Structure and dynamics of model colloidal clusters with short-range attractions

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We examine the structure and dynamics of small isolated $N$-particle clusters interacting via short-ranged Morse potentials. “Ideally prepared ensembles” obtained via exact enumeration studies of sticky hard sphere packings serve as reference states allowing us to identify key statistical-geometrical properties as well as to quantitatively characterize how nonequilibrium ensembles prepared by thermal quenches at different rates $\dot{T}$ differ from their equilibrium counterparts. Our results provide a theoretical framework for extending recent experimental studies of small colloidal clusters to examine nonequilibrium phenomena.

Understanding how varying the shape and strength of a pair potential affects the energy landscape and dynamics of systems composed of several particles interacting via that potential lies at the heart of theoretical cluster physics [1]. Variable-shape potentials are of particular utility in understanding common features of apparently disparate systems. For example, varying the dimensionless range parameter $\alpha D$ of the Morse potential

$$U_{\text{Morse}}(\alpha; r) = \epsilon \left[ \exp(-2\alpha(r - D)) - 2 \exp(-\alpha(r - D)) \right],$$

(1)
yields accurate models for clusters formed by constituents ranging from alkali-metal atoms to buckyballs to micron-sized colloids [2]. Studies of colloidal clusters are particularly valuable in this context since individual particle positions can be tracked. Most valuable are “model” systems with precisely controllable interparticle interactions and cluster size $N$. These systems are a veritable playground for studies of few-body statistical mechanics, and can (through the universality evident in cluster physics) provide insights into the behavior of their more microscopic counterparts.

Manoharan and collaborators have recently attracted great interest by characterizing the structure and dynamics [3, 4] of colloids interacting via hard-core-like repulsive and (variably) short-ranged attractive interactions. While published experimental studies and related theoretical modeling [3, 4, 5, 6] of these systems have focused on equilibrium phenomena, rapid advances in experimental particle-tracking techniques [4, 10, 11] suggest that much of their nonequilibrium physics may soon become experimentally observable. For example, the room-temperature transition rate between the two degenerate ground-state clusters (GSC) of $N = 6$ particles is of order $10^{-3} - 10^0\text{s}^{-1}$. Since their longest relaxation times should increase dramatically with increasing $N$ and decreasing $T$, it seems plausible that these model colloidal systems could soon be utilized for fundamental studies of nonequilibrium few-body statistical mechanics.

In this Letter, we provide theoretical guidance for such studies by elucidating the key nonequilibrium phenomena in small ($N \leq 13$) clusters that mimic the systems studied in experiments [3, 4]. Exact enumeration and molecular dynamics simulations are used in concert to rigorously characterize these systems’ zero-temperature equilibrium structure and perform a quantitative study of the preparation-protocol-dependent, nonequilibrium structure as well as their dynamics. Our key results include: (i) the fraction of “off-pathway nuclei” that are incompatible with close-packed crystallization grows rapidly with increasing $N$, and while it decreases with increasing hyperstaticity, it remains significant even for the lowest-energy clusters: (ii) fast temperature quenches produce ensembles retaining memory of equilibrium ensembles at high $T$, e.g. favoring structures that are more stable against excitation because they lie in deeper energy wells: and (iii) systems exhibit nonexponential relaxation indicative of both glassy dynamics and differing stabilities of degenerate clusters with different structures.

We extend the work of Refs. [3, 5] by obtaining all mechanically stable [12] packings of $N \leq 13$ sticky hard spheres. Extending $N$ to 13 is important because $N = 13$ clusters can form complete core-shell structures (i.e. HCP and FCC crystallites), and our work will aid experimental studies of core-shell structures where observation of the inner-core particles is difficult. The interaction potential for sticky hard spheres with diameter $D$ is [13]:

$$U_{ss}(r) = \begin{cases} \infty & , r < D \\ -\epsilon & , r = D \\ 0 & , r > D, \end{cases}$$

(2)

where $\epsilon$ is the energy at contact. A key feature of sticky hard-sphere clusters is that their isoenergetic, isocontacting states are in general highly degenerate. In general, systems of $N$ spheres with $N_c$ contacts possess $\mathcal{M}(N, N_c)$ nonisomorphic “macrostates” [8]. Our enumeration procedure for determining $\mathcal{M}(N, N_c)$ is very similar to that extensively described in Ref. [8]; the main difference is that we use NAUTY [14] to generate complete sets of nonisomorphic adjacency matrices.

In conjunction with exact enumeration studies of sticky hard spheres, we perform MD simulations using a continuous, modified Morse potential $U_{MM}(r)$ with shape and range (Figure 1) similar to the effective interactions be-
tween colloids in systems with micellar depletants \cite{3,4};
\[
U_{MM}(\alpha, b; r) = \begin{cases} 
\frac{U_{Morse}(\alpha; r) - c(\alpha, b)}{1 + c(\alpha, b)}, & r \leq r_c(\alpha, b) \\
0, & r > r_c(\alpha, b).
\end{cases}
\]

The structure and dynamics of Morse clusters with large \(aD\) are contact-dominated \cite{2}. In particular, rearrangements can be understood in terms of contact breaking and reformation. However, defining “contact” is ambiguous for potentials that decrease smoothly to zero. One advantage of using \(U_{MM}(r)\) rather than \(U_{Morse}(r)\) is that it facilitates contact identification and concomitant analyses of transitions between macrostates; \(F_{MM}(r) = -dU_{MM}/dr\) remains finite at \(r_c\), allowing us to define contact as finite-force interaction. The shift/stretch term \(c(\alpha, b)\) is defined to make \(U_{MM}\) continuous at \(r = r_c\), i.e. \(c(\alpha, b) \equiv U_{Morse}(\alpha; r_c(\alpha, b))\).

Here we study systems with \(aD = 150\) and \(b = \alpha/(30 \log(2))\), yielding \(r_c(\alpha, b)/D = 31/30\) \cite{2}. We have verified that replacement of \(U_{Morse}\) with this \(U_{MM}\) has minimal effects on the structural and dynamic properties of interest here. In particular, note that \(U_{MM}\) is long-range enough to avoid the thermodynamic and dynamic anomalies that are known to arise in the \(\alpha \to \infty\) “Baxter” limit \cite{10}. Our results should thus be scalable \cite{17} to both larger \(\alpha\) and smaller \(\alpha > \alpha_{conv}(N)\) using (for example) the Noro-Frenkel law of corresponding states \cite{18} and/or the “geometrical” free energy landscape techniques of Holmes-Cerfon et al. \cite{19}.

Another advantage of using \(U_{MM}(r)\) (for large \(\alpha\) and small \(r_c\)) is that it allows us to use well-defined “ideally prepared ensembles” (IPE) as initial \(T = 0\) states for our MD simulations. We define IPE as follows: Suppose a given potential has \(\mathcal{M}(N)\) strain-free, energetically degenerate \(N\)-particle ground state clusters (GSC) with permutational entropies \(\omega_k\). Statistical mechanics predicts that the equilibrium population fraction of each GSC at \(T = 0\) is \(\omega_k/\Omega\), where
\[
\Omega = \Omega(N) = \sum_{i=1}^{\mathcal{M}(N)} \omega_k(N).
\]

An IPE is an ensemble of molecules containing all of (and only the) \(\mathcal{M}(N)\) GSC, such that the population fraction of every GSC is equal to \(\omega_i/\Omega\). IPEs for modified-Morse potentials with sufficiently large \(\alpha > \alpha_{conv}(N)\) \cite{20} and small \(r_c\) are automatically produced by exact-enumeration studies of maximally contacting sticky hard sphere packings since sampling the adjacency matrices of all \(N\)-sphere packings with \(N_c = N_{n_{\text{max}}(N)}\) contacts yields the configuration and permutational entropy of every strain-free GSC.

We use IPE of \(N_m = f(N)\Omega(N)\) \(N\)-particle molecules as initial conditions for our MD simulations \cite{21}. These are performed using an in-house code that employs per-cluster parallelization. All particles have mass \(m\) and diameter \(D\). Each cluster is confined to a cubic cell with hard reflecting walls and side length \(L(N)\) chosen to give a particle number density \(\rho\) in the dilute limit \((\rho = N/L^3 = 0.01D^{-3})\). Thus while all particles in a given molecule interact via \(U_{MM}(r)\), different clusters do not interact with each other. This choice of simulation protocol and boundary conditions is motivated by the experiments \cite{3,4}, which also examined ensembles of isolated \(N\)-colloid systems in dilute solution. MD integration is performed using the velocity-Verlet algorithm with a timestep \(\delta t = 0.1\tau/\alpha\), where the unit of time is \(\tau = \sqrt{mD^2/\epsilon}\) \cite{22}. Temperature is controlled using a strong Langevin thermostat (with damping time \(\tau_{\text{lang}} = \tau\)) that mimics the strong damping experienced by colloids in a solvent. Comparing to experimental values \(\epsilon \approx 0.1eV, D = 1\mu m, m \approx 10^{-15} kg\) \cite{4} gives \(\tau \approx 10^{-4}s\). Our simulations extend as long as \(2.5 \cdot 10^5\tau\); this maps to \(25s\), which is comparable to the duration of a typical experiment \cite{4}.

Results of the exact enumeration study are shown in Table I. We report results for the total number of macrostates \(\mathcal{M}\), as well as the the numbers of macrostates with rhp (“Barlow” \cite{23}), stack-faulted, and five-fold symmetric structural motifs, as a function of \(N\) and \(N_c\). The latter three structural motifs are shown in Figure 2(a-c), preclude Barlow order, and thus correspond to “off-pathway” nuclei incompatible with close-packed crystallization. The fraction of “on-pathway” macrostates possessing Barlow order increases rapidly with increasing hyperstaticity \(H = N_c = N_{1SO}\), where isostatic packings have \(N_c = N_{1SO} = 3N - 6\). However, for the range of \(N\) considered here, many packings retain non-Barlow order for \(H\) as large as three. Many of these possess stacking faults; \(\mathcal{M}_{\text{stack-fault}}\) decreases with increasing \(H\) but remains nonzero for \(H\) up to three. Fivefold-symmetric motifs are highly prevalent.

![FIG. 1: Standard (red) and modified (blue) Morse potentials for \(aD = 150\). The inset highlights differences between \(U_{Morse}\) and \(U_{MM}\) for \(r \approx r_c\). For \(r \lessapprox r_c\), \(U_{MM}\) and \(U_{Morse}\) are essentially indistinguishable.](image-url)
in isostatic packings, and while their prevalence decreases rapidly with increasing $H$, they are still relevant motifs in these more-stable, lower-energy nuclei. Both stack-faulted and fivefold symmetric structures are known to play key roles in inhibiting crystallization in bulk particulate systems by promoting dynamical arrest and glass formation [24, 25].

The above results provide a potential explanation for the propensity of sticky hard sphere systems to jam and glass-form in both simulations and experiments [23, 26]. As discussed in Refs. [8, 19], high energy barriers are expected between off-pathway and Barlow-ordered nuclei since many bonds must be rearranged to change from one ordering to the other. The key parameter controlling the growth of ordered crystalline nuclei is thus the ratio of the particle attachment rate $r_a$ to the cluster reorganization rate $r_r$ [27]. When $r_a/r_r$ is large, the larger entropy $\frac{r_a}{r_r}$ of disordered (yet mechanically rigid) nuclei lacking close-packed order should promote growth of amorphous clusters. Conversely, when $r_a/r_r$ is small, enthalpy should rule, and close-packed nuclei will experience stable growth. Below, we examine these and other ideas via MD simulations.

The top panel of Figure 3 shows the eight degenerate GSCs for $N = 13$. Two are core-shell structures (respectively HCP and FCC) wherein a single center sphere contacts twelve neighbors, while the rest are irregularly shaped Barlow and stack-faulted clusters. The permutational entropies of these structures range over a factor of 48. In our simulations, to prepare for examination of nonequilibrium effects, IPEs were heated from

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**TABLE I:** Numbers of macrostates $\mathcal{M}$, macrostates with Barlow order $\mathcal{M}_{\text{Barlow}}$, stack faults $\mathcal{M}_{\text{stack-fault}}$, and fivefold-symmetric substructures $\mathcal{M}_{\text{fivefold}}$. Results for for $N \leq 11$ were reported in Ref. [8].

| $N$ | $N_c$ | $\mathcal{M}$ | $\mathcal{M}_{\text{Barlow}}$ | $\mathcal{M}_{\text{stack-fault}}$ | $\mathcal{M}_{\text{fivefold}}$ |
|-----|-------|----------------|-------------------------------|--------------------------------|-------------------------------|
| 12  | 30    | 11638          | 339                          | 8420                           | 6657                          |
| 12  | 31    | 174            | 77                           | 88                             | 16                            |
| 12  | 32    | 8              | 4                            | 4                              | 0                             |
| 12  | 33    | 1              | 1                            | 0                              | 0                             |
| 13  | 33    | 95799          | 1070                         | 69897                          | 53265                         |
| 13  | 34    | 1318           | 363                          | 859                            | 248                           |
| 13  | 35    | 96             | 42                           | 46                             | 8                             |
| 13  | 36    | 8              | 5                            | 3                              | 0                             |

The abovementioned trends are further reinforced by considering the fraction of microstates with these motifs. For motifs associated with a pattern $X$, we identify the fraction of microstates $f_X$ including these patterns via the values

$$\mathcal{M}_X(N, N_c) = \sum_{k=1}^{\mathcal{M}(N, N_c)} G_k(X),$$

reported in Table I where $G_k(X)$ is 1 if structure of the $k^{th}$ macrostate matches the pattern and 0 otherwise, and

$$f_X(N, N_c) = \Omega^{-1} \sum_{k=1}^{\mathcal{M}(N, N_c)} \omega_k G_k(X),$$

where $\{\omega\}$ and $\Omega$ are given by Equation II. The quantity $f_X$ corresponds to the total percentage of clusters in IPEs possessing motif $X$ (at $T = 0$). Figure 2 (bottom panel) shows $f_{\text{Barlow}}$, $f_{\text{stack-fault}}$ and $f_{\text{fivefold}}$ for $7 \leq N \leq 13$ and $0 \leq H \leq 3$. Notably, $f_{\text{Barlow}}$ for isostatic nuclei decreases monotonically with increasing $N$ to only about 1% for $N = 13$. This means that 99% of the highest-energy mechanically stable $N = 13$ nuclei are off-pathway, and nucleation of structures with Barlow order is likely to be a rare event. While $f_{\text{Barlow}}$ is far higher for hyperstatic ($H > 0$) nuclei, the same trend of decrease with increasing $N$ persists. In contrast, $f_{\text{stack-fault}}$ and $f_{\text{fivefold}}$ are relatively flat at 50 – 80% for isostatic nuclei in the range $10 \leq N \leq 13$, and while they decrease sharply with increasing $H$, still increase in hyperstatic systems to large values with increasing $N$.

The above results provide a potential explanation for the propensity of sticky hard sphere systems to jam and
FIG. 3: Top: The eight $N = 13$, $N_c = 36$ ground states. Labels above the structures indicate ordering (FCC, HCP, Barlow, or stack-faulted) and numbers below indicate relative permutational entropies. Bottom: Results from MD simulations for $N = 13$ Morse clusters: (Left) Mean cluster energy vs. reduced temperature for fast, medium, and slow quench rates from top to bottom. (Middle) The population fractions of each of the eight Morse clusters: (Left) Mean cluster energy vs. reduced temperature for fast, medium, and slow quench rates from top to bottom. (Middle) The population fractions of each of the eight $N = 13$ ground states at time $t$ after various quench simulations to their equilibrium predictions. Bottom: Results from MD simulations for $T = 0$ to $T = 2.5$ (well above the melting point) at a rate $\dot{T}^c = 10^{-5}/\tau$. The left panel shows results for the average molecular energy $\langle U(T) \rangle$ (from Eq. 3) for three quench rates: $|\dot{T}| = 10^{-3}/\tau$, $10^{-2}/\tau$, and $10^{-1}/\tau$. At the fastest quench rate, $\langle U(T) \rangle$ remains well above $-(N_{ISO})\epsilon$ even at $T = 0$ because systems freeze into multiple rather than single clusters. For the slower two quench rates, systems freeze into single clusters, but $\langle U(T) \rangle$ remains above $-36\epsilon$, indicating that many clusters freeze into mechanically stable excited states. The middle panel shows the population fraction $\omega_k/\Omega$ of these GSCs as a function of $T$ during the $|\dot{T}| = 10^{-5}/\tau$ quench; even at this low rate, about 2% of clusters remain in excited states at $T = 0$. The left edge of the panel compares the $\omega_k/\Omega$ from these quench simulations to their equilibrium $T = 0$ counterparts. The FCC and HCP clusters populate the quenched ensemble in excess at low $T$ because they form at slightly higher $T$, and as described below, rearrange more slowly. Conversely, the other clusters’ populations are somewhat lower than equilibrium predictions, showing that for this slow quench rate, clusters inhabiting deep, narrow wells on the potential energy landscape are favored, that is, on-pathway crystal growth is favored. Higher quench rates (not shown) reverse these trends.

It is also interesting to examine the traversal of clusters through their various GSCs at finite $T$. The right panel of Figure 3 shows the decorrelation $f_{mad}(t)$ of macrostates via state-to-state transitions (beginning from equilibrium ensembles) at various $T$ well below $T_{melt}$, as a function of time $t$. At high $T$, excitations from GSCs are very common, energy barriers are easily overcome, and relaxation is nearly exponential. As $T$ decreases, clear shoulders develop in $f_{mad}(t)$, and relaxation becomes very clearly non-exponential. One reason for this is that different GSCs possess different stability (i.e. lie in potential energy wells of different depths), and so decay at different rates. These varying decay rates are consistent with the abovementioned evolution of the population fractions during the quench. Another potential reason, which has been suggested by energy landscape analyses of related systems [2] and will be further examined in forthcoming work, is that these systems possess glassy dynamics.

In this Letter, we characterized the equilibrium and preparation-protocol-dependent structure and dynamics of small clusters interacting via hard-core-like repulsions and short-range attractions. Our results provide a theoretical framework for extending recent experimental studies [2] of small colloidal clusters to examine nonequilibrium phenomena. They should be relevant to understanding both the nonequilibrium self-assembly of such clusters as well as the role they play in the competing crystallization and glass transitions in bulk systems, and should ultimately be experimentally observable in real systems using plausible extensions of currently available experimental techniques [4, 11].

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\[ c(\alpha, b) = -[4^{-b}(2^{b+1} - 1)]\epsilon. \]

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\[ [15] \text{We define $b$ to produce a well controlled approximation in which} \lim_{b \to \infty} c(\alpha, b) = 0 \text{ and hence} \lim_{b \to \infty} U_{MM}(\alpha, b; r) = U_{\text{Morse}}(\alpha; r). \text{ Choosing} \]

\[ r_c(\alpha, b)/D = 1 + b(r^* - 1), \text{ where the attractive force} \]

\[ |dU_{\text{Morse}}/dr| \text{ is maximal at} r^*/D = (\alpha + \log(2))/\alpha, \text{ gives} \]

\[ \text{For} \ N \leq 13 \text{ systems and the form of} U_{MM} \text{ described herein,} \]

\[ \alpha_{\text{cons}}(N) < 30. \text{ Choosing} \]

\[ f(N) = 1 \text{ simply corresponds to multiplying the systems’ partition functions by a constant; its value should not (apart from statistical error) alter any results. Here} \]

\[ f(N) \text{ is chosen to be sufficiently large to give good statistics yet sufficiently small for computational tractability. For the} \ N = 13 \text{ systems studies here we employ} \]

\[ f(13) = 1/12972960, \text{ yielding} \]

\[ N_m(13) = \Omega(13)/12972960 = 1290. \]

\[ \text{We have verified} \]

\[ \delta t \text{ is sufficiently small by checking that the velocity autocorrelation function is insensitive to varying} \delta t \text{ over the range} \]

\[ [0.002\tau/\alpha, 0.007\tau/\alpha] \text{ in systems at} \]

\[ k_B T/\epsilon = 1. \]

\[ \text{We verified that these are near-equilibrium results by} \]

\[ \text{gradually decreasing $T_{eq}$ until} U(T) \text{ and} \]

\[ C_V(T) \text{ converged to within a few percent for the entire range of} \]

\[ T \text{ considered.} \]

\[ \text{Also see} \]

\[ \text{http://arxiv.org/pdf/1407.3289v1.pdf} \]