Sublattice Melting in Binary Superionic Colloidal Crystals

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(Dated: January 24, 2022)

We model binary colloidal crystals of oppositely charged nanoparticles, one large and one small, by controlling the ionic strength of the solution. The small particles undergo first order transitions from localized ionic compounds to delocalized states as temperature increases, showing sublattice melting in ionic colloids. In contrast to the fixed stoichiometric ratio in atomic compounds, the smaller particles hold the larger particles in crystal lattice positions with an adjustable stoichiometric ratio. This generates a coexistence of an ionically bonded stoichiometric phase with a non-stoichiometric phase where the small particles are melted and hold the large particles in crystal lattice positions. The coexistence of ionic-like bonding with metallic-like bonding provides a platform to create multicomponent colloidal assemblies with unexpected properties.

Crystalline colloidal assemblies of functionalized metallic or magnetic nanoparticles, nanodots or proteins are of great interest to various research fields [1–4]. Colloidal crystallization studies have served as experimental models to study phase behavior [5, 6] and self-assembly processes [7] akin to atomic and molecular systems. Unlike chemical compounds in atomic systems, colloidal assembly does not have constraints from the number, symmetry, or energy of orbitals. This significantly diversifies possible crystal structures. In the past few decades, several types of lattices of binary colloidal crystals have been prepared [8–10]. Experiments and computer simulations have shown that the size ratio [11] or charge ratio [10, 12] of the two components as well as the ionic strength in solution [10] are important factors that affect the assembled binary superlattices. Most of the work on binary charged colloidal crystals retain the restricted structures of classical atomic ionic compounds in which all particle positions are fixed.

In contrast, atomic “superionics” possess different kinds of structures and properties. In atomic superionics, due to the low energy barrier along cation migration paths [13], one of the components, termed the fast ion, is mobile and has a delocalized density distribution within the crystal lattice [13, 14]. Superionic phases have been found in other microscopic condensed systems such as ammonia [15] ice [15, 16], and polymers [17]. Here we explore the possibility of assembling superionic conductors in oppositely charged colloids without the charge neutrality restriction by tuning the salt concentration. That is, the charge neutrality restriction in traditional ionic and superionic atomic compounds can be removed in charged colloidal crystals in salt solutions [10, 18]. Moreover, the range of the interaction potential can be readily tuned by controlling the salt concentration in regimes where the Debye–Huckel approximation is valid [12, 18]. Therefore, if the superionic phase exists in charged colloidal crystals, the advantage of less stringent stoichiometry requirements in these systems may substantially expand the scope of colloidal crystal engineering and superionic materials.

Recently, a related superionic phase has been predicted in binary colloidal mixture of large DNA-functionalized gold nanoparticle (DNA-AuNP) and complementary small DNA-AuNPs that hybridize only to the large DNA-AuNPs [19]. The small DNA-AuNPs, when grafted with only a few DNA strands, become diffusive in the crystal of the large DNA-AuNPs. As the number of small to large DNA-AuNPs increases, the degree of delocalization increases. Only smooth variations in lattice spacing and diffusivity going from ionic-like to metallic-like bonding were predicted and many predictions were not collaborated due to experimental limitations in controlling the DNA hybridization in small DNA-AuNPs [19]. Here, we find a sharp transition from ionic to superionic phases in charged colloidal mixtures characterized by a discontinuous jump in the lattice spacing and in the diffusion coefficient as temperature increases, both properties accessible experimentally, as well as by the double-well shape of the free energy landscape. Moreover, we find regions of coexistence between phases such as ionic-like phases of different stoichiometry at low temperatures and ionic-like phases coexisting with superionic-like phases at intermediate temperatures, which we analyze by examining defects and the time average density of the small particles (TAMD) [20]. Finally, we show that the attractions provided by the small particles in the superionic-like phases are not depletion type interaction.

We analyze the nature of the transition from ionic-like phases to superionic-like phases by molecular dynamics (MD) simulations. We consider binary colloidal mixtures in salt solutions where the two types of colloids have charges of opposite signs. Since ionic colloidal mixtures...
with components of similar sizes are not expected to show superionic phases, we concentrate on binary charged colloids whose components differ in size substantially. In the MD simulations, both large particles (A) and small particles (B) were modeled as hard spheres with isotropic charged surfaces. The co-ions and counterions are accounted implicitly by applying the Debye-Hückel approximation, which functional form describes well charged nanoparticle pair potentials at salt concentrations up to roughly 300 mM of NaCl [21]. Particle interactions consists of two parts: one is the excluded volume effects given by the Weeks-Chandler-Andersen (WCA) potential with energy scale $\epsilon = 1.0$ and cutoff distance $r_{\text{cut}}^{ij} = 2^{1/6} \sigma_{ij}$, where $\sigma_{ij}$ is pair-dependent and is calculated from the Lorentz-Berthelot mixing rules $\sigma_{ij} = R_i + R_j$; the other one is the screened Coulombic interactions given by the hard-core Yukawa potential:

$$U_{\text{Yukawa}}(r_{ij}) = \frac{q_A q_B e^{-\kappa (r_{ij} - R_i - R_j)}}{(1 + \kappa R_i)(1 + \kappa R_j)r_{ij}}.$$  

(1)

Here the radii of the two species were fixed at $R_A = 5\sigma$ and $R_B = 1\sigma$, where $\sigma$ is the unit length in MD simulations. The impact of screening strength $\kappa$, charge ratio $q_B/q_A$, number ratio $N_B/N_A$ and temperature are explored in this work.

A zero pressure isobaric-isothermal (NPT) ensemble simulation is used to quickly test if there is a stable solid state and estimate the equilibrium density and other properties of that state. Large particles are initialized in perfect face centered cubic (FCC) crystal positions in a periodic cubic box, with small particles randomly placed throughout the lattice while avoiding strong overlap. The number of crystal unit cells in each direction is 6. The system is first thermalized in the canonical (NVT) ensemble with a Langevin thermostat. Then the simulation box size is slowly decreased until the volume fraction of large particles is slightly smaller than the closest packing value, 74%. After the system is equilibrated for $10^6$ timesteps, it is switched to the isobaric-isothermal (NPT) ensemble with a large enough external pressure to keep the system compressed and run for another $10^6$ timesteps. The pressure is subsequently relaxed to exactly 0 and the system is further equilibrated for $10^7$ timesteps. The system remains in a sufficiently stable condensed phase if there is one, otherwise the system would expand in principle to an infinite size since zero density is exactly the equilibrium density corresponding to zero pressure [22]. The cubic symmetry of simulation box is maintained during the run.

We first investigate under what salt conditions a stable colloidal crystal can form. When the salt concentration is low, we assume the colloidal crystals have to be charge-neutral because of insufficient screening from implicit ions. In the simulation we chose $\kappa \sigma = 0.1$, and fixed the charge on large particles at $q_A = -10e$. The charge on small particles was then determined based on the number ratio by $q_B = -q_A N_A / N_B$. We tested $N_B/N_A = 1, 2, 4, 8$, but all attempts resulted in rapid expansion of the simulation box and colloidal particles melting into the gas state as pressure was relaxed to zero, even at low temperature $T = 0.1$ (Fig. 1A). Although the formation of colloidal crystals via Yukawa potential has been proved to be viable in theory [23], it is not observed in our simulations. The reason might be that the Yukawa potential is weak compared to Coulombic interactions, hence the cohesive energy is not large enough to fight against the fluctuation toward expansion to larger volumes (which means larger entropy) in zero-pressure NPT simulations. Entropic effects then dominate and this results in an equilibrium gas state where large particles stay far apart with small particles surrounding each of them. On the contrary, when the salt concentration is high, strong screening allows us to circumvent the charge-neutral restriction and decouple $q_B$ from $N_B/N_A$. We explore this regime by fixing $\kappa \sigma = 0.7$, $q_A = -10e$, $N_B/N_A = 8$, $T = 0.3$, and increased the magnitude of $q_B$ to induce the aggregation between large and small particles. Results show that when $q_B \geq +3e$, the simulation box is able to maintain a finite size during the entire simulation and the equilibrium state of system is no longer a gas state but a crystal state stabilized by the attraction between the two species. When $q_B$ is

![FIG. 1](image-url) (A) The melting process of charge-neutral systems ($\kappa \sigma = 0.1$) as pressure approaches 0 in MD simulations. The simulation box is expanding to infinity simultaneously. (B) The simulation box size under different small colloid charge ($q_B$) when charge neutrality restriction is removed ($\kappa \sigma = 0.7$), which shows two distinct phases: sublattice-molten (superionic) and sublattice-frozen (ionic).
about $+3\epsilon$ or $4\epsilon$, the attraction strength is large enough to hold the large particles on a FCC lattice, yet small enough that the small particles are not trapped in interstitial positions and can diffuse throughout the lattice, leading to a superionic structure; further increasing $q_B$ enhances the attraction that freezes the small particles into a fixed sublattice, yielding the “sublattice molten-frozen” transition (Fig. 1B).

By simulating the heating process of the system we reveal that this transition is a first order phase transition at the number ratio $N_B/N_A = 8$. To characterize the transition temperature, we chose the equilibrated size of the simulation box to be the order parameter, which is approximately six times of the lattice constant when large particles (A) remain stable on the lattice. After equilibrium, we calculated the diffusion coefficient of small particles (B) from the mean-square-displacement (MSD) $\langle r(t)^2 \rangle$ over $5 \times 10^6$ timesteps using $D = \langle r(t)^2 \rangle / 6t$. Heating curves of different number ratios $N_B/N_A$ (Fig. 2A) show that the lattice monotonically expands as temperature increases, however, at $N_B/N_A = 8$ the expansion is discontinuous at a certain temperature ($T = 0.68$). The jump in the magnitude of the order parameter corresponds to the sublattice melting of small particles, which also indicates that this melting is a first order phase transition. $N_B/N_A = 8$ is a special number ratio because the interstitial positions in FCC crystals are the $32f$ Wyckoff positions, whose number is eight times larger than the number of large particles. At these positions, small particles attach to both sides of the triangular voids formed by large particles in order to maximize the attraction. Thus in low temperature regime adding more small particles ($N_B/N_A$ increasing from 5 to 8) can hold large particles tighter and hence a decrease in lattice constant, as shown in Fig. 2A. At $N_B/N_A = 8$, small particles fulfill all $32f$ positions and can barely move within the lattice. The system is frozen in the most enthalpically-favorable ionic state until temperature reaches high to drive it to entropically-favorable superionic state by expanding the lattice spacing to create channels for small particles previously trapped in the $32f$ positions to diffuse. This results in a more delocalized small particle density distribution and a rapid increase in diffusion coefficient at the transition point (Fig. 2B). The “ionic-superionic” transition is continuous at other number ratios $N_B/N_A \leq 8$ because the movement of small particles in those systems does not require the lattice expansion. Instead, small particles can hop to neighboring vacant interstitial positions regardless of the compactness of system [13, 24]. The existence of hopping in ionic phases greatly reduces the entropic advantage of superionic phases and the driving force for a sudden lattice expansion. Therefore we only observed a natural smooth thermal expansion and a continuous melting process.

At $N_B/N_A = 9$ we observe the coexistence of two phases with different stoichiometric ratios. To determine the stoichiometric ratios, we divided the simulation box into $12 \times 12 \times 12$ cubic bins (each cube is $1/8$ the volume of the FCC unit cell). After equilibrium, the average number of small particles in each cube $N_B^{\text{local}}$ was counted from 1000 frames taken every 5000 timesteps and local number ratio is then given by $N_B/N_A = 2N_B^{\text{local}}$ as one cube has $1/2$ particle As. The histogram of $N_B^{\text{local}}$ at different temperatures combined with corresponding simulation snapshots (Fig. 3) show that at $T = 0.2$ the system is in the ionic state, but the two peaks located at $N_B^{\text{local}} = 4.0$ and $N_B^{\text{local}} = 5.0$ indicate that in fact there are two separate phases with stoichiometric ratios $N_B/N_A = 8$ and $N_B/N_A = 10$, respectively. When temperature is increased to 0.4 the $N_B/N_A = 10$ phase melts into the superionic phase and thus we see an ionic phase with $N_B/N_A = 10$ coexisting with a superionic phase with an undefined stoichiometric ratio. Further increasing temperature melts the sublattice in the $N_B/N_A = 8$ phase and the whole system forms a homogeneous superionic phase with $N_B/N_A = 9$. This is because after fulfilling the $32f$ Wyckoff positions, additional small particles can stabilize in the 8c positions which are twice as many as large particles, forming the $N_B/N_A = 10$ ionic phase, however, this phase is only stable at low temperature because the 8c positions have higher energy than the $32f$ positions. From the phase

![FIG. 2. (A) Heating curves of the box size under different number ratios $N_B/N_A$. $q_A = -10\epsilon$, $q_B = +8\epsilon$, $\kappa\sigma = 0.7$. (B) Comparison of the box size and diffusion coefficient of small particles at $N_B/N_A = 8$.](image-url)
coexistence it is clear that the most stable stoichiometry for the ionic phase in FCC crystals is \( \frac{N_B}{N_A} = 8 \), but the existence of such an optimal stoichiometric ratio for the superionic phase is uncertain. Revealing it is a subject of future work involving equal chemical potential simulations.

The relative Helmholtz free energy landscapes were calculated by thermodynamical integration methods and midpoint approximation was used to numerically evaluate the integrals:

\[
F_{rel}(V) = -\int_{V_0}^{V} PdV \approx -\sum_i (P_{i+1} + P_i)(V_{i+1} - V_i)/2
\]

A series of NVT simulations with a Langevin thermostat were done for different volumes \( V_i \) at \( \frac{N_B}{N_A} = 8 \). The system was first initialized in the same way as in previous NPT simulations. After thermalized in NVT ensemble with a Langevin thermostat in a large simulation box for \( 10^6 \) timesteps, the simulation box was deformed to the volume \( V_i \) and further equilibrated \( 10^7 \) timesteps to obtain the corresponding ensemble averages of pressure \( P_i \). Figure 4 shows that at either low (\( T = 0.3 \)) or high temperature (\( T = 0.8 \)), the free energy has only one minimum in the compact state, marking the ionic and superionic phases, respectively. The double-well shape around transition temperature (\( T = 0.68 \)) again proves that the sublattice melting is a first order phase transition when the system is at the optimal stoichiometry. Volumes at the free energy minima match well with the equilibrium volumes obtained in previous NPT simulations, although when there are double wells, NPT simulations tend to sample the state with smaller volume because we initialized the system in denser configurations.

Depletion force is widely recognized as the driving force for assemblies in mixtures of colloidal particles with different sizes [11, 25], but we clarify that it is not important in stabilizing the superionic structures and the depletion force applied by small particles is not responsible for holding large particles on site after the B-sublattice melts, either. First, in our system we do not have explicit salt which can cause depletion attraction between charged nanoparticles [21]. Second, depletion effect is significant when a large size difference exists [25], where larger particles aggregate in order to create more free space for smaller particles. Hence this effect is entropy-driven and should be enhanced by increasing temperature. However in our simulations, all colloidal crystals melt into gas phases when temperature is further in-

**FIG. 3.** Phase coexistence in the system with \( \frac{N_B}{N_A} = 9 \). (Top) The histogram of average number of small particles in sub-unit cubic bins at different temperatures \( T = 0.2, 0.4, \) and 0.6. Each cube has a size of 1/8 FCC unit cell. \( N_c \) is the number of cubes. (Bottom) Snapshots of the equilibrium distribution of small particles at \( T = 0.2 \) (left), 0.4 (middle), and 0.6 (right).

**FIG. 4.** Calculations of relative Helmholtz free energy using thermodynamical integration methods at \( \frac{N_B}{N_A} = 8 \). (Top) Overall free energy landscapes at \( T = 0.3, 0.68, \) and 0.8. The reference volume \( V_0 \) is \((88\sigma)^3\) for all three temperatures. (Bottom) Locations of free energy minima. The reference volumes are \((89\sigma)^3\) for \( T = 0.3 \), \((90.5\sigma)^3\) for \( T = 0.68 \), and \((96\sigma)^3\) for \( T = 0.8 \). Black arrows mark the state sampled by previous NPT simulations.
increased up to 1.3, indicating that the stability of the superionic state is not enhanced at high temperature and thus cannot be entropy-driven. Third, because the box size is not constrained in our zero pressure NPT simulation, the system is supposed to expand infinitely if it was favorable to add more free volume for the small particles, but instead the system is equilibrated at a finite size \( L \) (see Fig. 2A). The average distance between two neighboring large particles \( d \) can be calculated by \( d = L/6\sqrt(2) \). In our simulation, it satisfies \( 2R_A < d < 2\sigma_{AB} \) where \( \sigma_{AB} = R_A + R_B \). \( 2R_A, 2\sigma_{AB} \) in fact is the regime where depletion effects can exist. However, in this regime the free volume for the B particles \( V_{free} \) as a function of \( d \) in the FCC structure is given by \( V_{free}(d) \propto d^3-2\pi(R_A+R_B)^3/3+\pi(R_A+R_B-d/2)^2(4(R_A+R_B)+d) \) which monotonically increases in \( (2R_A, 2(R_A+R_B)) \). Thus the colloidal superionic structure is not stabilized at any local maximum of \( V_{free} \). These observations elucidate the crucial contribution of appropriate attraction strength in stabilizing colloidal superionic structures.

To conclude, we have identified a superionic-like crystal structure in size-asymmetric charged colloidal systems where the smaller particles lose long-range order and become diffusive holding the larger component on a crystalline lattice via electrostatic interactions. By cooling down the system, the small mobile particles condense to interstitial positions, resulting in an ionic-like structure. At the stoichiometric ratio where the number of small colloids equals the number of interstitial positions, this colloidal “superionic-ionic” transition is demonstrated to be first order by the discontinuous change in lattice constant and the double-well shape in the free energy landscape. The addition of more small colloids inside the lattice leads to the coexistence of “ionic-like” and “superionic-like” phases. This coexistence state of the system may provide new insights for growing heterostructures. Overall, our findings provide guidelines to assemble metallic or superionic conductor colloidal crystals and set up the foundation for discovering new and exciting properties and functions of multicomponent colloidal crystals.

Acknowledgement: This work has been funded by NSF DMR Award No. 1611076. We thank Wei Li for helpful discussion. We also thank the computational support of Sherman Fairchild Foundation.

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