“Colloid–Atom Duality” in the Assembly Dynamics of Concave Gold Nanoarrows

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ABSTRACT: We use liquid-phase transmission electron microscopy (TEM) to study self-assembly dynamics of charged gold nanoarrows (GNAs), which reveal an unexpected “colloid–atom duality”. On one hand, they assemble following the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory for colloids when van der Waals attraction overruns slightly screened electrostatic repulsion. Due to concaveness in shape, GNAs adopt zipper motifs with lateral offset in their assembly matching with our modeling of inter-GNA interaction, which form into unconventional structures resembling degenerate crystals. On the other hand, further screening of electrostatic repulsion leads to merging of clusters assembled from GNAs, reminiscent of the coalescence growth mode in atomic crystals driven by minimization of surface energy, as we measure from the surface fluctuation of clusters. Liquid-phase TEM captures the initial formation of highly curved necks bridging the two clusters. Analysis of the real-time evolution of neck width illustrates the first-time observation of coalescence in colloidal assemblies facilitated by rapid surface diffusion of GNAs. We attribute the duality to the confluence of factors (e.g., nanoscale colloidal interaction, diffusional dynamics) that we access by liquid-phase TEM, turning takes to dominate at different conditions, which is potentially generic to the nanoscale. The atom aspect, in particular, can inspire utilization of atomic crystal synthesis strategies to encode structure and dynamics in nanoscale assembly.

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and 84 nm, respectively) and varying minimum. (e) The calculated Movie S2. Inset schematic de.

repulsion (with the zipper motif. The weak attraction strength (\(E_{\text{vdW}}\) and electrostatic repulsion (\(E_{\text{el}}\) \(E = E_{\text{vdW}} + E_{\text{el}}\) following DLVO theory) as a function of different pairing configurations. As shown in Figure 1d, \(E\) has a minimum at \(\Delta x = 66\) nm and \(\Delta y = 29\) nm, matching with the zipper motif. The weak attraction strength (\(\sim 0.5 k_B T\)) suggests thermal fluctuations are sufficient to overcome the net inter-GNA attraction, consistent with our experimental observation of dynamic assemblies. The concaveness accounts for the misalignment, consistent with previous studies illustrating the role of surface curvature in dictating assembly; conversely, when we consider hypothetical flat GNAs (f-GNAs, Figure S1c) with a cuboidal body (no concaveness) while keeping all the other features the same, the minimum of \(E\) occurs at \(\Delta y = 0\) nm with no offset (Figure 1e).

The zipper motif is essential to further assemble into unexpected structures resembling degenerate crystal (DC). The three preferred alignments of the GNAs (Figure 2a) and connections (Figure 1b). The tracked nearest neighboring distances \(r_{nn}\) of all the GNAs in the view average at a finite length of 82.8 nm (Figure S2a–b), confirming net inter-GNA attraction despite fast shuffling of GNAs. As an example, the distance between GNAs 1 and 2 (labeled in Figure 1b) fluctuates between 80.3 and 91.5 nm (Figure S2c), suggesting dynamic reorganization, differing from irreversible aggregation in previous liquid-phase TEM studies.

Statistical tracking of the configurations of a connected GNA pair shows single-peaked distribution of the \(\Delta x\) spacing (averaged at 65.9 nm, defined as the distance between the centroid of one GNA and the long axis of the other GNA) and the \(\Delta y\) offset (averaged at 30.1 nm) along the long axis of parallel GNAs (Figure 1c), favoring the “zipper” motif.

Our interaction modeling elucidates the key role of local concaveness generic to the GNA shape in favoring the dynamic “zipper” motif. Using a three-dimensional (3D) discretized model built on the measured shape descriptors (Figure S1b–c), we compute the pairwise interparticle interaction \(E\) from the interparticle van der Waals attraction (\(E_{\text{vdW}}\)) and electrostatic repulsion (\(E_{\text{el}}\) \(E = E_{\text{vdW}} + E_{\text{el}}\) following DLVO theory) as a function of different pairing configurations. As shown in Figure 1d, \(E\) has a minimum at \(\Delta x = 66\) nm and \(\Delta y = 29\) nm, matching with the zipper motif. The weak attraction strength (\(\sim 0.5 k_B T\)) suggests thermal fluctuations are sufficient to overcome the net inter-GNA attraction, consistent with our experimental observation of dynamic assemblies. The concaveness accounts for the misalignment, consistent with previous studies illustrating the role of surface curvature in dictating assembly; conversely, when we consider hypothetical flat GNAs (f-GNAs, Figure S1c) with a cuboidal body (no concaveness) while keeping all the other features the same, the minimum of \(E\) occurs at \(\Delta y = 0\) nm with no offset (Figure 1e).

The zipper motif is essential to further assemble into unexpected structures resembling degenerate crystal (DC). The three preferred alignments of the GNAs (Figure 2a) and triangular ordering (see the labeled GNA lobes in Figure 2b) are typical of a DC structure, potentially allowing for polarization control of incident light. The 6-fold bonding symmetry of each lobe \(j\) measured using the modulus bond-orientational...
order parameter \( |\psi_{ij}| \) shows a consistent high order spanning the whole structure (Figure 2b). This periodicty of DC structure can produce diffractive waves by GNAs scattering light, which can narrow plasmon resonances for applications in optoelectronics, photovoltaics, and biosensing.\(^{41,42}\) Besides the specific zipper motif favored at \( I = 6.4 \, \text{mM} \) (Figure S2d), another “boomerang” motif (\( \Delta \beta = 60^\circ, \Delta x = 94.2 \, \text{nm}, y' = 18.1 \, \text{nm} \)) defined in Figure 2c) is also essential for the DC-like structure to form. Our calculated pairwise interaction \( E \) for a GNA pair at fixed \( \Delta \beta \) and \( \Delta x \) (Figure 2c) reaches its minimum at \( y' = 19 \, \text{nm} \), validating the enthalpic preference for the boomerang motif.

The concaveness in our GNAs allows for a wide range of interaction tunability: at \( I = 120 \, \text{mM} \), GNAs are further screened electrostatically and exhibit a surprising coalescence growth analogous to that in atomic crystallization. Interaction modeling rationalizes that GNAs assemble into clusters of various motifs (Figure 3c). At low GNA concentration, the clusters are small (<30 GNAs), diffusing and rearranging quickly as a whole after coalescence (Movie S3, Figure 3a–b). In comparison, at high GNA concentration, the clusters are large (>100 GNAs) and diffuse slower than the small clusters,\(^{72}\) exhibiting the formation of a neck as some surface GNAs of the two clusters come into physical contact (Movie S4).

New surfaces are formed at the neck periphery of high curvature (Figure 3d–f). The neck’s apexes are tracked over time \( t \) with the interapex distance measured as the neck width \( d_{\text{neck}} \). In atomic crystallization, volume diffusion and surface diffusion of atoms are the dominant mass transport paths during coalescence. We measure a power law of \( d_{\text{neck}} \sim \rho^{0.34} \) (Figure 4a), indicating surface diffusion \( (d_{\text{neck}} \sim \rho^{0.18}) \) as predicted by the classical continuum theory.\(^{34,44}\)

Coalescence is usually attributed to the minimization of the free energy by reducing surface area. Indeed, the upper contour of the coalescing neck (Figure 4b) shows a decrease in the high-curvature regions, while regions of low curvature remain (Figure 4c). The curvature–growth rate histogram (Figure 4d) shows a positive interrelation of these two factors, consistent with a curvature-dependent flattening effect to minimize surface area.\(^{45}\) We measure the surface energy gain for coalescence following a capillary wave theory (CWT) \(^{46}\) (Supporting Information), which describes how thermal fluctuation equilibrates with surface energy in defining the spatiotemporal fluctuation of a surface. Specifically, we track the regional surface profile of a cluster (Movie S5, Figure 4e), from which we derive a height function \( h(x, t) \). The height function is then decomposed into a series of sinusoidal waves of wave vector \( k \), based on which we verify that the squared time-averaged Fourier coefficient \( \langle |A(k)|^2 \rangle \) fits with \( k^{-2.2} \) (Figure 4f), consistent with the prediction of CWT \( ((|A(k)|^2) \sim k^{-2}) \). This applicability of CWT allows us to calculate the surface energy as \((1.26 \pm 0.02) \times 10^{-13} \, \text{J/m} \) (Figure S3). That our observation of the neck formed during coalescence starts from \( d_{\text{neck}} = 104 \, \text{nm} \), corresponding to a surface energy gain of 3.2k_B T, sufficient for coalescence to happen.

We attribute the observation of such coalescence behavior in GNAs to the faster diffusion of nanoparticles than that of micron-sized colloids, which makes it hard for micron-sized colloids to exhibit a similar collective mass transport. In fact, the diffusion dynamics can be regulated by particle–substrate interaction for solvent-evaporation-driven or templated assemblies. For example, Figures S4 and S5 show that the same GNAs can exhibit suppressed motions at a lower \( I \) following Langmuir-like adsorption on the SiN membrane. The “colloid–atom duality” illustrated here suggests that modification of diffusional dynamics of nanoparticles could facilitate atom-resembling behaviors as an unexplored playground in nanoscale assembly, offering more routes toward diverse functional and reconfigurable structures.\(^{37,48}\)
Materials and Methods, Image and Data Analysis, Interaction Modeling, Figures S1–S5, Supplementary Movie Legends, and Supplementary References (PDF)

Movie S1: Liquid-phase TEM movie showing the zipper motifs of GNAs assembled at 1 = 6.4 mM. Dose rate: 7.4 e− A−2 s−1. The movie is played at 8 fps, real time. Scale bar: 100 nm. (AVI)

Movie S2: Synchronized movie including liquid-phase TEM movies of the self-assembly of GNAs into 2D degenerate crystal-like structure marked with single GNA orientation $\tilde{\beta}$ (top left) and the local modulus bond-orientational order parameter $|\psi|_{ij}$ (top right), and the corresponding standard deviation of the histogram of GNA orientations and the ensemble averaged local structure order parameter $|\psi|_{ij}$ vs time $t$ at 1 = 6.4 mM. Dose rate: 7.4 e− A−2 s−1. The movie is played at 2 fps, 0.25× real time. Scale bar: 100 nm. (AVI)

Movie S3: Liquid-phase TEM movie showing the coalescence of two small clusters assembled from GNAs, at low GNA concentration at 1 = 120 mM. Dose rate: 12.9 e− A−2 s−1. The movie is played at 8 fps, real time. Scale bar: 100 nm. (AVI)

Movie S4: Liquid-phase TEM movie showing the coalescence of the two large clusters at a high GNA concentration at 1 = 120 mM. The contours are colored to the local curvature $\kappa$. Dose rate: 12.9 e− A−2 s−1. The movie is played at 8 fps, real time. Scale bar: 100 nm. (AVI)

Movie S5: Liquid-phase TEM movie showing the fluctuating surface (highlighted by yellow) of a cluster at a high GNA concentration at 1 = 120 mM. Dose rate: 12.9 e− A−2 s−1. The movie is played at 8 fps, real time. Scale bar: 100 nm. (AVI)