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Clusters of Charged Janus Spheres

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ABSTRACT

We study the assembly of spherical particles with opposite electric charge on both hemispheres, in the case that the particle diameter exceeds the electrostatic screening length. Clusters result, not strings. The cluster shapes are analyzed by combined epifluorescence microscopy and Monte Carlo computer simulations with excellent agreement, indicating that the particles assemble in aqueous suspension to form equilibrated aggregates. The simulations show that charge asymmetry of individual Janus particles is preserved in the clusters.

Historically, colloid science has focused on understanding particle interactions when the surface composition is so uniform that the interaction potential depends only on separation.[1] Though magnetic effects comprise an obvious counter-example to the assumption of isotropic particle−particle interactions, studies of magnetic colloids have proceeded essentially independently.[2] Indeed, the assumption that the relevant interactions are nondirectional[3] is the premise for analyzing a vast number of ubiquitous technological and environmental problems involving colloids. Many applications have ensued, including their use as proxies for atoms in studying the dynamical structure of crystals and glasses,[4,5] and their self-assembly into colloidal crystals is useful in the important application of photonic materials.[6] However, surface chemistry is commonly spotty, patchy, and heterogeneous. Rather than dismiss this as imperfection, here we show that qualitatively new behavior follows when spherical symmetry is broken by anisotropic chemical composition.

Synthetic routes to create colloidal-sized particles with patchy surface chemical composition are known.[7,8] Also, *shape* asymmetry can be created by causing block copolymers to self-assemble in certain organic solvents.[8] In this communication, we ignore the complexity of such shape asymmetry and consider the "Janus" motif in which the surface of a spherical particle is divided evenly into two areas of different chemical composition. The effect of hemispherical interactions on the aggregation behavior of colloids appears hitherto unstudied. Bearing in mind that electrostatic potentials are better understood than those involving hydrophobic interactions, we consider the simpler case of hemispheres having opposite surface charge density. Although their net charge is zero, zwitterionic particles fail to behave as classical (ideal) dipoles because their size greatly exceeds the electrostatic screening length and the electrostatic interactions thus have much shorter range than the particle size. We study the structures into which zwitterionic Janus particles self-assemble and show that colloids with directional interactions can form clusters with definite shape and anisotropic distribution of electric charge.

Experimental and Computational Details. We prepared zwitterionic colloids using known methods for "Janus" particles.[9−11] A suspension of (fluorescent) colloids was spread onto a cleaned glass substrate such that a monolayer of colloid remained after the suspension liquid evaporated. A thin (15 nm) gold film was deposited using electron-beam deposition. Monolayers of *N*,*N*,*N*-trimethyl-(11-mercaptoundecyl)ammonium chloride were deposited from ethanol solution to produce positive charge and washed multiple times with 1% HCl ethanol solution to remove the electrostatic adsorption. On the other hemisphere, negative charge resulted from carboxylic acid groups on the untreated side of carboxylate-modified polystyrene colloids. When this procedure was performed with care, measurements of zeta potential showed that it yielded particles whose charge on two hemispheres was indeed nearly balanced. For example, the zeta potential of bipolar particles is 0.6 mV, whereas it is −41.6 mV for bare particles at the same salt concentration. The particles were then suspended in aqueous solution, and epifluorescence micrsocopy was used to image regions of relatively high concentration formed when the particles settled to the bottom of the glass sample container. In this thin volume ~5 μm from the surface, the maximum volume fraction of ~10^{-3} was still dilute.

The particles in the experiments (F8819 from Invitrogen, Inc.) had 1 μm diameter, but the size is not believed to be fundamental, provided that it much exceeds the screening length. The experiments were conducted in PBS buffer (pH

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= 6) at 1 mM ionic strength, such that the Debye screening length was approximately 10 nm.

Janus particles were modeled as spherical shells composed of 12 002 isotropically distributed spherical particles[12] (cf. Figure 1E). The large number of surface particles ensures a smooth representation of the charge distribution on each hemisphere. Each pair of surface particles interacts via an attractive or repulsive square potential (representing their screened electrostatic interaction), according to the sign of both hemispheres. We find that our results are insensitive to the precise range (and shape) of the nanoparticle potential (and hence to precise salt concentration), as long as this range is less than 30% of the colloid diameter. Because the equilibration time increases rapidly with decreasing interaction range, we have adopted a range of 10% of the size of a Janus particle. By systematically exploring all possible relative orientations of a pair of Janus particles, we obtained the *colloid* pair potential, which was then fitted to a functional form (cf. Figure 1A−D). We explicitly verified that variation of the number of surface particles does not change the shape of this potential, but merely rescales the contact energy of a pair of Janus particles. The magnitude of the colloid potential quickly decays to zero with increasing surface-to-surface distance.

Subsequently, we carried out Monte Carlo (MC) simulations in which the Janus particles were represented as monodisperse hard spheres with a pairwise interaction given by the functional form obtained. Use of this functional form allowed us to study systems containing relatively large numbers of particles for a large number of steps, which is essential to ensure that stable configurations are reached. The simulations employed a standard Monte Carlo algorithm and were all performed in the *NVT* ensemble with periodic boundary conditions. We explored potentials with contact interactions between 5 and 10 k_BT; reduced units were chosen such that T is equal to unity. Up to $N = 400$ particles were used in each simulation. The minimum-energy states were reached fairly quickly, but to ensure equilibration we continued all runs for a minimum of 10^6 MC steps.

We proceeded as follows. First, a dilute system of Janus particles with random orientation and position was allowed to evolve via local MC moves. Because of the strong contact interactions, clusters assembled relatively quickly. These clusters were identified, and their structure was analyzed visually and compared to the experimental images as well asto the known Lennard-Jones clusters of the same size.

Next, to check the stability of each cluster of size n, we also performed simulations where only n particles were placed within the simulation cell and allowed to self-assemble. As the number of metastable states increases quickly with increasing cluster size n, we started with a high temperature, to permit continuous rearrangements within the cluster. All different structural arrangements (i.e., aggregates of n Janus particles) were enumerated and each was quenched to a minimum-energy state using a standard simulated annealing technique. Finally, the energies of all resulting clusters were compared to find the absolute minimum energy. Although such an approach becomes inefficient for large n, our analysis only included rather small clusters, giving us confidence that the clusters presented below are indeed the most stable ones.

Last, we note that the rotational diffusion of the experimental clusters facilitated the careful and thorough visual comparison with the clusters obtained from the simulations. Clusters of size up to $n = 7$ were observed at least 20−30 times. The clusters of largest n were observed less frequently, but at least 2−3 times, validating the conclusion that the agreement between simulation and experiment was not coincidence.

Results and Discussion. The complexity of the interaction potential between Janus particles is obvious upon inspection. Consider a polar axis pointing north−south through the hemispheres. Only if the axes of the two particles lie in the same plane (Figure 1A) the interaction switches smoothly from repulsion to attraction depending on how the particles face one another. This is illustrated in Figure 1B; a switch between repulsion and attraction over a narrow range of rotation angle. Generally, the polar axes passing through the hemispheres do not lie in the same plane (Figure 1C) and the interaction potential depends on relative orientation as well as on separation. This multidimensional parameter space illustrates the rapid increase of complexity as one goes beyond the classical concept of isotropic potentials. Figure 1D presents the calculated dependence of the interaction potential between a pair of particles on the two polar angles describing the orientation of one particle for a *fixed* orientation of the second particle and for fixed particle separation. The key conclusion is the existence of multiple energetic minima, an energy “landscape” in the true sense of the word. It suggests that in nature particles of this kind might be prone to slide over one another by Brownian motion, toward configurations of lower electrostatic energy. Indeed, we observe this in our experiments.

The parameters in the modeling are selected to be consistent with the experimental conditions; the main point is that the particle size of 1 μm greatly exceeds the electrostatic screening length of ∼10 nm. On the basis of manufacturer’s specification and measurements of the zeta potential of unfunctionalized particles, we estimate their surface charge on the order of 1 elementary charge per square nanometer. In our modeling, we set the net particle charge equal to zero.

The epifluorescence images show that the particles cluster into definite geometrical shapes depending on the number of particles, as summarized in column A of Figure 2. Clusters larger than about 12 zwitterionic particles are not observed owing to the dilute concentration. Having validated the simulations (column B of Figure 2) by comparing to the shapes observed experimentally, we exploit the modeling to determine the mutual orientation of the charged hemispheres on neighboring particles, because this information is so far inaccessible experimentally. For the case of $n = 2$ particles, one observes that the particles find a low-energy state even if their polar axes are not strictly in the same plane. This broad energy minimum is expected, because the area of

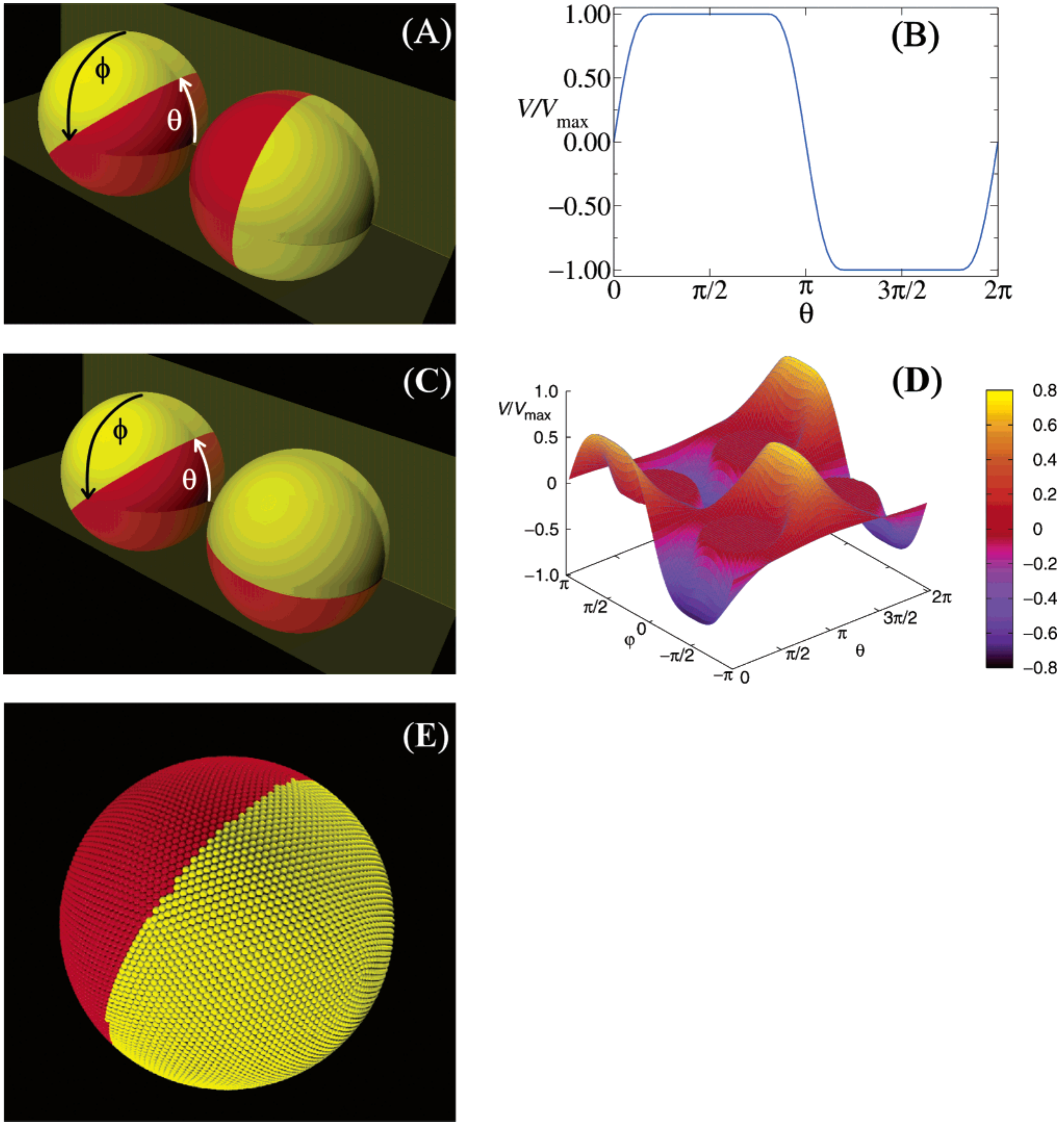

Figure 1. Two particles with bipolar charge, analyzed using simulations. The right-hand object is fixed; the angles (θ,φ) indicate the orientation of the left-hand object. Red denotes positive charge, and yellow denotes negative charge; these charges are equal in magnitude. (A) Charged hemispheres whose polar axes lie in the same plane. (B) Relative interaction energy for case A, plotted against angular displacement for two particles at contact. The interaction potential switches from repulsive to attractive as the left-hand object rotates in the θ direction even when the particle−particle separation does not change. (C) General case where the polar axes do not lie in the same plane. (D) For every orientation of the right-hand particle, a potential energy landscape must be determined. Thus, the parameter space become four-dimensional even at fixed surface separation, illustrating the rapid increase in complexity once one goes beyond the concept of isotropic potentials. The potentials shown are obtained numerically using a pair of composite particles having 6001 fixed and uniformly distributed "nanoparticles" per hemisphere, representing the surface charges (panel E). Each pair of nanoparticles interacts via an attractive or repulsive square potential (representing their screened electrostatic interaction), according to the sign of both hemispheres. We find that the shapes of the resulting clusters are insensitive to the precise range of the nanoparticle potential (and hence to precise salt concentration), as long as this range is less than 30% of the colloid diameter. Because the equilibration time increases rapidly with decreasing interaction range, we have adopted a range of 10% of the particle size. The magnitude of the resulting *colloid potential* quickly decays to zero with increasing surface-to-surface distance.

contact is so much smaller than the particle size. For clusters larger than $n = 2$, the polar axes of the hemispheres twist in space as neighboring particles circle the structure. One profound consequence is that if one considers the entire

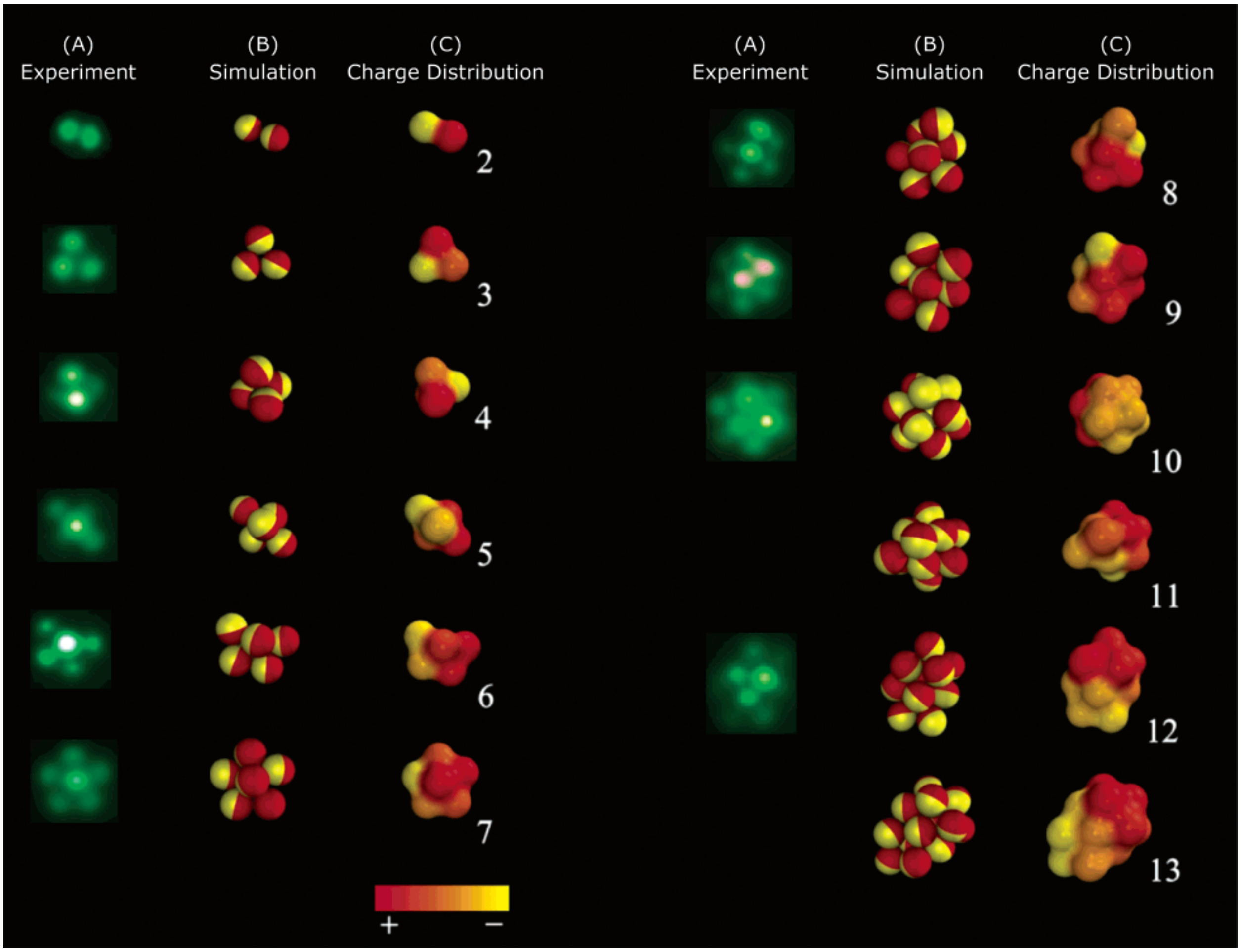

Figure 2. Comparison of experimental epifluorescence images and Monte Carlo computer simulations of the self-assembled structures of particles with near-equal positive and negative charges on the two hemispheres (denoted by red and yellow colors). Clusters form with monotonically decreasing energy as the number of colloidal particles increases. Their computed structures (column B) agree quantitatively with the observed structures (column A). The charge distribution in these clusters is also computed; the color goes smoothly from red to yellow depending on the inner product of the vector from the center of mass of the cluster to each colloid and the axial vector (pointing to the positive side) of this colloid (column C). In the charge distributions, a wrapping has been added to emphasize the outer surface. As described in the text, experimental measurements of zeta potential showed it to be <1 mV, confirming that charge on two hemispheres was nearly balanced.

cluster as a particle in its own right then the envelope of electrostatic charge is not distributed evenly. To quantify this, Column C of Figure 2 displays the envelope of electrostatic charge presented to the environment (the caption of Figure 2 describes the color coding). Charge is distributed asymmetrically; one half of each (non-spherical) cluster tends to be predominantly positive in charge, the other half predominantly negative. Thus, charge asymmetry on the elemental spherical particles is preserved in the surface charge asymmetry of the clusters into which they assemble.

In principle, there appears to be no limit to the size of clusters that can form from these electrostatic interactions; our modeling shows that each cluster of larger size is energetically more stable than all of the smaller ones. This implies that the clusters depicted in Figure 2 might merge into larger ones, if only their concentration were higher. This has not yet been possible to investigate experimentally owing to the limited quantity of sample available. However, because the charge anisotropy of individual particles is preserved in the clusters analyzed here, it is logical to conclude that energetically the positive side of one cluster will attract the negative side of another cluster, resulting in facile assembly into even larger aggregates, based on short-range, orientation-dependent interactions of the kind presented by our calculations summarized in Figure 1.

The compact shapes in Figure 2 differ fundamentally from the lines and rings formed by magnetic particles[2] and electric dipoles, which are much studied in recent literature.[13] Our particles would behave as ideal dipoles only at distances that much exceed the actual interaction range. It is appropriate to compare the shapes we observe to those of colloidal-sized spheres *without electrostatic interaction*. A pioneering study by Pine and co-workers of uncharged spheres that self-assemble owing to van der Waals attraction[14] revealed structures that are identical to those predicted mathematically for most favorable packing.[15] For $n = 2-5$ and $n = 7$, we observe the same overall shapes albeit with the internal structure and charge asymmetry depicted in Figure 2. An intriguing technical point is that packing considerations[14,15] lead, for $n > 7$, to structures different from those predicted by modeling spheres with Lennard-Jones interactions. By contrast, our findings differ from either prediction already for $n = 6$, but reproduce the Lennard-Jones clusters for $n = 7-10$. For cluster sizes of $n = 6$, 11, 12, and 13, the shapes found for hemispherical interactions differ from those obtained from isotropic interactions; the difference is that the shapes we observe are less symmetric. We anticipate even larger distinctions for particles of lesser symmetry, for example, unmatched positive and negative surface charge, and also for larger clusters.

A key aspect of these particles is that real-time imaging reveals the process of self-assembly. The constituent zwitterionic spheres assemble into clusters, the clusters coalesce with one another, and structural defects heal; all of this on the convenient time scale of seconds to minutes. In earlier work on colloid clusters, the conditions were such that in the ultimate structures the elements were quenched in place.[14] In the present system, the forces of interaction are relatively weak. From simulation we estimate them as on the order of $5-10\ k_BT$ and this is consistent with the unambiguous observation that equilibration events, dynamical particle attachment to and detachment from clusters, and reconfiguration of cluster shapes, can be observed in video images as these clusters self-assemble. This experimental approach will allow comparison with prior computer-based calculations of how patchy particles associate.[13,16−20]

Looking to the future, the idea of directional self-assembly between colloidal-sized particles suggests many possibilities. It is obvious to generalize the situation to consider colloids whose shape is not just spherical, as in this study, but also, for example, rodlike or oblate, more complex than the spherical shape considered in this study for simplicity. Also obvious is that the bipolar functionality studies in this communication can be generalized to ternary; a simple place to start will be to divide spheres into three regions of different chemical composition, as appears to be possible by vacuum deposition of metal at oblique angles. Finally, it is intriguing to note that asymmetric charge distribution has been proposed, based on experiments, to explain the aggregation of some proteins.[21] Thus, the model particle systems that we study here may have relevance to proteins and other more complex particles where the surface charge distribution is similarly patchy.

However, a limitation of our present method to produce Janus particles is that their yield is low. Methods to scale up the production of Janus particles to larger quantities are under development and will be reported presently.

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