Structural Color of Colloidal Clusters as a Tool to Investigate Structure and Dynamics

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Colloidal assemblies have applications as photonic crystals and templates for functional porous materials. While there has been significant progress in controlling colloidal assemblies into defined structures, their 3D order remains difficult to characterize. Simple, low-cost techniques are sought that characterize colloidal structures and assist optimization of process parameters. Here, structural color is presented to image the structure and dynamics of colloidal clusters prepared by a confined self-assembly process in emulsion droplets. It is shown that characteristic anisotropic structural color motifs such as circles, stripes, triangles, or bowties arise from the defined interior grain geometry of such colloidal clusters. The optical detection of these motifs reliably distinguishes icosahedral, decahedral, and face-centered cubic colloidal clusters and thus enables a simple yet precise characterization of their internal structure. In addition, the rotational motion and dynamics of such micrometer-scale clusters suspended in a liquid can be followed in real time via their anisotropic coloration. Finally, monitoring the evolution of structural color provides real-time information about the crystallization pathway within the confining emulsion droplet. Together, this work demonstrates that structural color is a simple and versatile tool to characterize the structure and dynamic properties of colloidal clusters.

1. Introduction

Colloids have a rich phase behavior that includes gels, glasses, and crystalline structures in two and three dimensions.

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interface in emulsion droplets then imposes internal elastic strain, which induces characteristic defects and enforces deviations from the fcc structure.\cite{13,46–48} Small clusters with less than a few hundred colloidal particles assemble into structures with varying geometry dictated by packing constraints at the droplet interface.\cite{49–51} Medium-size clusters with between a few hundred and about 10 000 colloidal particles favor icosahedral symmetry.\cite{13,52} These clusters can be particularly well-ordered near characteristic “magic” particle numbers that afford systems with closed icosahedral shells.\cite{15,16} In between magic numbers for icosahedral clusters, decahedral clusters can be observed.\cite{53,54} Ultimately, above $10^5$–$10^6$ constituent particles, clusters recovers the fcc structure of the bulk, possibly with the presence of stacking faults (ABA stacking instead of ABC stacking).\cite{12,33} Besides crystalline colloidal clusters, spherical colloidal clusters with onion-ring-like layers near the confining surface and a more disordered interior also occur and are in fact more common.\cite{19,36–38} These clusters form if liquid is removed too fast from the emulsion droplet for the system to reach thermodynamic equilibrium.\cite{16}

Both crystalline and spherical colloidal clusters give rise to structural color from diffraction of white incident light. While the structural color motif of spherical colloidal clusters, typically known as photonic balls,\cite{19,55} is isotropic because of its layer-like interior structure, the presence of grains in a crystalline cluster gives rise to an anisotropic structural color motif. Here, we demonstrate the utility of structural color to rapidly and reliably infer the internal cluster structure. The anisotropic nature of crystalline colloidal clusters allows following their rotational motion, which in turn provides important information about cluster interactions, the presence of flow fields and external forces. We also reveal details of colloidal crystallization by recording the evolution of structural color during the self-assembly process. Our results demonstrate that structural color imaging is a low-cost, versatile imaging tool that only requires an optical microscope in reflection mode.

2. Structure of Crystalline Colloidal Clusters

We synthesize negatively charged polystyrene (PS) colloidal particles with sizes between 190 and 244 nm by surfactant-free emulsion polymerization with acrylic acid as comonomer.\cite{56} These sizes are chosen to give structural color in the visible range.\cite{23} Next, we use droplet-based microfluidics\cite{19,57} with a PDMS microchip to fabricate emulsion droplets (size range 25 to 50 µm) of an aqueous colloidal dispersion in a continuous fluorinated oil phase. The emulsions are kept in glass vials with excess oil. As water slowly diffuses through the droplet interface into the oil phase, the droplet volume reduces. Eventually, the encapsulated PS colloidal particles consolidate into a compact colloidal cluster suspended in the oil phase. We vary the drying speed by controlling the opening of the storage glass vials, which regulates water evaporation to the ambient environment.

Fast droplet drying results in spherical clusters with a hexagonally close-packed monolayer of colloidal particles containing grain boundaries\cite{48} at the cluster surface.\cite{19,36,37} Commonly, a few concentric monolayers are stacked near the surface, forming onion-ring-like shells.\cite{19} Upon illumination, the periodicity of these stacked monolayers generates structural color when the size of the colloidal particles matches the constructive interference conditions with visible light. As a result of the spherical symmetry, such clusters show an isotropic color motif consisting of a colored circle at the cluster center when observed in a microscope.\cite{19,37} With decreasing drying speed, the system can equilibrate into its minimum energy configuration. Upon reaching a critical packing fraction, the colloidal particles undergo a phase transition from a fluid into a crystalline cluster,\cite{16,38} where symmetry is dictated by system size. Smaller numbers lead to icosahedral clusters, while larger numbers favor fcc clusters.\cite{33} Decahedral clusters occur less frequently and are irregularly distributed over a broad range of sizes.\cite{53} Before describing the observed, anisotropic structural color motifs resulting from these defined, crystalline colloidal clusters, we first introduce the sphere packing models describing the 3D structures of the different clusters (Figure 1).

The sphere packing model of a large icosahedral cluster (Figure 1a) is based on a Mackay icosahedron\cite{58} (upper inset), which consists of 20 slightly deformed tetrahedral fcc grains, each twinned at three faces with neighboring grains. The sharp vertices in the Mackay icosahedron are incompatible with the confined self-assembly in an emulsion droplet. Surface tension favors a spherical shape of the assembly. To mimic this effect, we apply spherical truncation that removes all spheres whose distance to the model center is larger than the truncation radius (lower inset, removed spheres are transparent). Spherical truncation results in a quasispherical cluster shape that exhibits the characteristic features of an icosahedral cluster. Twenty hexagonally close-packed {111} patches surround twelve fivefold symmetric axes at the cluster surface. In an SEM image of a complete icosahedral cluster (Figure 1b), five {111} patches surround a fivefold axis at the surface, in agreement with the model. We previously characterized the 3D structure of smaller icosahedral colloidal clusters by electron tomography, which confirmed that the crystal structure follows the truncated Mackay icosahedron model.\cite{16} The clusters in Figure 1 are larger and cannot be penetrated by electron beams. We therefore resort to a simpler method to reveal their interior structure. We ultrasonicate the dispersion containing the clusters and examine their fractured remains. A broken piece of an icosahedral cluster contains remains of six tetrahedral grains (Figure 1c). The model opened at a similar fracture point (inset) matches the experimental fracture surface.

The sphere packing model of a decahedral cluster (Figure 1d) is based on a pentagonal bipyramid, which consists of five slightly deformed tetrahedral fcc grains (upper inset), each twinned with two of its neighbors.\cite{59,60} These grains are slightly deformed in comparison to the ideal fcc lattice. While {111} planes form an angle of $\cos(1/3) = 70.5^\circ$ in the fcc lattice, the dihedral angle of grains in the decahedral cluster is $360^\circ/5 = 72^\circ$. The surface of the truncated structure (lower inset) exhibits ten {111} patches in direction of the face normals of the pentagonal bipyramid, five each in the upper and lower hemisphere, forming two rings surrounding the sole fivefold axis. Perpendicular to this axis, five square-packed {100} patches are found. The model is rotated to facilitate comparison with an experimental cluster in Figure 1e. In the SEM image, only one region with fivefold symmetry identified...
by the presence of five \{111\} patches surrounding a fivefold vertex is visible at the cluster surface. The remaining structure has alternating \{100\} and \{110\} patches perpendicular to the fivefold axis. The absence of other regions with fivefold symmetry is the main difference to the icosahedral cluster. The interior of a fractured decahedral cluster reveals two \{111\} planes joined at an angle (Figure 1f). Its structure agrees well with a constructed decahedral model from three tetrahedral grains with 144° dihedral angle (inset).

The sphere packing model of an fcc cluster (Figure 1g) is based on a single-crystalline octahedron-shaped grain without deformation, twinning, or stacking fault (upper inset). The octahedron has eight faces, which, after spherical truncation (lower inset) are converted to eight \{111\} patches. The six vertices of the octahedron are truncated to reveal six \{100\} patches. Truncating the twelve edges reveals \{110\} patches. The surface features of an fcc cluster in SEM are alternating \{111\} and \{110\} patches (Figure 1h, details in Figure S1 in the Supporting Information). A fractured fcc cluster (Figure 1i) shows a highly crystalline interior consisting of a single grain in agreement with the model (inset and Figure S2 in the Supporting Information).

### 3. Anisotropic Structural Color Motifs of Colloidal Clusters

We now analyze the structural color motifs of the three crystalline clusters with an optical microscope in reflection mode. Structural color is predominantly observed whenever a \{111\} plane is oriented perpendicular to incident light so that light reflected from the colloidal cluster is recollected by the objective lens. Only lightwaves that match the Bragg condition interfere constructively, thus producing structural color with wavelength determined by the size and refractive index of the colloidal particles. We now analyze colloidal clusters to identify crystal planes matching this condition and subsequently correlate the model structure to the observed color motifs.

#### 3.1. Fcc Colloidal Clusters

The model of an ideal fcc cluster without defects is a single fcc grain (Figure 2a). A few hexagonally close-packed \{111\} layers at the top (green) are lifted for illustration. All \{111\} layers throughout the cluster follow the ABCABC packing sequence.
(Figure 2b). However, the fcc clusters we find are rarely perfect single grains. This is seen in molecular dynamics simulations of colloidal clusters that closely match the experimentally prepared clusters[16,33] and therefore allow a detailed investigation of their interior structure. A large fcc cluster assembled in simulation exhibits a sequence of twinned fcc domains (Figure 2c). The first fcc domain consists of three stacked layers in ABC sequence (green). The next two layers are stacked in BA sequence (grey) and thus are twinned to the first domain, and so on. Importantly, all twinning planes are parallel throughout the fcc cluster, creating a laminated texture (Figure S3, Supporting Information). We now focus on three exemplary illumination scenarios of the fcc cluster as indicated in the figure.

In the first scenario, incident light impinges on the cluster from the top, perpendicular to the {111} plane (Figure 2c, incident light 1). All stacked layers are positioned periodically with identical distance, which is not affected by the twinning between laminated fcc domains. Figure 2d schematically illustrates this scenario by showing the cluster from the direction of the incident light. Particles that match the interference condition discussed above are marked in green. In this orientation, all particles within the cluster contribute to the structural color.[41,61] Figure 2e characterizes the fcc cluster by SEM and optical microscopy. The orientation perpendicular to the {111} plane can be seen from the close-packed layer right at the top center of the cluster. It agrees well with the structure of the simulated cluster. The entire cluster shows structural color in optical microscope images underlining that the fcc structure (with laminated twinning planes) persists throughout the cluster. The wavelength of structural color can be tuned over the visible range by changing the size of the particles (Figure 2e, inset). Structural color is observed throughout the spherical outline of the three clusters demonstrating a high degree of crystallinity for all colloid sizes.

In the second scenario, the direction of incident light is rotated by 60° and impinges on the cluster from the side (Figure 2c, incident light 2). Due to the symmetry of the fcc lattice, incident light from this angle meets the first domain perpendicular to another {111} plane (marked in green). However, because twinning changes the orientation of adjacent fcc domains, only every other domain is oriented in a way to create structural color. The simulated cluster depicted from the direction of the incident light (Figure 2f) then contains stripes alternating between domains that reflect light (marked in green) and domains that do not reflect light (marked in grey). Close inspection of experimental fcc clusters with an orientation matching the orientation of the simulated cluster reveals multiple twinning planes as inferred from the surface structure (Figure 2g; Figure S3, Supporting Information). Optical microscopy produces the expected stripe-like motifs (Figure 2g),

Figure 2. Structural color of an fcc colloidal clusters. a) Structure model highlighting stacked hexagonally closed-packed {111} layers. b) ABC stacking sequence of the layers. c) Simulated fcc cluster from 90 000 hard spheres in spherical confinement after removing surface defects and shrinking the spheres for clarity. The side view image reveals a sequence of fcc domains with alternating orientation (green and grey) separated by stacking faults. Three illumination scenarios are indicated. d,f,h) Views of the simulated cluster along the three incident light directions. Particles in {111} planes perpendicular to the direction of incident light are marked in green. Only these particles contribute to the structural color of the cluster. e,g,i) Experimental characterization of colloidal clusters oriented in the three incident light directions using SEM (left images) and optical microscopy in reflection mode for colloidal particles of three sizes (small insets). PS particle size: 230 nm unless noted differently (“col”). Scale bars: 10 µm.
corroborating the structure model. As before, the wavelength of structural color can be tuned via the size of the colloidal particles (Figure 2g, inset). Note that all twinning planes in fcc clusters are parallel, which is in contrast to earlier observations of multigrain textures with uncorrelated orientations caused by independent nucleation events.\(^{[62,63]}\)

In the third scenario, the incident light is not aligned perpendicular to any \(\{111\}\) crystal plane of the cluster (Figure 2c, incident light 3). Although higher order crystal planes may be oriented to fulfill a Bragg condition, their larger separation distance does not produce structural color in the visible range. The analysis of the simulated cluster predicts no structural color (Figure 2h), which is also confirmed by optical microscopy for all particle sizes (Figure 2i). Fcc clusters suspended in a liquid phase are mobile. They continuously change their color appearance by rotating through the different illumination scenarios (Video S1, Supporting Information).

### 3.2. Decahedral Colloidal Clusters

In the model of a decahedral cluster one grain is marked in green and lifted for illustration (Figure 3a). As before, structural color is observed only if the incident light impinges perpendicular to a \(\{111\}\) plane. Two types of cluster orientations afford such conditions and therefore produce structural color. In Figure 3b, a fan-shaped color motif covering the center of the cluster is observed in optical microscopy when one of the five grains is oriented with its \(\{111\}\) plane perpendicular to the incident light. The side view image of the model shows how the layers of the grain penetrate through the cluster, while the top view image illustrates the expected structural color motif (green particles). Model and optical microscopy (OM) color patterns match. Figure 3c depicts a different orientation affording structural color. The decahedral cluster is oriented with one of its five twinning planes towards the incident light, the vertex region points to the side. In this orientation, two neighboring grains are oriented with their \(\{111\}\) plane perpendicular to the incident light (Figure 3c, side view). The resulting color motif is a semicircle (Figure 3c, top view), which matches experimental observation. A rotating decahedral cluster suspended in liquid transitions through the different illumination scenarios (Video S2, Supporting Information).

### 3.3. Icosahedral Colloidal Clusters

We have previously shown that icosahedral clusters at intermediate system sizes (from a few hundred to about 10 000 particles) are accurately described by a Pentakis dodecahedron model (Figure 4a).\(^{[16]}\) In this model, the icosahedral core is complemented by anti-Mackay\(^{[64,65]}\) layers at the surface, which produce the characteristic rectangular surface features. Anti-Mackay layers are twinned with respect to the underlying Mackay icosahedron at the core. In the figure, one of the 20 tetrahedral grains is lifted to show the different regions of such clusters. Three anti-Mackay layers (dark green) are twinned with a tetrahedral grain of the Mackay core over the icosahedral face. A few additional particles in the anti-Mackay region (yellow) locate over icosahedral edges. The symmetry of the icosahedral cluster produces a number of complex structural color motifs.

In Figure 4b, the icosahedral cluster is oriented with a three-fold axis parallel to the incident light, as most clearly seen at the top of the side view image of the model. In this scenario, two of the 20 tetrahedral grains have a \(\{111\}\) plane oriented perpendicular to the incident light and thus contribute to the structural color (marked in green). The expected color motif is a triangle (top view) in agreement with OM. When the focal plane is moved to the lower hemisphere, a mirrored triangle

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Figure 3. Structural color of decahedral colloidal clusters. a) Structure model consisting of five twinned fcc grains reminiscent of the segments of an orange. b,c) Appearance of structural color under two illumination scenarios. Model clusters are depicted perpendicular to (side view, particles shrunken for clarity) and along (top view) the incident light. Green spheres in top view illustrate the geometry of the expected color motif. Experimental color motifs in reflection-mode optical microscopy (OM) agree with the models. PS particle size: 230 nm. Scale bar: 5 \(\mu\)m.

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is observed as predicted by the opposite orientation of the tetrahedral grain in the lower part of the cluster (Video S3, Supporting Information).

In Figure 4c, the incident light impinges on a twofold axis of the icosahedral cluster. In this scenario, two tetrahedral grains located in the cluster interior (marked in green) are oriented with \{111\} planes perpendicular to the incident light (side view). In addition, a part of the surface anti-Mackay layers (marked in yellow) aligns with a \{110\} plane perpendicular to the incident light. The crystal planes have a slightly larger lattice distance compared to the one of the Mackay core resulting in a redshift of the structural color to yellow. The relative position of the two tetrahedral grains and the anti-Mackay layers generates a bowtie motif, in which a narrow rectangle connects two triangles (top view, OM).

The signature fivefold symmetry of icosahedral clusters can also be captured in a structural color motif (Figure 4d). When observed along a fivefold axis, no tetrahedral grain fully aligns with the incident light. Nevertheless, the surface anti-Mackay layers in the lower hemisphere of the cluster have \{111\} planes that are nearly perpendicular to the incident light (side view) resulting in star-like motif with five dots at the rim of the cluster (top view, OM). This is confirmed by observing the same cluster in SEM and under microscope (Figure S4, Supporting Information). Fivefold motifs are difficult to observe in the optical microscope because they are highly sensitive to cluster orientation and are strongly affected by structural defects that tend to accumulate in the surface region [15]. Furthermore, clusters outside magic number regions [15] with incomplete icosahedral symmetry are expected to show weak fivefold structural color motifs [15]. Icosahedral cluster rotating through the different illumination scenarios in Video S4 in the Supporting Information.

4. Evolution of Structural Color

4.1. Cluster Dynamics

Structural color is a useful tool to monitor the dynamics of colloidal clusters suspended in liquids. To study such dynamic effects, we suspend a group of colloidal clusters in oil and deposit the suspension on a glass substrate. Oil evaporation induces convective flow that sets selected clusters into motion (Videos S5 and S6, Supporting Information). Figure 5a, showing time-lapse images of Video S5 in the Supporting Information recorded with a high-speed camera shows details of the cluster motion. In about 0.04 s, an icosahedral cluster with diameter of about 6 \( \mu \text{m} \) rotated about 2 \( \mu \text{m} \) away from original position. Its bowtie-shape motif disappeared and reappeared with around...
60° in-plane rotation. As the change of color motifs is dictated by cluster symmetry and rotation axis, we infer that the cluster rotated around an axis perpendicular to the incident light (viewing angle). Around this axis, every 36° rotation produces the reoccurrence of bowtie motifs (Figure S5, Supporting Information). When the translation of the cluster is caused solely by rotation on substrate, it equals to the cluster circumference \(6\pi \approx 19\ \mu m\), multiplied by the amount of rotation \(36°/360°\), which gives 1.9 \(\mu m\), in close agreement with experiment. We therefore deduce that the cluster is rolling on the substrate. Further following this icosahedral cluster (Figure 5b), after 0.3 s, its bowtie motif rotates in-plane continuously. In this case, the rotation axis is parallel to viewing angle (Figure S6, Supporting Information), otherwise triangle or star-like motifs would have appeared (Figures S7 and S8, Supporting Information). As in-plane rotation does not contribute to translation, the displacement of the cluster is caused by cluster sliding, likely due to the loss of direct contact to the substrate or low friction due to the suspending oil. In a second experiment, a thin oil film containing two icosahedral clusters is deposited on a glass substrate (Figure 5c). Threefold symmetry motifs are visible. During drying, the receding meniscus forms a circular shape and induces capillary attraction between the two clusters (Figure 5d). The meniscus has normal component to the substrate which cause stronger friction between clusters and substrate. At the end of drying, capillary forces rotate the clusters while pulling them together as evidenced by the change in color motif (Figure 5e). As these examples demonstrate, anisotropic color motifs of colloidal clusters are a simple indicator for rotation. Potential applications are the design and testing of microfluidic devices, investigation of rotational diffusion at liquid interfaces,\cite{66} in colloid suspension,\cite{67,68} and comparison of sliding and friction on solid substrates.\cite{69,70}

4.2. Crystallization Pathway

The evolution of structural color, paired with the ability to identify the cluster type from its structural color motif, can be utilized to observe and analyze confined colloidal crystallization in real time. Figure 6 shows a time series of optical microscope images. The droplet contains approximately 500 000 colloidal particles. The system size is large enough to approximate bulk behavior, which favors crystallization into the fcc structure.\cite{33} At the beginning of the evaporation process, the droplet has a whitish overall appearance (Figure 6a). The colloidal particles are in the liquid state and cause random scattering of incident light. As the droplet shrinks and the packing fraction of colloids increases, a homogenous low-intensity red hue emerges (Figure 6b). This hue originates from short-range
correlations developing among the colloidal particles. Upon further increase in packing fraction, a central red spot appears, accompanied by five regions of grating-like color near the rim (Figure 6c). This color motif is characteristic of an onion-ring-like concentric layer structure near the droplet surface, usually observed in spherical photonic balls fabricated by fast droplet drying. It is surprising that long-range correlation is present already at this early stage when the majority of the colloids still remains in the liquid state. The fivefold symmetry of the motif even suggests icosahedral ordering within these surface layers.

Figure 6d captures the onset of colloid crystallization within the droplet. A red quasicircular region extends from the center to the circumference. The color intensity of the quasicircular region keeps increasing (Figure 6e). This suggests that nucleation and growth occur predominantly from one region, in contrast to the nucleation of icosahedral clusters. Because optical images are 2D projections, it is difficult to decide whether nucleates starts at the center or at the droplet surface. However, the central red dot, present already in Figure 6c, remains unaffected by the changes in color around it, demonstrating that the onion-ring-like surface layers persist through the initial crystallization process. Figure 6f finally shows uniform color throughout the droplet outline. At this stage, crystallization into an fcc colloidal crystal has been completed. We note that some experiments see the onion-ring-like surface layer structure remaining until the end of the crystallization process even though the interior exhibits fcc ordering (Figure S9, Supporting Information). This suggests that in these cases all or parts of the surface layers remain intact around an fcc crystalline core. Returning to the time series, after the end of the crystallization process the colloidal cluster consolidates further. Interparticle distances continue to decrease continuously as the remaining water evaporates. The result is a blueshift of structural color from red to orange to yellow to green (Figure 6g,h).

5. Conclusion

Crystalline colloidal clusters with icosahedral, decahedral, and fcc structure were formed by colloidal self-assembly in the confinement of emulsion droplets. Structural color emerges from these clusters as a result of constructive interference of light at {111} planes in the colloidal crystals. The resulting structural color motifs are characteristic for the type of colloidal cluster and its orientation relative to the incident light. Detecting these motifs by observation in an optical microscope is a simple, versatile technique to obtain information about the structure of colloidal clusters. The anisotropy of the structural color motif can be further utilized to monitor dynamic processes. Preformed colloidal clusters are micrometer-scale probes for convective flow and interactions. The evolution of structural color during droplet drying captures the transformation pathway of confined colloid crystallization from liquid to solid in real time. The information encoded in the evolving structural coloration may be further used to extract quantitative information, such as the volume fractions at different stages of the process, which can be inferred by Bragg’s law once a crystal is formed, or the correlation length in amorphous phases, which characterizes non-crystalline structures as well. Theoretically, structural defects and size and twinning of grains, which both influence the interference of light, may also be deduced from the coloration. Even more complex assemblies such as colloidal cluster structures formed by binary or polyhedral particles may be characterized by their distinct structural coloration.

6. Experimental Section

Particle Synthesis: Styrene, acrylic acid, and ammonia peroxidisulfate (Sigma Aldrich) were used as received. Surfactant-free emulsion
polymerization produced PS particle with diameters 190, 230, and 244 nm and <5% size dispersity using ammonia peroxodisulfate as initiator and acrylic acid as co-monomer.[19,56]

Microfluidic Device: Water-in-oil emulsion droplets were produced in a PDMS microfluidic device. The microfluidic chip was created following literature procedure.[19] In short, a thin layer of negative photoresist SU-8 was spin coated on silicon wafer surface and patterned with UV light through designed photomask to produce the master. PDMS (Sylgard 84, Dow Corning) was mixed in 10:1 ratio with curing agent. After degassing in reduced pressure, the mixture was poured onto the structured master to reproduce the microstructure. PDMS was cured at 85 °C overnight, cut and peeled off from the master. 0.75 mm biopsy punch (Harris Uni-Core; Ted Pella) created inlets and outlets on the PDMS chip. The PDMS chip was bonded to a cleaned glass substrate after oxygen plasma treatment for 18 s. Immediately after bonding, Aquapel (PPG Industries) was injected into the microfluidic channel to render the surface hydrophobic.

Emulsion Droplet Fabrication: An aqueous dispersion of PS particles and fluorinated carbon oil (Novec, HFE 7500, 3M) fluorinated oil was pumped into the microfluidic channel as inner and out phases (Harvard Apparatus). Emulsion droplets were stabilized by 0.1 wt% perfluoropolypropylene glycol-block-polyethylene glycol-block-perfluoropropylenglycol surfactant.[82,83] Flow rates varied from 100 to 300 µL h⁻¹, and 400 to 800 µL h⁻¹ for inner and outer phase, respectively. Droplets were collected in 1.5 mL glass vials (Ritotlab, Carl Roth).

Colloidal Cluster Fabrication: The opening of glass vials was sealed by parafilm with different numbers of holes created by 0.4 mm syringe needle (BD) and stored at 5 °C to further slow down evaporation. The number of holes controls the evaporation rate of water and oil to the ambient environment, the latter has a typical mass loss of 0.11 mg per day. Excess oil was used, in comparison to water, to ensure water droplets were always suspended freely in oil. After complete water evaporation from the droplet, the consolidated colloidal clusters remained suspended in oil.

Characterization of Colloidal Cluster Structure: Droplets of oil containing solid clusters were deposited on silicon wafers. Samples were imaged in SEM (Zeiss Gemini 500). To fracture colloidal clusters, glass vials filled with oil and samples were immersed in ultrasonic bath for 10 s. An optical microscope (Leitz, Ergolux) characterized consolidated colloidal clusters with bright field 50 × 0.63 N.A. objective (Leitz) in reflection mode. An inverted microscope (Nikon Eclipse Ti) characterized drying droplet with bright field 40 × 0.60 N.A. objective (Nikon) in reflection mode. Images and videos were used captured by high-resolution CMOS camera (Thorlab) and high speed camera (Mikrotron Eosens mini).

Computer Simulation of Crystallization: A two-step simulation protocol was employed to produce colloidal clusters as observed in experiment.[16] In a first step, colloidal particles were modeled as hard spheres in spherical confinement. Packing fraction was gradually increased in event-driven molecular dynamics to emulate evaporation. In the second step, capillary forces were mimicked by replacing hard sphere interaction with a Morse potential. Energy was minimized with the fast inertia relaxation engine (FIRE) implemented in HOOMD-blue.[84,85] Bond orientational order parameter identified local symmetry of each particle with respect to neighbors using spherical harmonics. Grain detection employed DBSCAN clustering of bond orientational order parameters.[86]

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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