Angewandte Chemie 125 Jahre

Self-Assembly

DOI: 10.1002/ange.201301520

# Colloidal Clusters by Using Emulsions and Dumbbell-Shaped Particles: Experiments and Simulations**

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In the last decade, there has been a significant increase in the complexity of colloidal building blocks, which were developed with self-assembly (SA) steps in mind.[1] An important reason for this increase in complexity is the realization that with more complex, anisotropic building blocks significantly more potential structures and symmetries can be realized, thus increasing the ability to realize and optimize materials properties.[1] Also, these particles are interesting model studies for answering questions which cannot be easily addressed with spheres. Emulsion droplets of a water phase in oil, the focus of this communication, or vice versa, are powerful platforms for the SA of colloidal particles.[2] Velev et al.[3a] pioneered shells of many particles ($\geqslant 10$) which could be generated using droplets, and are now generally called "colloidosomes".[3b] Manoharan et al.[4] investigated the limit of small numbers, $N$, of particles adsorbed onto droplets ($N < 15$) wherein the particles remained stable as the oil was slowly and completely evaporated. Surprisingly, this procedure, which has now been performed with quite a number of different particles, leads to regular clusters (for relatively small $N$ values) where all clusters of the same $N$ value have the same shape.[5] It was noted already by Manoharan et al.[4] that the structures of the packing of particles in the clusters seem to minimize the second moment (M2) of the mass distribution of each $N$-mer. The method of Manoharan et al. has been extended to binary systems,[6a] to more monodisperse emulsion droplets made by shear as reported by Zerrouki et al.,[6b] combined with the "over-swelling" method used in emulsion and dispersion polymerization to arrive at anisotropic particles,[6c] and to clusters of particles with a smaller size (< 200 nm) from smaller emulsion droplets as reported by the group of Wittemann.[5c–e]

Despite the strong interest and the general character of this method, there have not been many theoretical investigations into the mechanism or into the reasons behind the observation that the second moment of the mass distribution seems to be minimized. Lauga and Brenner[7] have shown that the resulting unique structure of each $N$-mer can be correctly predicted by minimization of the surface free energy of the complex oil-water interface during the drying process by considering individual droplets having different numbers of particles attached to the interface. Unfortunately, the calculations to minimize the ever changing surface between the particles are quite involved and thus slow, and are not so easily adapted to more complex starting particles.

The present communication has a double focus: By using dumbbell (DB)-shaped polymethylmethacrylate (PMMA) particles, which are both sterically stabilized and can be made in high purity and yield relatively easily,[8] we extended the method of Manoharan et al.[4] using the evaporation of emulsion droplets to generate particles having an anisotropic shape. Specifically, we are interested in finding out if regular and thus unique structures are still formed for each $N$-mer, and if so, whether their second moments are still minimized. Particles with DB shapes have the important property that, if arranged into clusters or strings,[9a] they can form enantiomeric structures or structures with a certain handedness similar to that of helices.[9b]

The second focus of this communication is on exploring a simple simulation procedure which correctly predicts the structures formed. The parameter space for possible structures, which can be made using the evaporation driven SA method, if it is performed by not starting with spheres but with colloids already having a more complex shape,[1] is huge and it would be quite efficient if optimized conditions could be found for desirable structures by using simulations. As mentioned already, a full calculation minimizing the surface area which drives the SA is not a simple and quick procedure, especially for clusters of particles with more complex shapes. We mimicked the SA process by a two-step simulation in which single droplets having $N$ particles, which interact through hard interactions only, are considered. In the first step the particles are confined to the surface of a spherical shrinking shell and after the long-time self-diffusion of the particles has stopped and the pressure increases sharply, the M2 of the particle mass distribution is minimized in a second step (see the Supporting Information).

As a test for our method, we first applied it to clusters of spherical particles,[10] with cluster sizes of $4 \leq N \leq 14$ (see SF-1a and ST-1 in the Supporting Information). As expected, the experimentally observed clusters for $N \leq 12$ match with the simulated particles after M2 minimization. For larger clusters ($N > 12$), no clear match between simulations and experiments can be found.

To judge if we can expect the presence of chirality with a certain cluster structure we applied the theory developed to

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[**] We thank J. de Graaf for fruitful discussions. B.P. was supported by the EU Nanodirect FP7-NMP-2007-SMALL-1, project 213948. F.S. was supported by an NWO-VICI grant.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201301520.

describe the symmetry of molecules to these colloidal clusters. Chiral molecules necessarily belong to point groups $C_1$, $C_n$, and $D_n$ (or, albeit rarely, to $T$, $O$, or $I$), that is, groups which have only proper symmetry axes. All other point groups, that is, those that have alternating (improper) axes ($S_n$), including reflection planes and inversion centers, planes of symmetry ($\sigma$) or a center of symmetry ($i$) are associated with achiral molecules.[11]

Our symmetric DBs are characterized by the following average parameters: radius of 0.71 μm, polydispersity of 2.2 % (see SF-1c in the Supporting Information). As mentioned in the methods section (see the Supporting Information) the clusters with different $N$ values were purified by density gradient centrifugation (see SF-3 and 4 in the Supporting Information). Close-ups of the clusters found for different $N$ values are shown in Figure 1 and compared with those found from computer simulations. According to the chirality considerations mentioned above, the clusters from the symmetric DBs lack chirality when $N=2$ (because of a symmetry plane $\sigma$), $N=4$ (a $\sigma$), $N=6$ (a $S_3$ alternative axis, or a $i$ for the one shown as inset in Figure 1), and $N=7$ (a σ; see Figure 1). In contrast, the trimer and pentamer are chiral colloidal clusters in which a $C_3$ axis and no symmetry elements, respectively, are present. We find good agreement between the experimentally observed clusters and the structures predicted using the simulation method where the particles are adsorbed to the interface, as is the case in our experiments. Of course, at the moment it is not yet possible to separate the stereoisomers from each other, but this applies to molecular chiral mixtures as well, and provides an interesting avenue for research. In particular, if these kinds of chiral clusters could be made from, for example, optically active materials, their handedness would also be of interest for photonic applications.

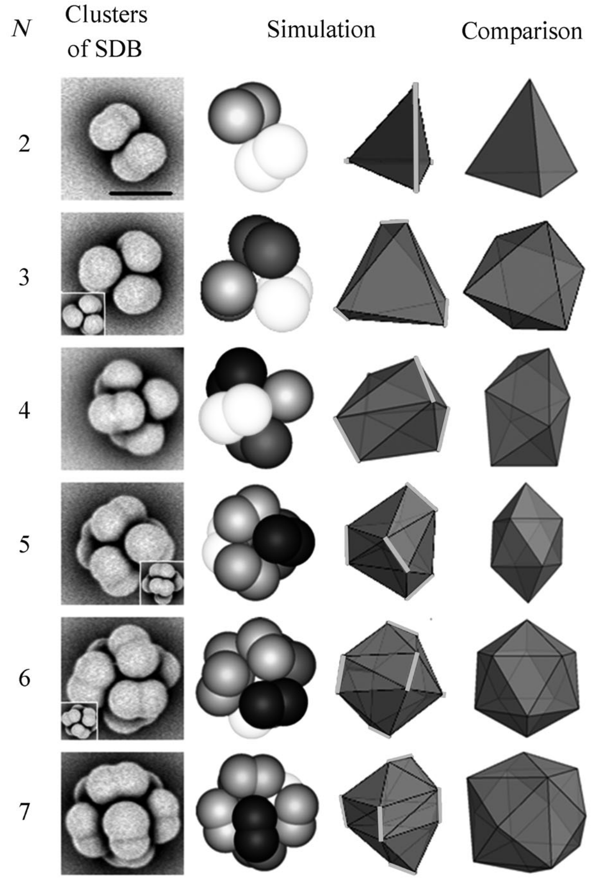

***Figure 1.*** Cluster configurations for the symmetric DB (SDB) particles. The first column denotes the cluster size $N$. The second column shows experimental SEM micrographs of clusters of size $N$. The insets show enantiomeric clusters ($N=3$ and 5) or isomeric clusters ($N=6$). The third and fourth columns show the corresponding simulations packing results and their schematic packing models (the bold grey lines stand for DBs and each bulb is connected with its neighbors by thin black lines), respectively. The fifth column shows the corresponding simulation structures of clusters of spheres of $2N$ when the DBs are regarded as two independent spheres. Scale bar: 2 μm.

It is interesting to see how closely the structures consisting of symmetric DBs resemble those made of twice as many spherical particles. In other words, which clusters having $N$ DBs correspond to clusters having $2N$ spheres? For small clusters ($N<5$), the clusters formed by the symmetric DBs are indeed the same as those formed by $2N$ spheres. Whereas the configurations partly coincide at $N=5$ and 6, for the larger sizes the relevant clusters from spheres are totally dissimilar. This difference is caused by the DB being made of two overlapping spheres, which prevents a closer packing of the DBs as would be possible for spheres.

We now turn our attention to clusters of monodisperse asymmetric DBs. Their shape is given by the average parameters: $R_s$ of 0.71 μm with a polydispersity of 2.3 %, $R_p$ of 0.52 μm with a polydispersity of 3.7 %, and a contact angle of (49 ± 3)°. They were also used as packing units (see SF-1d in the Supporting Information). All distinct structures of the clusters observed for low numbers of particles ($N=2$,3, and 4) are summarized in Figure 2. We observed two configurations for both $N=2$ and 3. According to the theory of the symmetry of molecules referred to before,[11] for the dimeric clusters the absence of any symmetry elements directly predicts a pair of enantiomeric colloidal clusters, and the enantiomers should occur with equal probability (Figure 2 a). For the trimeric clusters, two isomers are present because these have a plane of symmetry. Hence, they are achiral. However, these two configurations do not have the same yield: the one in which the protrusions have a heterogeneous orientation is the favorable configuration (the yield is 76 % based on around 100 counts), compared to the other, with homogeneously oriented protrusions (the yield is 24 %; Figure 2 b). A ratio of 1:3 is expected if the up-down orientation of the DBs would be random.

For increasing $N$ values, the number of configurations of clusters increased dramatically, both experimentally and in the simulations. For $N=4$, we observed eight configurations (Figure 2 c). The top-left configuration in Figure 2 c is predicted by the simulations and is a diastereomeric cluster (having a $S_4$ axis). The bottom-left cluster is achiral (with a $i$). Three pairs of chiral colloidal tetramers are displayed in Figure 2 c, and are mirror images of each other. Surprisingly, if the protrusions were removed from the tetramer cluster, all the configurations of the asymmetric DBs are superimposable

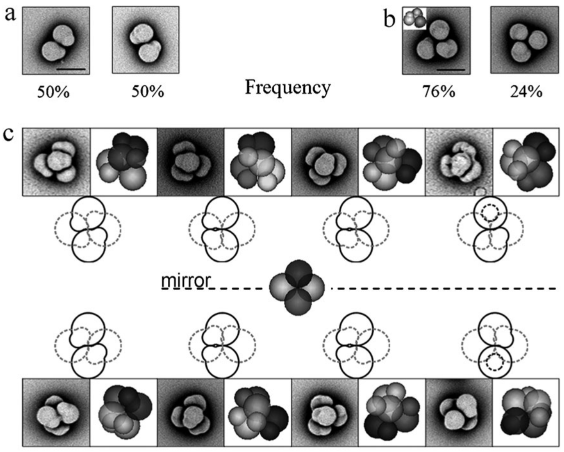

*Figure 2.* Simple cluster structures with $N=2,3$, and 4 made of the asymmetric DBs (size ratio of 0.73, overlap see SF-1b and d in the Supporting Information). Some shrinkage and deformation of the particles occurred during drying and exposure to the electron beam, but the structures are still recognizable. a) The experimental frequencies of the clusters for $N=2$ are given next to the SEM micrographs of the pair of chiral clusters. b) The experimental frequencies of clusters at $N=3$ are given next to SEM micrographs of the two structures of clusters found. The inset is the result of a computer simulation, which matches the observed cluster configuration. c) The first and last rows show SEM micrographs and translucent schematic images of the clusters observed in simulations for $N=4$, while the second and third rows are two-dimensional perspective views of each corresponding cluster. Note that the large spheres are always in the same configuration. Scale bar: 2 μm.

on a common cluster which is structurally identical to the tetramer formed from spheres. One can conclude that the asymmetric DB packing leads to bigger bulb-dependent clusters, while the smaller bulb simply attaches to the bigger bulb with a relatively free orientation. Since the particles were confined to lie horizontally in the interface of a spherical droplet, and they always stay at the interface, this restriction causes the loss of one rotational degree of freedom. Indeed, we never observed a small bulb hiding in the center of a cluster.

The landscape underwent a quantitative change for $N>4$, as there were too many configurations to catalogue experimentally. We therefore show some typical examples of the experimental observations and simulation results in Figure 3. We again observed that the large spheres were arranged in the same configurations as those seen in clusters of spherical particles, and the small protrusions oriented themselves more or less randomly against the clusters thus formed. These variations break the symmetry of the main frame of the clusters, and could for instance be exploited by changing the composition of the smaller bulbs. In this case, the index contrast of the smaller part of the DB could be used to add more or less randomness to the scattering signal if the clusters were placed on a photonic lattice. Also, the intercluster interactions could be randomized depending on the properties of the composition of the smaller bulb.

When applying the same simulation method to this system of asymmetric building blocks, the configurations found directly after the compression step, that is, before the M2 minimization step, did not agree with the experimental snapshots. Clear differences in the positions of the large spheres could be seen, and the small spheres had a limited freedom of movement before M2 minimization, rather than being mechanically arrested as a result of contact with other spheres as seen in the experimental snapshots. When minimizing the second moment of the mass distribution, the resulting configuration is influenced by the mass ratio $m_p/m_s$

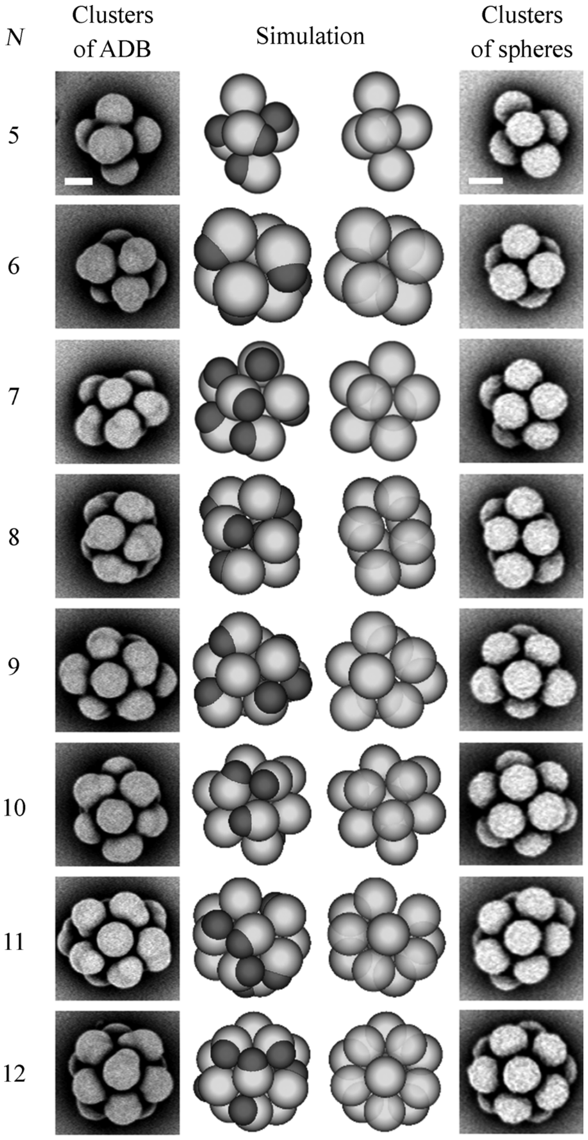

*Figure 3.* Cluster configurations for asymmetric DBs (ADBs) of $N>4$. The first column indicates clusters of size $N$, while the second and fifth columns show the cluster configurations of the asymmetric DBs (size ratio of 0.73) and spheres, respectively, as determined by SEM. All the clusters of spheres for a specific cluster size $N$ have identical configurations, while the configurations shown for clusters of the asymmetric DBs are typical configurations taken from the many corresponding examples found both in the experiments and simulations (third column). The fourth column lays out the configurations of clusters in which the small protrusions were removed from the simulation results, thus showing the resemblance to the cluster configurations in the last column. Scale bars: 1 μm.

of the seed (big) and protrusion (small) spheres. Of course, as the minimization of M2 is only an empirical model for the final stages of droplet evaporation, for which no strong theoretical basis has been given, the mass in this context is not physically linked to the real mass of the sphere. Simply letting the mass of each sphere scale with its volume, such that $m_p/m_s = R^3_p/R^3_s$, generally led to configurations where the smaller spheres preferentially resided in the center of the cluster, and therefore deviated from the experimental observations. Reducing the effect of the positions of the small spheres on M2 yielded much better agreement with the experimental observations. The resulting clusters were independent of the exact mass ratio, as long as $0 < m_p/m_s \ll R^3_p/R^3_s$: all that appeared to be required was a strong preference for the large spheres to be near the center of the cluster, and a weak contribution of the small spheres to prevent any freedom of movement in the final configuration. For all the investigated clusters sizes, the structure of the large spheres in the final configuration agrees with those seen in experiments, and the positions of the small particles vary between different simulation runs and experimental snapshots.

As was already mentioned (Figure 3) it is quite clear that if one neglects the smaller bulbs in the structure, the cluster structures found experimentally, up to $N = 12$, are equal to those of the clusters of the single spheres. These data indicate that the principle of minimizing the M2 of the mass distribution is not a general rule in this kind of SA processes as it leads to incorrect structures when this minimization was used for these particles.

We investigated the SA of anisotropic DB-shaped particles confined onto the interface of water emulsion droplets dispersed in an oil phase while the water was evaporated. We also investigated whether a simple simulation scheme could predict the structures formed. The simulation procedure correctly predicted structures of the $N$-mers formed for both spheres and symmetric DB particles for $N < 8$. However, for the results for the asymmetric DBs were predictable only if the minimization of the mass distribution was performed by giving less weight to the smaller bulb. For the asymmetric DBs it was found that the structures formed were identical to those of spheres if the positions of the smaller bulbs were ignored. If the whole particle was taken into account, the uniqueness of the structures formed was lost for $N > 2$, whereas for $N = 2$ two chiral enantiomers were found. Our results also indicate that minimization of the second moment of the mass distribution is not a general rule for this kind of SA.

For the symmetric DBs unique structures were found (at least for $N < 8$) both for the experiments and the simulations. Several of the structures were completely unique, whereas for others two isomers were found, that is, for $N = 6$ without chirality and for $N = 3$ and $N = 5$ with chirality. The chiral structures are interesting as they are not present in clusters of single spheres. Chiral structures also are interesting for photonic applications as they interact differently with light.

Received: February 21, 2013

**Keywords:** chirality · colloids · isomers · particle aggregates · self-assembly

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