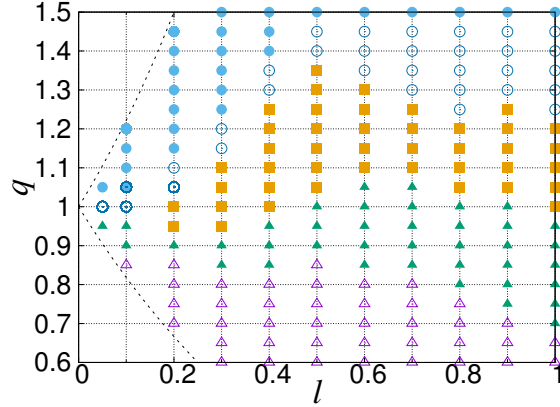


Fig. 4. (color online) Dependence of self-assembled structure on q and l . Filled circles, open circles, filled squares, filled triangles, and open triangles represent the formation of small micelles, elongated micelles, straight strings, meshlike structure, and clusters with voids, respectively. Patchy colloidal dumbbells are not formed for the parameters to the left of the dashed lines are not formed.

with small l and large q . The straight strings are formed easily with increasing l when $l < 0.5$ and $q > 1$. The other is the parameter region with large l and small q . The formation of clusters with voids becomes difficult with increasing l when $l > 0.5$ and $q < 1$. Thus, the effect of l on the self-assembled structure seems to be more complicated than that of q .

4. Summary

In this paper, we carried out Monte Carlo simulations and studied the dependence of self-assembled structures on the shape of patchy colloidal dumbbells composed of attractive and repulsive circles in a two-dimensional system. Self-assembled structures in a three-dimensional system have already been studied in Ref. 22, in which a small volume fraction was used and only the change in the form of small clusters was focused on. In our study, we carried out simulations with a high area volume. Not only small clusters but also the self-assembled structures as large as the system size were formed in the simulations.

The dumbbell shape is characterized by two parameters: the ratio of the diameter of the repulsive circle to that of the attractive circle, q , and the dimensionless distance between the two circles, l . When q is small, the periphery of repulsive part is smaller than that of attractive part. In this case, the steric effect of the repulsive part is small. Thus, the colloidal dumbbells aggregate and form clusters with voids. With increasing q , the steric effect increases and the colloidal dumbbells cannot form clusters with voids.

The self-assembled structure changes into a meshlike structure formed by two rows of colloidal dumbbells because the steric effect caused by the repulsive circle is too small to prevent for the colloidal dumbbell rows from bending. When q increases further, the bending of colloidal dumbbell rows is suppressed and straight strings are formed. Then, with the increasing steric effect, the strings are torn off and elongated micelles are formed. Finally, the elongated micelles are changed to micelles with increasing q . This tendency is almost independent of the value of l .

On the other hand, increasing in l has two effects: the attractive periphery increases and anisotropy of the particle shape increases. These effects are large in the upper-left region and lower-right region in Fig. 4. When $q > 1$ and $l < 0.5$, the steric effect caused by the anisotropy of the colloidal dumbbells is small. Since the colloidal dumbbells are regarded as patchy circles, the main effect of increasing l is to increase the attractive area. Thus, the straight strings are formed easily by large q with increasing l for large q . When $q < 1$ and $l > 0.5$, the increase in the anisotropy of the particle shape is more dominant than the increase in the attractive periphery. In this parameter region, the steric effect caused by the repulsive circle becomes significant: thus, the formation of clusters with voids becomes difficult with increasing l .

Because the volume fraction was small in Ref. 22, a three-dimensional self-assembled structure corresponding to the meshlike structure was not observed. If we carry out a three-dimensional simulation with a high volume fraction, a self-assembled structure corresponding to the meshlike structure may be formed. Liquid droplets and faceted polyhedra were observed in Ref 22, although their internal structure was not studied in detail. If voids were present in their interior, these structures would probably correspond to the three-dimensional version of the cluster with voids.

In the case of spherical patchy colloids, the two-dimensional structures have been studied. In Refs. 24 and 25, the dependence of the ordering of the patch direction on the patch size²⁴⁾ and the formation of a kagome lattice²⁵⁾ were studied for two-patch particles. In the case of patchy colloidal dumbbells, the two-dimensional self-assembled structures have not been studied experimentally, but experiments similar to those for spherical patchy colloids^{24,25)} are probably possible.

In our simulation, we set Δ to $0.5\sigma_r$. In Ref. 21, Preisler et al. showed that the phase diagram is markedly changes with Δ for Janus particles. By controlling Δ , new structures that did not appear in our simulations may be formed. We intend to study the effect of Δ on self-assembled structures.

Acknowledgments

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