Two-dimensional clusters of colloidal tetramers via droplet emulsion templating

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Abstract. In this report, using a kinetic Monte Carlo simulation method we considered a hierarchical assembly of planar square tetramers, constrained in a plane, via droplet evaporation. We found that colloidal tetramers undergo a structural transition from initial square-shape tetramers to diamond-like tetramers. A variety range of novel cluster configurations belongs to a particular class of geometrical shape, that has not been previously reported to the clusters of single colloids. Considering potential applications of colloidal clusters in electronics, photonic materials, our result could provide an effective way to control the formation of complex colloidal cluster structures.

1. Introduction
Recent advances in the physical, chemical technique enable a new generation of colloids with a huge number of shape-anisotropic particles, including rods, plates, chains, dumbbells, cubes, octahedra, tetrahedral or particles with anisotropic interactions, e.g. patchy colloids [1]. This raises the questions of which complex structures can be formed from such colloids via self-assembly process.

In 2003, Manahoran et al [2] reported an intriguing strategy for preparing clusters of small colloids into well-defined structures. Starting from polystyrene spheres (PS) confined in a oil-water interface, the oil droplet was subsequently evaporated so that the PS were packed together by a strong attraction. Interestingly, the final configurations of clusters containing a number \( N \) of constituent spheres were unique, which is independent on the nature of colloidal materials or colloidal sizes. Lauga and Brenner [3] later have shown that the unique configuration of each \( n_c \)-sphere cluster can be correctly predicted by minimization of the total surface energy of the droplet-colloid interface. These configurations with \( (n_c) \) exactly reproduce those observed from the spherical packing problem that minimizes the second moment of the mass distribution (namely \( M_2\)-cluster) [4]. In addition to \( M_2\)-clusters, there are several categories of sphere packing structures that can be obtained by optimization theories, including Lennard-Jones clusters [5], Coulomb clusters [6], spherical codes [7], and hard-sphere packing with a short-range interaction [8]. Remarkably, all of these packings have exactly the same structures for the number of constituent particles up to six, but differ at most values \( n_c < 6 \).

However, until now, the reports concerning with the topics have mainly focused on the self-assembly of spherical-shape colloids with isotropic interactions. As a result, the obtained structure types are significantly restricted to simple motifs. Several recent works attempted to
extend to anisotropic-shape colloids in two (2D) [9, 10] and/or three dimensions (3D) [11, 12, 13], such as dumbbells, triplets, tetrahedra, octahedra, suggesting that a higher complexity of cluster structures was predictable. In a prior work, we considered the configuration of 2D clusters of single colloids constraint to the interface of liquid droplets in the plane and found that 2D clusters have degenerate configurations that seem to be similar to those of polyiamonds, i.e a mathematical category of plane geometries formed by joining congruent equilateral triangles edge to edge [9]. In the current, we restrict ourselves to the small cluster of square planar as building blocks to study hierarchical assembly. Our aim is to predict the formation as well as possible configurations of high-order clusters via droplet template.

2. Model and method

The simulated system is composed of $N_c$ colloids of diameter $\sigma_c$ and $N_d$ droplets of diameter $\sigma_d$. The pair interactions between the particles are given as follows.

2.1. Droplet-droplet pair interaction

The droplet–droplet interaction, $\phi_{dd}$, is simply taken as a hard-sphere repulsion, given by

$$\phi_{dd}(r) = \begin{cases} \infty & r < \sigma_{\text{eff}} \\ 0 & \text{otherwise} \end{cases}$$

where $r$ is the center-to-center distance, $\sigma_{\text{eff}}$ is the effective diameter, defined by $\sigma_{\text{eff}} = \sigma_c + \sigma_d$ in such a way that any colloid cannot be shared by two droplets.

2.2. Colloid-colloid pair interaction

Similar to our previous work [9], the colloid-colloid interaction $\phi_{cc}$ is a combination of a short-ranged attraction, together with a long ranged repulsion to model the Yukawa potential that is a typical interaction between electrostatic particles dispersed in the liquid [14].

$$\phi_{cc}(r) = \begin{cases} \infty & r < \sigma_c \\ -\epsilon_{\text{SW}} & \sigma_c < r < \lambda \sigma_c \\ \epsilon_{\text{Y}} \exp[-\kappa(r - \sigma_c)]/r & \text{otherwise} \end{cases}$$

with $\epsilon_{\text{SW}}$, $\Delta$ being the depth and width of the square-well potential, respectively; $\lambda = 1 + \Delta/\sigma_c$. To make an irreversible bond, the separation between the two colloids must be smaller than $\lambda \sigma_c$. The parameter $\epsilon_{\text{Y}}$ in Eq. (2) indicates the intensity of the Yukawa repulsive potential and the inverse shielding length $\kappa$ characterize the Yukawa interaction range.

2.3. Colloid-droplet pair interaction

Consider the Pickering emulsion stabilized by the colloids which are adsorbed onto the oil-water interface [15]. The adsorption energy $\Delta E$ is given by

$$\Delta E = \pi \rho_p^2 \gamma_{\text{OW}} (1 - |\cos \theta_{\text{OW}}|)^2,$$

where $\rho_p$ is the particle radius, $\gamma_{\text{OW}}$ is the interfacial tension, and $\theta_{\text{OW}}$ is the contact angle.

To mimic the Pickering emulsion, as shown in Eq. (3), we employed a simple colloid-droplet ($\phi_{cd}$) model as follows [9]. For $\sigma_d > \sigma_c$, as

$$\phi_{cd}(r) = \begin{cases} -\mu l & \frac{\sigma_d - \sigma_c}{2} < r < \frac{\sigma_d + \sigma_c}{2} \\ 0 & \text{otherwise} \end{cases}$$


and $\sigma_d < \sigma_c$,

$$
\phi_{cd}(r) = \begin{cases} 
-\mu \frac{\sigma_d}{2} & r < \sigma_c - \sigma_d \\
-\mu l \frac{\sigma_c - \sigma_d}{2} & \sigma_c - \sigma_d < r < \sigma_c + \sigma_d \\
0 & \text{otherwise}
\end{cases}
$$

(5)

where $\mu$ is the line tension and $l$ is the length of the contact line, determined by

$$
l = \frac{\sigma_d}{2} \cos^{-1}\left[\frac{1}{\sigma_{qr}} \left(\frac{\sigma_d^2}{4} - \frac{\sigma_c^2}{4} + r^2\right)\right].
$$

(6)

2.4. Simulation method

A series of colloidal tetramer-droplet mixtures was simulated by kinetic Monte Carlo method in the canonical ensemble (NVT). To start the simulation, we assigned starting configurations of a liquid to all particles. The maximum displacement of colloids and droplets were set to be $0.01\sigma_c$ and $0.01\sigma_c \sqrt{\sigma_c/\sigma_d}$ to mimic the realistic Brownian dynamics [16]. During the simulation, the droplet diameter was slowly reduced to zero after $5 \times 10^6$ MC steps, leaving another $5 \times 10^6$ MC steps for equilibration. As two any tetraters came close to each other, they can make a bond, and therefore formed a cluster. The collective motion of tetraters and/or clusters were taken account through the use of translational and rotational moves suggested by Frenkel and Smit [17]. Specifically, a rotation of clusters was performed by rotating around a random axis with a maximum angle $\theta_{\text{cls}} = 0.01\sigma_c/\sigma_{\text{cls}}$, whereas a maximum displacement of clusters was $d_{\text{cls}} = 0.01\sigma_c / \sqrt{n_c}$, where $n_c$ is number of constituent particles belong to the cluster and $\sigma_{\text{cls}}$ is the effective diameter of the cluster taken to be $\sigma_{\text{cls}} = \sqrt{n_c \sigma_c}$.

All simulations were carried out in a square with periodic boundary condition along the two directions with the total number of particles of 512. A set of simulated parameters was given as follows: the packing fraction of tetraters $\eta_c = 0.1$; the packing fraction droplet $\eta_d = 0.15$; the parameters of the attractive interaction $\Delta = 0.1\sigma_c$, $\epsilon_{SW} = 15k_B T$; the parameters of repulsive interaction $\kappa = 10\sigma_c^{-1}$, $\epsilon_Y = 25k_B T$; the line tension $\mu = 100k_B T/\sigma_c$. For each set of above parameters, we performed at least five simulation runs to improve the statistical accuracy.

3. Results and Discussion

3.1. Cluster formation

Figure 1 shows the snapshots of the binary mixture at different stages during the simulation process. Each tetrater contains four colloidal particles (purple) arranged in a square planar, while the pink spheres represent the droplets. The initial position of all particles (Fig. 1(a)) was randomly distributed in the liquid phase in which no overlapping spheres and tetraters are allowed. In Fig. 1(b), during the subsequent shrinkage of the droplets, some tetraters, displayed by the green spheres, have been adsorbed onto the droplet surface. These tetraters once trapped at the surface were stabilized due to the Pickering emulsion (see Eq. (3)), as shown in Fig. 1(c). In the early half stage of the simulation (Fig. 1(d)-(e)), all the droplets become vanishing. At this time, few tetraters assembled to form hierarchical clusters that maintain stable configurations until the final stage of the simulation (Fig. 1(f)). It can be seen that all single tetraters adsorbed at the droplet surface occur a structural transition from an initial square planar shape to a diamond-like shape. In addition, a variety of clusters with higher complexity also appears. Detailed structures of such complicated clusters will be analyzed later.

3.2. Pair correlation functions

Further information on the dynamics of cluster formation can be quantitatively analyzed by the pair correlation functions. For a two-component system, we consider the pair correlation
functions as follows [18].

\[ g_{cc}(r, r') = \frac{\rho_{cc}^{(2)}(r, r')}{\rho_c^{(1)}(r)\rho_c^{(1)}(r')} , \]  

(7)

\[ g_{dd}(r, r') = \frac{\rho_{dd}^{(2)}(r, r')}{\rho_d^{(1)}(r)\rho_d^{(1)}(r')} , \]  

(8)

and

\[ g_{cd}(r, r') = \frac{\rho_{cd}^{(2)}(r, r')}{\rho_c^{(1)}(r)\rho_d^{(1)}(r')} , \]  

(9)

where \( \rho_c^{(1)} \), \( \rho_d^{(1)} \) are the one-particle density for the colloid and the droplet, respectively; \( \rho_{cc}^{(2)} \) is two-particle density of the colloid in the presence of the droplet, and \( \rho_{cd}^{(2)} \) is two-particle density between the colloid and the droplet.

Figure 2 shows three pair correlation functions for colloid-colloid, \( g_{cc}(r) \), colloid-droplet, \( g_{cd}(r) \), and droplet-droplet, \( g_{dd}(r) \), at different “time” of the simulation. As shown in Fig 2(a), all the \( g_{cc}(r) \) shows two pronounced peaks, which can be attributed to the nearest and second nearest neighbor separation between the colloids. The first peak is located at ca. \( 1.05\sigma_c \) due to the fact that attractive range \( \lambda \) is setting at \( 1 + \Delta/\sigma_c \) with \( \Delta = 0.1\sigma_c \) (see Eq. 2). The second peak with a lower probability is at \( 1.45\sigma_c \) corresponding to the length of the diagonal.
Figure 2. Pair interaction potential between colloid-colloid (a), colloid-droplet (b) and droplet-droplet (c). Shown in legend are time step as Fig. 1, \( t_6 \) is the final stage of the simulation.

of a square tetramer of edge 1.05\( \sigma_c \). Note that since the number of clusters formed is much smaller than the number of initial tetramers, there is no significant change of \( g_{cc} \) during the dynamics. In contrast, the colloid-droplet \( g_{cd} \) (Fig 2(b)) exhibits an apparent variation of both the peak position and peak strength as a function of time. We interpreted the increase of the peak strength in \( g_{cd} \) as a result of a larger number of colloids adsorbed to the droplet surface as the dynamic time increases, in agreement with the observation in Fig. 1. In addition, at a given time, \( g_{cd} \) shows two peaks: the one ascribed to the distance from the droplet center to the first colloid of tetramers, the other to the second colloid of tetramers. In Fig 2(c), the droplet-droplet correlation function \( g_{dd} \) displays random errors at the distance larger than \( 7\sigma_c \), which is initial separation between the droplets, indicating an extremely slow dynamics of droplets during the simulation.

3.3. Cluster configurations

In Fig. 3, we show the typical cluster configurations obtained in the final stage of the simulations. The number of tetramers in the cluster is represented by \( N \), while the total number of bonds in the cluster is represented by \( N_B \). To easily visualize the geometrical symmetry of each cluster, the colloid is colored accordingly based on its bond number to all the neighboring colloid. For example, the red colloid indicates its bond number to be 2, the cyan colloid indicates the bond number to be 3, etc. It can be seen that for \( N = 1 \) only one cluster structure is found, that is a diamond-like tetramer. This means that all square tetramers that are trapped at the droplet surface transform to diamond-like structure. Meanwhile, for each \( N > 1 \) the multiple configurations (multiple isomers) were observed. Specifically, at \( N = 2 \) two square tetramers
can be connected to each other in two ways by sharing one colloid or two colloids, making the cluster of 9 bonds and of 11 bonds, respectively. However, as discussed later, the probability of finding the 11-bond cluster is much higher than that of 9-bond cluster. Similarly, for \( N = 3 \) and \( N = 5 \), two isomers of clusters are obtained, but three isomers for \( N = 4 \) (see Fig. 3). Compared to a large number of possible isomers from an assemble of single colloids [9], the number of isomers from the tetramer assembly are significantly smaller. For instance, at the same number of constituent colloid, three isomers of tetramers for \( N = 4 \) were found, while the number of isomers of single colloids is 12 [9]. A large reduction in the possible isomers is directly related to the constraint of the colloid in the square tetramer and the confinement of tetramers onto the droplet surface as well. Apparently, the degree of freedom of the cluster containing \( n_c \) colloids is \( 3n_c \), while the degree of freedom of the cluster containing \( N \) tetramers (with \( N = 4n_c \)) is only \( 3n_c - 4 \).

Also note that most configurations of the clusters, as shown in Fig. 3, differs from those of the clusters of single colloids. The cluster configuration of single colloids all belongs to a particular class of the plane geometry, namely polyiamonds that is formed by joining the triangles. The bond number of the most tightly packing polyiamond is determined by a simple relationship, \( N_B = 3(n_c - 2) \). However, here the bond number of the cluster of tetramers is smaller, meaning the less packing structures.

### 3.4. Cluster size and bond distribution

Figure 4 shows the histograms of the cluster size distribution, i.e. the number of clusters as a function of cluster size (\( n_c \)) (upper panel) and the number of clusters as a function of bond
The height of each column in the histogram equals to the number of clusters with different isomers. The largest cluster size obtained in the simulation is 28, while the largest cluster bond is 51. For a given cluster size, each cluster possess at least three isomers where the isomers with the more tightly packing structures are favored. In addition, the cluster of $N = 3$ ($n_c = 12$) occupies the highest probability. Note that the cluster size distribution can be simply tuned by changing the colloid(droplet) packing fraction and/or the initial diameter of the droplets [16].

**Figure 4.** Cluster size distribution and bond distribution
4. Conclusions
In summary, using the Monte Carlo simulation method we have studied the two dimensional templated-assembly of tetramers, a colloidal “molecule” consisting of 4 colloids arranged in a square planar, into defined configurations. We found that the clusters have multiple (degenerate) isomers, in agreement with those obtained by a similar strategy but for single colloid [9]. However, differently from clusters of single colloids, clusters of tetramers have relatively smaller number of isomers due to a strong constraint of tetramers. In addition, among the isomers, the isomers with the more tightly packing configurations favors. Note that the current pair interaction model can be controlled via pH, concentrations of salt solution and particles, wettability of colloids [19]. Thus, our work could be helpful for fabrication complex colloidal “molecule” as building blocks of nanostructured materials.

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