

Two-Dimensional Clusters of Colloidal Spheres: Ground States, Excited States, and Structural Rearrangements

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We study experimentally what is arguably the simplest yet nontrivial colloidal system: two-dimensional clusters of six spherical particles bound by depletion interactions. These clusters have multiple, degenerate ground states whose equilibrium distribution is determined by entropic factors, principally the symmetry. We observe the equilibrium rearrangements between ground states as well as all of the low-lying excited states. In contrast to the ground states, the excited states have soft modes and low symmetry, and their occupation probabilities depend on the size of the configuration space reached through internal degrees of freedom, as well as a single “sticky parameter” encapsulating the depth and curvature of the potential. Using a geometrical model that accounts for the entropy of the soft modes and the diffusion rates along them, we accurately reproduce the measured rearrangement rates. The success of this model, which requires no fitting parameters or measurements of the potential, shows that the free-energy landscape of colloidal systems and the dynamics it governs can be understood geometrically.

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Colloidal clusters containing a few particles bound together by weak attractive interactions are among the simplest, nontrivial systems for investigating collective phenomena in condensed matter. Such clusters can equilibrate on experimental time scales and display complex dynamics, yet are small enough that the ground states can be enumerated theoretically, and the positions and motions of all the particles can be measured experimentally. Theoretical and experimental work on isolated three-dimensional (3D) colloidal clusters of monodisperse particles has shown how the number of ground states changes with the number of particles N [1–6] and how the free energies of the rigid states are related to entropy-reducing symmetry effects and entropy-enhancing vibrational modes [7–9]. The importance of entropy in colloidal clusters stands in stark contrast to the case of atomic clusters, where potential energy effects dominate. The entropically favored clusters are important clues to understanding nucleation barriers in bulk colloidal fluids [4,10] and the local structure of gels [11].

However, the excited states and structural rearrangements in such clusters have not yet been studied experimentally. In bulk materials, local structural rearrangements are important to a variety of dynamical phenomena, including the glass transition [12], aging [13,14], epitaxial growth [15], and the jamming transition [16]. A better understanding of the internal dynamics in colloidal clusters could reveal local mechanisms underpinning these bulk phenomena. Only a few experimental studies have explored internal dynamics in colloidal clusters: Perry and co-workers examined transitions between two states of a

3D six-particle cluster of spherical particles [17], Yunker and co-workers studied relations between the vibrational mode structure and the contact network in disordered, two-dimensional (2D) clusters of polydisperse particles as a function of N [18,19], and Chen and co-workers examined the interconversion and aggregation pathways in clusters of particles with directional attractions [20]. As yet, however, a quantitative understanding of the rearrangement rates and the pathways through the excited states remains challenging. Transition-state models [21–24], which relate dynamics to the heights of saddle points on the energy landscape, are not easily applied to colloids because the fluid surrounding the particles damps and hydrodynamically couples their motions, and the short-ranged interactions typical of colloidal particles are not easily measured, making the topography of the landscape difficult to accurately compute. Indeed, as we shall show, the excited-state occupation probabilities and the transition rates are sensitive to fine details of the potential, which are not easily measured.

We study experimentally the excited states and rearrangement rates in perhaps the simplest type of colloidal cluster: isostatic arrangements of equal-sized, spherical colloidal particles, constrained to lie on a plane and held together by well-controlled, short-range attractions a few times the thermal energy $k_B T$ in depth [Fig. 1(a)]. Because the clusters are isostatic, all excited states have zero-frequency modes, or soft modes, in their vibrational spectra (Fig. 1(b), [25]). By tracking the particles over long times, we quantify the equilibrium probability of each excited state and the motions of the particles within each soft mode. Surprisingly, the dynamics that emerge from this landscape

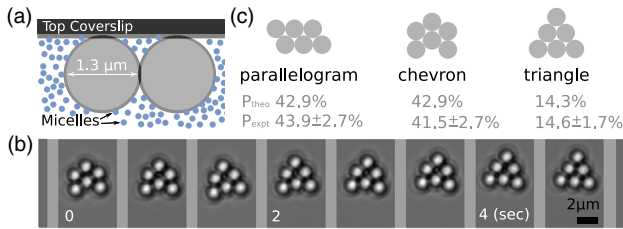


FIG. 1 (color online). (a) SDS micelles induce a short-range depletion attraction between polystyrene microspheres and between the microspheres and the nearby glass coverslip. (b) Time-lapse images demonstrate a transition. (c) The three rigid ground states and their theoretical and experimental probabilities with 95% confidence intervals [25] (the probabilities for the parallelogram include both chiral enantiomers).

can be quantitatively described by a simple geometric model involving only two parameters, a “sticky parameter” that characterizes both the depth and curvature of the attraction, and a diffusion coefficient, which we find to be insensitive to the mode. Both parameters can be easily measured. Therefore, no detailed knowledge of the interactions or hydrodynamics is required to reproduce the rates of rearrangement between ground states.

To make clusters, we first load an aqueous suspension of $1.3 \mu\text{m}$ -diameter sulfate polystyrene microspheres into a cell made from two plasma-cleaned glass coverslips separated by $35 \mu\text{m}$ DuPont Mylar® A spacers [25]. The only additional component in the suspension is sodium dodecyl sulfate (SDS), a surfactant that forms negatively charged micelles in solution. The micelles create a weak depletion interaction [30–32] between the particles and a stronger depletion interaction between the particles and coverslip [33,34], as illustrated in Fig. 1(a). At 33.4 mM SDS, we observe that 2D clusters bound to a coverslip frequently transition between states but rarely split apart or merge

[25]. At this concentration, the sodium counterions from the surfactant reduce the Debye length to 2.85 nm, setting the effective hard-sphere depletion range of the micelles to 30 nm, just 2.3% of the particle diameter [32,35]. As a result, the electrostatic and depletion interactions between the particles are short ranged. There is likely also a short-range van der Waals attraction, which we estimate tapers off to $k_B T$ when the particle surfaces are 145 nm apart [36].

At the beginning of the experiment, we assemble clusters at the top of the sample cell using optical tweezers. We then turn off the tweezers and record digital micrographs for the remainder of the experiment. The clusters, which would normally sediment, remain at the underside of the upper coverslip, confirming the depletion attraction. We use particle tracking algorithms to locate the particles [37], link the locations into trajectories through time, and automatically identify the cluster configurations [25].

We focus on six-particle clusters because this is the smallest system with multiple ground states. Because these clusters are bound by short-range interactions, the potential energy is proportional to the number of contacts or “bonds” between particles. The six-particle clusters adopt three ground states with nine bonds each [Fig. 1(c)]: the parallelogram (which has two enantiomers), chevron, and triangle. In aggregate, the clusters occupy the parallelogram and chevron states for equal amounts of time but spend only one third as much time in the triangle state [Fig. 1(c)]. The measured occupation probabilities agree with the expectation for a statistical mechanics ensemble in equilibrium. To calculate the probabilities, we assume that the translational, rotational, and vibrational degrees of freedom are independent, the vibrational modes are harmonic, and the translational contributions and potential energy differ negligibly among the three states [25]. As seen previously in 3D clusters, the differences in

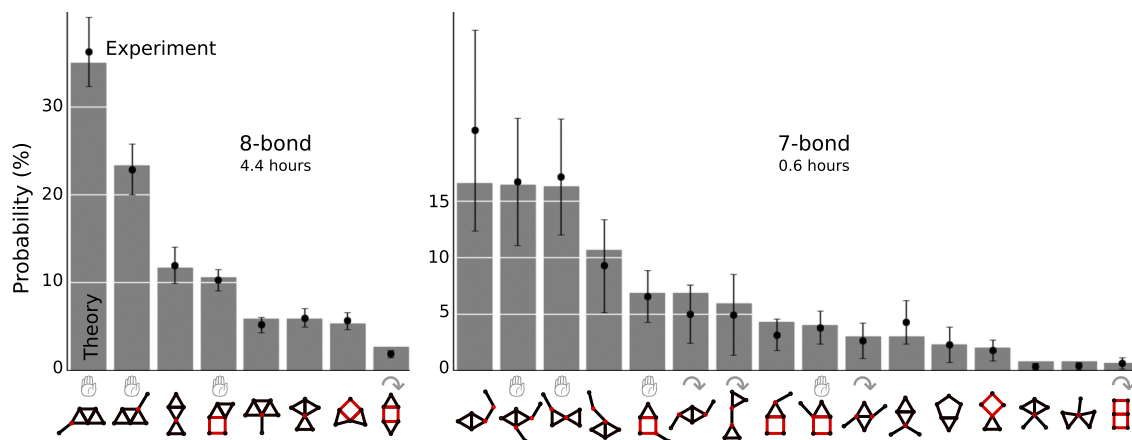


FIG. 2 (color online). Theoretical (bars) and experimental (points) probability distributions of the eight- and seven-bond excited states. Each bar-point pair is labeled by a connectivity diagram of the excited state, with hingelike joints and nonrigid squares labeled in red. Hand symbols mark the chiral states, and curved arrows mark the states with twofold rotational symmetry (in 2D the only accessible symmetry axis is perpendicular to the plane of confinement). The total observation time is 25.6 h; for comparison, the clusters spend 19.5 h in the nine-bond states. Error bars represent 95% confidence intervals [25].

TABLE I. Structural rearrangement rates between each of the ground states: parallelogram (P), chevron (C), and triangle (T). In total, we observed 820 transitions in 25.6 h of data from 44 clusters. Measured values used in postfactor: $D = 0.065 \mu\text{m}^2/\text{s}$ ($234 \mu\text{m}^2/\text{hr}$), $\kappa = 30.5$, and $d = 1.3 \mu\text{m}$.

		Theory						Experiment			
		(nondimensional) end state			$\times(D/\kappa d^2) =$	(per hour)			(per hour)		
		P	C	T		P	C	T	P	C	T
start state	P	1.17	1.43	0.67		5.3	6.5	3.0	4.4	5.5	2.5
	C	1.43	2.31	0.56		6.5	10.5	2.5	5.4	7.7	1.9
	T	0.67	0.56	0		3.0	2.5	0.00	2.5	2.2	0.04

occupation probabilities are primarily due to symmetry, which enters into the rotational contribution [7,10].

The excited states of the system have more complex and interesting structures. All of them have zero-frequency modes. The modes we see at the eight-bond energy level have either hingelike joints or diamond-square-diamond [38] flexibility (Fig. 2). Although the seven-bond energy level has twice as many states, nearly all of the zero-frequency modes are simply combinations of these two types of motion (Fig. 2). The exceptions are a state with a flexible ring of five spheres and a state with a single sphere detached from the cluster. We do not include this disconnected state in our seven-bond probability calculations because it is not a true six-sphere cluster.

The fraction of time the clusters spend in the excited energy levels depends on the surfactant concentration. At a concentration of 33.4 mM SDS, the clusters spend 95.5% of the time in states with seven or more bonds. Of this time, 79.6% is spent in ground states, 18.0% in eight-bond excited states, and 2.4% in seven-bond excited states. As we decrease the surfactant concentration, the distribution shifts toward the excited energy levels. Qualitatively, this shift makes sense, since decreasing surfactant concentration corresponds to decreasing depletion strength. To understand the energy level occupation probabilities quantitatively, we must consider the entropy of the soft modes. We return to this point later.

Despite the wide variety of structures in the excited states, few have any symmetry. Surprisingly, the few symmetric states do not occur as infrequently as we might expect, given the dominant role symmetry—more specifically, permutational entropy [7,39]—plays in the probabilities of six-sphere ground states in both 2D and 3D. Furthermore, the asymmetric states have a highly nonuniform distribution that is only partially explained by the increased probability of states that are pairs of chiral enantiomers (Fig. 2). These observations suggest that the variation in probabilities arises from entropic factors other than the permutational contribution.

We also measure the rate of rearrangements between ground states and find that the matrix of rearrangements per unit time is symmetric (Table I), as expected in equilibrium. Most of these rearrangements involve a single bond

breaking, followed by the cluster diffusing along the soft mode in its excited state and finally forming a new bond to arrive at a ground state (Fig. 3).

Understanding the excited-state probabilities and rearrangement rates requires us to consider the entropy of the soft modes and the dynamics along the resulting free-energy landscape. In contrast to typical molecular-scale transitions, in which the potential energy varies along the entire reaction coordinate, our clusters first break out of a narrow attractive well and then freely diffuse in soft modes at constant potential energy under only an entropic driving force. We therefore expect the transition rates to depend on the entropy along the modes, the hydrodynamic drag, and the distance to diffuse in the soft modes.

To calculate the entropy, we use the geometrical model of Ref. [40]. In this model, the potential energy landscape is represented as a collection of manifolds, each at constant potential energy. The dimension of each manifold equals the number of internal degrees of freedom of the cluster: for example, the ground states are zero-dimensional manifolds (points), and the eight-bond states live on one-dimensional manifolds (lines). To compute the partition function, we numerically parametrize each manifold and integrate the vibrational and rotational entropies over its entire volume.

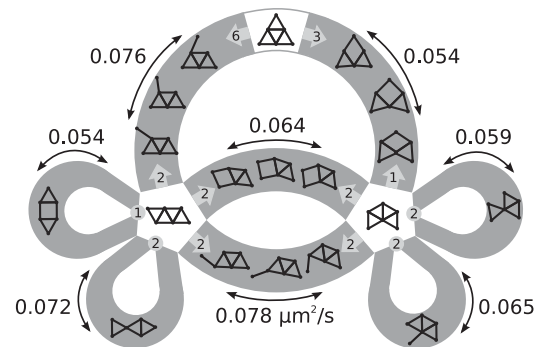


FIG. 3. The eight-bond excited states form transition pathways (gray background) between the ground states (white background). The numbers at the edges of the ground states show the number of bonds that lead into each nearby pathway. The measured diffusion coefficients of the modes range from 0.054 to 0.078 $\mu\text{m}^2/\text{s}$ [25].

This calculation of the entropy is purely geometrical and requires no knowledge of the actual pair potential; the only assumption is that the harmonic vibrational degrees of freedom equilibrate quickly compared to motion along the soft modes.

The model reproduces our experimental measurements of the excited-state probabilities within experimental error (Fig. 2). The agreement validates the model's assumption and shows that for the excited states, the entropy associated with the soft modes dominates the permutational entropy associated with asymmetry. In particular, the entropy of the zero-frequency modes explains the surprisingly high probability of seven-bond structures with twofold symmetry.

To understand the relative populations of the excited-state energy levels (eight-bond versus seven-bond), we must consider the interparticle potential. Measuring the potential well is difficult because the interaction is short ranged—only a few tens of nanometers for the depletion component [32] and similarly ranged for the electrostatic and van der Waals contributions. However, the short range makes it possible to use a “sticky sphere” approximation, in which a single parameter κ , called the sticky parameter, characterizes the interaction. κ is the partition function for a single bond and as such is proportional to the amount of time two particles are bound versus separated. In the limit where the potential becomes both infinitely narrow and infinitely deep [40],

$$\kappa = \frac{e^{-\beta U_0}}{d\sqrt{\frac{2}{\pi}}\beta U_0''}, \quad (1)$$

where $\beta = (1/k_B T)$, U_0 is the depth of the potential well, d is the microsphere diameter, and U_0'' is the curvature at the potential minimum. The advantage of this approximation is that we need only measure κ , and not the full potential.

We measure κ from ratios of occupation probabilities of ground and excited energy levels. The total time t_n for which a cluster has n bonds is proportional to $Z_n \kappa^n$, where Z_n is the sum of the partition functions of the n -bond manifolds [25]. By taking ratios of the time spent at different energy levels and calculating the Z_n we obtain a measurement of the sticky parameter as $\kappa = (t_{n+1}/t_n)(Z_n/Z_{n+1})$. We use observations of smaller clusters to determine κ independently of our six-particle data. For three-particle clusters, with three-bond and two-bond energy levels, we find $\kappa = 29.3$. We make two more measurements of κ using four-particle clusters: a comparison of five-bond to four-bond energy levels yields $\kappa = 26.8$, and that of four-bond to three-bond levels yields $\kappa = 35.3$. Using the mean of these measurements (30.5) in the n -bond partition function $Z_n \kappa^n$, normalized by $\sum_{n=7}^9 Z_n \kappa^n$, where $[Z_7, Z_8, Z_9] = [11900, 3320, 498]$, we predict six-particle occupation probabilities of $p_7 = 2.1 \pm 0.6\%$, $p_8 = 17.6 \pm 2.0\%$, and $p_9 = 80.3 \pm 2.5\%$, where the uncertainties are based on the range of measured

κ values. The calculations agree with our measured occupation probabilities.

The transition rates are calculated using transition path theory [40,41]. To simplify the calculations we suppose that each transition occurs by a single bond breaking, followed by the cluster diffusing along a one-dimensional path and forming another bond. We calculate the flux of probability along each path and from this extract the nondimensional rates, exactly as in Ref. [40]. The dimensional rates are obtained by multiplying by $D/\kappa d^2$, where D is the average diffusion coefficient and d is the microsphere diameter (Table I). As our implementation of the model ignores the time the clusters spend with fewer than eight bonds, we expect it to slightly overestimate the rates.

To determine the second parameter in our model, D , we measure the mean-square displacements along each pathway [25]. The measured diffusion coefficients range from 0.054 to 0.078 $\mu\text{m}^2/\text{s}$ with a mean of 0.065 $\mu\text{m}^2/\text{s}$ (Fig. 3). The error bars on the measured diffusion coefficients [25] are smaller than the variation in these values between the different modes. Thus, the variation is likely due to differences in hydrodynamic friction factors between these modes, and not measurement error.

Nonetheless, the dimensional transition rates predicted from a simple model using a single, average diffusion coefficient agree with the measured rates, as shown in Table I. Using different diffusion coefficients for each pathway yields values that agree equally well, though not better, with the data. This shows that the variation in diffusion coefficients among the different modes is not significant compared to the error in the measured transition rates. However, it also raises the question of why the diffusion coefficients for different pathways vary by only about 20% from the mean value. To understand this variation, we measure the diffusion coefficient for a rearrangement in a three-sphere cluster and find a value of $D = 0.070 \mu\text{m}^2/\text{s}$, close to the average value for the six-sphere rearrangement pathways. This agreement, along with the fact that these diffusion coefficients are all lower than that for a single sphere diffusing on the plane ($D = 0.10 \mu\text{m}^2/\text{s}$), suggests that the hydrodynamic friction factor along each pathway is dominated by flows between those spheres that must slide or roll past one another (as in the three-sphere cluster), rather than by hydrodynamic interactions between larger moving subunits of the clusters. This would explain why the diffusion coefficients are similar for both diamond-square-diamond and hinge-like modes.

Taken together, these results shed new light on the free-energy landscape, and the dynamics along it, in colloidal systems. As in 3D clusters, the short-range interaction in our 2D system leads to degeneracy in both the ground and excited states. Whereas the occupation probabilities of the ground states are determined primarily by symmetry (permutational entropy), those of the excited states are

determined primarily by the entropy of the soft modes. The agreement between the measured probabilities of the excited states and those predicted from our geometrical model shows that the harmonic vibrational modes equilibrate quickly compared to motion along the soft modes. This separation of time scales is another consequence of the short-range interactions. From our geometrical model of the free energies, we can reproduce the measured rearrangement rates between ground states by incorporating only a single diffusion coefficient and the partition function of a single bond, both of which are easily measured.

Our model easily extends to 3D clusters. Its success in describing the 2D experimental data suggests that, at least near the isostatic limit, it may be possible to use similar geometrically inspired models to understand the free-energy landscape and predict dynamics in more complex systems with soft modes, such as bulk colloidal phases. Indeed, such models are beginning to be developed [42].

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