Assembling nanocrystal superstructures
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Revealing Driving Forces in Quantum Dot Supercrystal Formation

We must accept finite disappointment, but never lose infinite hope.

— Martin Luther King Jr.

The assembly of semiconductor nanoparticles, quantum dots (QD), into dense crystalline nanostructures holds great promise for future optoelectronic devices. However, knowledge of the sub-nanometer scale driving forces underlying the kinetic processes of nucleation, growth and final densification during QD assembly remains poor. Emulsion-templated assembly has recently been shown to provide good control over the bulk assembly of QDs by condensation into highly ordered three-dimensional supercrystals. Here, we combine emulsion-templated assembly with in situ small-angle X-ray scattering to obtain direct insight into the nanoscale interactions underlying the nucleation, growth and densification of quantum dot supercrystals. We show that at the point of supercrystal nucleation, nanoparticles undergo a hard sphere-like crystallization into a hexagonally close-packed lattice slowly transforming into a face-centered cubic lattice. The ligands play a crucial role in balancing steric repulsion
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against attractive van der Waals forces to mediate the initial equilibrium assembly, but cause the QDs to be progressively destabilized upon densification. The rich detail of our kinetic study elucidates the assembly and thermodynamic properties that define QD supercrystal fabrication approaching single-crystal quality, paving the way towards their use in optoelectronic devices.
3.1 Introduction

Colloidal semiconductor nanocrystals or quantum dots (QDs) represent an important class of materials that has drawn considerable attention in the last few years: The possibility of bandgap tuning by varying dot size is attractive for both lighting and energy industry, enabling applications such as full-color screens and light emitting diodes, photodetectors, solar cells, and lasers. Most applications require the assembly of QDs into thin films at the highest possible packing fraction: In lasing the threshold for stimulated emission depends linearly on the volume fraction of QDs; in electronics, three-dimensional charge percolation is only possible when the volume fraction is higher than 15 %. While many different QD superstructures have been assembled, spanning the parameter space in compositional and structural complexity, the nanoscale interactions directing the assembly process remain poorly understood. Importantly, the ligands are believed to play a crucial role in the assembly process, yet their function in mediating QD interactions during kinetic assembly and final aggregation remains unclear. Recently, an emulsion droplet-templated assembly method was developed to produce high-volume fraction nanoparticle superstructures: The method relies on the evaporation of a volatile hydrophobic solvent from an oil-in-water emulsion where each oil droplet contains a dispersion of nanoparticles, and allows excellent control over slow drying rates. After complete evaporation, the final product consists of spherical colloidal superstructures composed of visually ordered nanoparticles, or supercrystals. The approach is applicable to nearly any kind of nanoparticle, both hydrophobic and hydrophilic, by using respectively oil-in-water or water-in-oil emulsions. The controlled slow evaporation sets the rate of change of volume fraction of the QD dispersions, enabling direct control over the crystallization process, which ultimately determines the crystal quality. Consequently, this technique is uniquely suited to achieve high-quality superstructures, and study the kinetic driving forces of their assembly in detail, unlike other drying techniques such as drop casting or spin coating that are less controlled and convenient to study. Understanding the driving forces in QD crystallization is paramount to maximizing order in superstructures, which is the first step towards unraveling novel physical properties, such as minibands, that will ultimately set the performance limits of QD devices. In this chapter, we use in situ synchrotron X-ray scattering to obtain direct insight into the formation of QD supercrystals and elucidate the underlying particle interactions during assembly. We implement a new method to collect small angle X-ray scattering (SAXS) patterns in real time during evaporation of QD-containing emulsion droplets and follow the nucleation, growth and final crystal densification process. By imposing a limit on the rate of evaporation, we are able to follow key moments of the QD assembly in great detail. We find that QD supercrystals nucleate into a hexagonally close-packed lattice which slowly transforms...
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into a face-centered cubic lattice and densifies. While nucleation and early growth are consistent with effective hard sphere behavior of ligand stabilized QDs, a balance of sterically repulsive ligands and attractive van der Waals interactions dictates the later stages of assembly until permanent aggregation of the supercrystals. These results demonstrate the important interplay of entropic nucleation and nanoscale interactions in the drying-induced assembly of nanostructures.

3.2 Experimental details

Hydrophobic CdSe QDs are synthesized following a reported procedure. Oleate ligands grafted on the QD surface provide colloidal stability for several years in apolar solvents by steric repulsion and are well suited as colloidal building blocks for close-packed superstructures. X-ray scattering from a dilute dispersion of the synthesized CdSe QDs in hexane yields a form factor consistent with spheres of diameter $\sigma_{QD} = 5.4\text{nm}$, and a polydispersity of 7% (Figure 3.1a). Adding this dilute QD dispersion to an aqueous solution of surfactant, we obtain a two-phase system that we emulsify by vortexing the container, leading to polydisperse droplets of QD dispersion suspended in water and stabilized by the surfactant (Figure 3.1b). Upon evaporation of the hexane droplets, the volume fraction, $\phi$, of the QDs increases, eventually forcing the system from a dilute colloidal gas phase with negligible particle-particle interactions to a dense solid phase with interacting particles. The rate of evaporation sets the rate of change of volume fraction in time, $d\phi/dt$; the colloidal equivalent to the rate of temperature quench in atomic systems which plays a crucial role in the crystallization and final quality of atomic crystals. The evaporation rate is ultimately defined by the temperature and solubility of the apolar solvent in the aqueous polar phase. To control the evaporation rate while simultaneously measuring SAXS, we develop a setup in which the emulsion is continuously flowed through a 10$\mu$m-walled quartz capillary while evaporating from a thermo-stated reservoir (Figure 3.1c). Two-dimensional scattering patterns taken at a rate of $0.6\text{min}^{-1}$ permit following the kinetic details of the QD crystallization process.

3.3 Results and discussion

3.3.1 Assembly kinetics and structure of QD supercrystals

Scattering patterns show the evolution of the QD superstructure in Figure 3.2. Initially, we observe a diffuse pattern (Figure 3.2a), which after a few minutes of drying at 40°C develops a broad ring (Figure 3.2b), followed by the sudden occurrence of narrower and more pronounced rings (Figure 3.2c), which sharpen as they expand outward and the diffuse background vanishes (Figure 3.2d). The initial diffuse pattern
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Figure 3.1: Quantum dot dispersions and emulsions. (a) Azimuthally averaged scattering pattern for a 5mg/mL dispersion of oleate capped CdSe quantum dots dispersed in hexane. The intensity decay has been fit to a spherical form factor accounting for particle polydispersity. (b) Bright-field light microscope image of a polydisperse hexane-in-water emulsion droplets (20% hexane) stabilized by sodium dodecyl sulfate (SDS, 6g/L). The image was taken immediately after preparing the emulsion. (c) Schematic of the custom-built setup used for the kinetic SAXS measurements. The prepared emulsion is flowed by means of a peristaltic pump through tubing in a closed cycle ending in a temperature-controlled reservoir.

reflects the form factors of both the micrometer-sized emulsion droplets and the dilute dispersion of nanometer-sized QDs. Subsequently, the appearance of a broad ring indicates the emergence of short-range order within the concentrated QD dispersion. The sudden occurrence of narrower and more pronounced rings reveals the formation of crystals within the dense QD dispersions (Figure 3.2e); their azimuthal symmetry indicates the presence of many supercrystals within the scattering volume, whose superposition results in a powder-like diffraction pattern. Finally, the expansion of the rings and disappearance of the diffuse background indicates a compression of the QD crystal lattice and simultaneous drying and vanishing of the emulsion droplets. Inspecting the final product under the electron microscope reveals spherical supercrystals of diameters between 50 and 1000nm (Figure 3.3a), exhibiting clear hexagonal order at the surface, as shown in Figure 3.3b. The six-fold symmetry is confirmed by the fast-Fourier-transform of the real-space image as shown in inset.

To follow the crystallization process in more detail, we plot the azimuthally averaged scattered intensity $I(q, t)$ in Figure 3.2e. The corresponding structure factor $S(q, t)$ is obtained by dividing $I(q, t)$ by the effective form factor, which arises from the scattering of dispersed QDs within the emulsion droplets, the emulsion droplets themselves, and the surfactant in the aqueous phase. As direct modeling of the evolving form factor is challenging due to droplet polydispersity and size-dependent rates
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Figure 3.2: In situ observation of QD supercrystal assembly. (a-d) Two-dimensional SAXS patterns obtained from crystallizing CdSe quantum dots confined in oil droplets of an oil-in-water emulsion. Patterns are recorded during drying of the oil droplets, at (a) 0 minutes, (b) 282 minutes, (c) 312 minutes, and (d) 420 minutes. Scale bars indicate $1 \text{nm}^{-1}$. Insets show sketches of the drying oil droplets containing the QDs. (e) Azimuthally averaged scattering profiles $I(q)$ of dilute quantum dots dispersed in hexane (upper black curve), and quantum dots during crystallization in the drying oil-in-water emulsion (colored curves). Intensity profiles have been shifted for clarity. (f) Effective structure factor $S_{\text{eff}}(q)$ of the crystallizing quantum dots extracted from the intensity $I(q)$ in (e) (colored curves), and structure factor of the final dried supercrystals, re-dispersed in water with surfactant (black curve). Starting from $S_{\text{eff}}(q) \approx 1$, typical for non-interacting particles, the structure factor develops peaks characteristic of face-centered cubic (FCC) and hexagonal close packed (HCP) crystal order. Ticks at the bottom demarcate the expected positions of FCC and HCP diffraction peaks for the final dried supercrystals. (g) Contour plot showing the full time evolution of the effective structure factor $S_{\text{eff}}(q,t)$ during the self-assembly process. Color bar on the right indicates the magnitude of $S(q)$.

Of evaporation, we take $F_{\text{eff}}(q) \equiv I(q,t = 0)$ as effective form factor and calculate $S_{\text{eff}}(q,t) = I(q,t)/F_{\text{eff}}(q)$. This choice is reasonable since at the beginning of the experiment the QD dispersion is very dilute ($\phi \approx 0.09\%$) and therefore $S(q,0) \approx 1$. The resulting $S_{\text{eff}}(q,t)$ displays the emergence of the reflections, as
Figure 3.3: Electron microscopy of supercrystals. (a) Histogram of supercrystal diameters extracted from the image in inset. (b) SEM micrograph of an 800 nm spherical supercrystal showing highly ordered 5.4 nm quantum dots. Scale bar indicates 200 nm. Inset: fast-Fourier-transform of the SEM image displaying six-fold symmetry.

shown in Figure 3.2. Reflections emerge at $t \sim 280 \text{min}$, and grow and sharpen in time as shown by the full time evolution of $S_{eff}(q, t)$ in Figure 3.2. The detectable onset of nucleation at $t \approx 275 \text{min}$ is clearly reflected in the emergence of the first reflection of the structure factor at $q \approx 0.8 \text{nm}^{-1}$, while the s-shaped evolution of $S_{eff}(q, t)$ between 300 and 310 minutes demarcates the complete phase transition from fluid to crystal, at which the particles densify rapidly and the reflections shift to higher $q$. Limited by the ability to discern the broad reflections ascribed to small crystallites, crystals can only be detected when they have reached a large enough size, which occurs at $t \geq 275 \text{min}$; however the actual moment of nucleation takes place slightly earlier, around $t \approx 250 \text{min}$ (data now shown). We also show the structure factor of completely dried and re-suspended supercrystals in Figure 3.2 (bottom), which we extracted using $S(q) = I(q)/F_{QD}(q)$, where $F_{QD}(q)$ is the form factor of the fully dispersed QDs in hexane. The positions of reflections show ratios $q_i/q_1 = 1, \sqrt{4/3}, \sqrt{8/3}, \sqrt{11/3}, 2$, where $q_i$ is the position of the $i$-th reflection; these ratios are consistent with face-centered-cubic packing, FCC, as shown by comparison with the reference positions of reflections. Interestingly, at early times, additional features reveal the occurrence of a minority crystal phase. These features are consistent with the hexagonal close-packed (HCP) crystal structure. In fact, FCC and HCP differ from one another merely by the stacking sequence of hexagonal close-packed layers (Figure 3.4a). As their free energy difference is extremely small, of the
order of $10^{-3}k_B T$ favoring FCC, both lattices often occur together in hard sphere systems. Therefore either FCC or HCP could stabilize critical nuclei. From the intensity of the relative contribution of FCC and HCP to the structure factor, we conclude that initially, HCP dominates, while at later stages supercrystals are primarily FCC with a minority HCP phase.

We further quantify this phase change using the peak widths and heights determined by Gaussian fitting to extract, respectively, mean crystalline domain size, $\xi(t)$, and relative fraction of FCC and HCP crystalline phases. These are shown together with the FCC (111) and HCP (100) peak positions in Figure 3.4b-d; the s-shaped pattern is clearly reproduced with both crystal phases shifting synchronously towards higher q. Remarkably, within only 30 minutes, the average crystal size quickly increases to $600\, nm$ for the FCC phase and $200\, nm$ for the HCP phase (Figure 3.4c), each crystallite containing approximately $10^4 - 10^6$ QDs. A comparison with literature values reveals that these crystal sizes are $6 - 60$ times larger than what has been achieved so far for interfacial assembly, as well as spin-coating, and are comparable to early reports for complex, ultra-slow self-assembly methods. The relative fractions, $f_{\text{FCC}}$ and $f_{\text{HCP}}$, of FCC and HCP crystalline phases (Figure 3.4d) show that, indeed, the early stages of assembly are governed by a dominance of HCP, with sizes of $100\, nm$, suggesting a critical radius of nucleation of $50\, nm$. Remarkably, $f_{\text{FCC}}$ and $f_{\text{HCP}}$ cross over at around 275 minutes transitioning supercrystals to mostly FCC at the end of the experiment, $f_{\text{FCC}} \approx 0.85$. These findings indicate that while FCC is the thermodynamically preferred bulk phase, HCP is the preferred phase at nucleation. The slope with which $f_{\text{FCC}}$ approaches the end of the experiment is small yet positive and amounts to $df_{\text{FCC}}/dt \approx 10^{-4}\, \text{min}^{-1}$. Simulations have computed the rate of growth of FCC crystals at the expense of the HCP phase for hard spheres; accordingly, this change should take only $\Delta t_{\text{sim}} \approx 1.8 \times 10^{-1}$ minutes for a mixture of FCC and HCP crystal phases composed of $5.4\, nm$ hard spheres to transition to a $1000\, nm$ FCC crystal. However, experimentally we estimate $\Delta t_{\text{exp}} = (1 - 0.85)/(df_{\text{FCC}}/dt) \approx 1.5 \times 10^3\, \text{min}$ as the time for all the superstructures to show exclusively FCC ordering, a factor 8000 times larger than simulation predictions. This discrepancy may point to the impossibility of treating QDs as hard spheres at high volume fractions, and suggests that the role of the ligand may be crucial in the late-stage crystallization. Further insight into the crystallization kinetics is obtained by calculating the lattice parameter, $a_{\text{FCC}}(t) = 2\pi/\sqrt{3}/q_{111}(t)$, the surface to surface distance between nearest neighbors, $d_{\text{FCC}}(t) = [a_{\text{FCC}}(t)/\sqrt{2}] - \sigma_{\text{QD}}$, and the solid volume fraction $\phi_{\text{FCC}}(t) = \left(\frac{2\pi}{3}\right) \times \left[\frac{\sigma_{\text{QD}}}{a_{\text{FCC}}(t)}\right]^3 \times 100\%$, with a relative uncertainty, $\Delta \phi/\phi \leq 1\%$, estimated by the full-width at half-maximum $\Delta q_{111}$ of the FCC(111) peak as shown in Figure 3.4e-g. During densification of the crystal, $a_{\text{FCC}}$ decreases from 13.8 to 10.8\, nm, corresponding to a decrease in $d_{\text{FCC}}$ from 4.2 to 2.1\, nm and an increase in $\phi_{\text{FCC}}$ from 14 to 30\%. The smallest $d_{\text{FCC}}$
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Figure 3.4: Supercrystal size, lattice parameter and phase fraction. (a, left) Schematic relating the CdSe quantum dots (Cd atoms in red, Se in green) with ligands to effective hard spheres. The self-assembly kinetics can be described in terms of hard sphere behavior when including the effective ligand length $\ell \approx 1\text{nm}$. (a, right) Schematic showing FCC and HCP hard sphere packing. (b) Peak position $q(t)$ followed in time for FCC (111) and HCP (100) peaks. (c) Average crystal domain size $\xi$ estimated with the Scherrer formula $\xi(t) \approx 2\pi K/\Delta q(t)$, where $K \approx 1$ for a spherical crystal and $\Delta q(t)$ is the full-width-at-half-maximum of FCC (111) and HCP (100) peaks. (d) Phase fraction $f_{\text{FCC}}$ and $f_{\text{HCP}}$ of FCC and HCP crystals calculated as $f_{\text{FCC, HCP}}(t) = A_{\text{FCC, HCP}}(t)/[A_{\text{FCC}}(t) + A_{\text{HCP}}(t)]$, where $A_{\text{FCC, HCP}}(t) = I_{\text{FCC, HCP}}(t) \times \xi_{\text{FCC, HCP}}(t)$ and $I_{\text{FCC, HCP}}$ is the height of the 111 (110) peak. (e-g) Evolution of structural parameters for the FCC phase: (e) Lattice parameter $a_{\text{FCC}}(t) = 2\pi\sqrt{3}/q_{111}(t)$, (f) quantum dot surface-to-surface distance $d_{\text{FCC}}(t) = [a_{\text{FCC}}(t)/\sqrt{2}] - \sigma_{QD}$, and (g) volume fraction $\phi_{\text{FCC}}(t) = (2\pi/3) \times [\sigma_{QD}/a_{\text{FCC}}(t)]^3 \times 100\%$, (black symbols). To include the ligand contribution we substituted $\sigma_{QD}$ with $\sigma_{eff} = \sigma_{QD} + 2\ell$ (green symbols).
values correspond to twice the effective ligand length, $\ell$, such that $\sigma_{\text{eff}} = \sigma_{QD} + 2\ell$ represents the effective hard sphere size of the nanoparticle. An effective ligand length of $\ell \approx 1\,\text{nm}$ then results in an effective surface to surface distance $d_{\text{eff},\text{FCC}} \approx 0\,\text{nm}$ and effective volume fraction reaching $\phi_{\text{eff},\text{FCC}} \approx 73\%$ at the end of the experiment (Figure 3.4f-g), which is indeed in good agreement with the highest hard sphere packing fraction of the FCC phase of $74\%$. This supports the idea that at high volume fractions, the oleate ligands bound to the QD surface behave as a $\ell \approx 1\,\text{nm}$ thick, hard shell stabilizing the QD cores. In addition to average structural parameters, our X-ray measurements also provide insight into basic thermodynamic quantities and particle interactions. While the hard sphere model is tempting and has been used to explain basic packing considerations, [75] nanoscale interactions mediated by ligands play an important role in the later stages of the dynamic assembly process. To obtain insight into these nanoscale interactions and their impact on crystallization, we increase the quench rate $d\phi/dt$ by raising the temperature from 40 to $80\,^\circ\text{C}$, thus increasing the rate of evaporation of the emulsion droplets. The resulting evolution of the effective volume fraction shows $\sim 15$ times faster rate, as indicated by the earlier sharp increase in volume fraction (Figure 3.6a). Remarkably, the characteristic shape is preserved for all quench rates, suggesting a common mechanism of self-assembly and densification of the QD supercrystals. To show this most clearly, we rescale the time axis using $t^* = (t - t_x)/t_{70\%}$, where $t_x$ corresponds to the inflection point in the volume fraction curves and $t_{70\%}$ is the characteristic time interval, in which the volume fraction reaches $70\%$ (see Figure 3.6b); the rescaled curves show good agreement, with growth proceeding in a similar fashion independent of the quench rate. The crystal quality, however, is affected: Crystal domain sizes decrease overall with increasing quench rate, indicating deteriorating crystal quality as shown in Figure 3.6c.

The crystal quality also depends on the choice of hydrophobic solvent, QD polydispersity and surfactant concentration (Figure 3.5). Specifically:

- **Choice of hydrophobic solvent:** We have investigated how the use of a specific solvent affects the crystallinity of QD supercrystals while driving the assembly at a fixed temperature, $20^\circ\text{C}$ (Figure 3.5a). While the overall FCC symmetry is unaffected, we find that cyclohexane yields the largest crystals, followed by chloroform, hexane and pentane. Our findings suggest that the solvent’s boiling point is the main contributing factor, with pentane (boiling point $36^\circ\text{C}$) yielding the smallest crystals and cyclohexane (boiling point $81^\circ\text{C}$) the largest.

- **QD polydispersity:** For a fixed temperature, $20^\circ\text{C}$, and average QD diameter $\sigma_{QD} = 5.5 \pm 0.1\,\text{nm}$, we find that the particle polydispersity greatly affects the structural properties of QD superstructures (Figure 3.5b). For polydispersity values $PD \leq 8\%$ the FCC symmetry is retained, with the most monodisperse sample yielding the largest crystals. However, for the most polydisperse sam-
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ple, \(PD = 11\%\), we find a fully amorphous, or glassy, superstructure. These results are in line with the expected suppression of crystal nucleation in hard sphere systems for increasing particle polydispersity. [61]

- **Surfactant concentration:** The surfactant SDS stabilizes the droplets of hydrophobic solvent in water. We find that increasing the concentration of SDS also increases the crystallite size (Figure 3.5). Increasing surfactant concentration in the bulk of the aqueous phase likely causes an increase in concentration of surfactant molecules bound to the surface of the droplet, decreasing the surface tension. This decrease makes the liquid-liquid interface more flexible allowing QDs to rearrange more readily at the curved interface which acts as a defect or hindrance to crystal formation; we speculate that this effect causes the observed improvement in crystal quality.

![Figure 3.5: Influence of colloidal parameters on the crystallinity of CdSe QD supercrystals.](image)

(a) Supercrystal structure factor measured for supercrystals prepared from CdSe QDs of diameter \(\sigma_{QD} = 5.4\text{nm}\) and polydispersity \(PD = 7\%\) at \(20^\circ\text{C}\) for different hydrophobic solvents. (b) Supercrystal structure factor measured for supercrystals prepared from CdSe QDs of the same size, \(\sigma_{QD} = 5.5 \pm 0.1\text{nm}\), and different polydispersity values (PD). (c) Supercrystal structure factor measured for supercrystals prepared from CdSe QDs of diameter \(\sigma_{QD} = 5.4\text{nm}\) and polydispersity \(PD = 7\%\) at \(40^\circ\text{C}\), for different SDS surfactant concentration.

3.3.2 Thermodynamic parameters

Taking full advantage of the X-ray measurements, we use the structure factor for \(q \to 0\text{nm}^{-1}\) to determine the compressibility, \(\chi\), and virial coefficient, \(B_2\), of the crystallizing particles. The osmotic compressibility is related to the low-q limit of the structure factor through \(S(0) = b\chi\), where \(b\) is a positive constant. [51][91][92] As the volume fraction increases, the compressibility decreases monotonically from...
Figure 3.6: Evolution of experimental thermodynamic parameters. (a-c) Effective volume fraction of the FCC phase (a), osmotic compressibility $\chi$ (b), and negative second virial coefficient $-B_2$ (c) as a function of time. Three quench rates are shown: fast quench (blue, 80°C), medium quench (green, 60°C), and slow quench (red, 40°C). For the fast quench rate cyclohexane has been used as apolar solvent rather than hexane because of the higher boiling point. For all quench rates, the compressibility vanishes when the quantum dots have fully crystallized. (d) Effective volume fraction of the FCC phase as a function of rescaled time $t^*$ indicating good overlap for the three quench rates (e) Final resulting average crystalline domain size for the three quench rates. (f) Schematic illustrating extraction of $S(0)$ and $\Delta S(0)$ from $S(q)$ data. To determine $S(0)$, $\log(S)$ is plotted as a function of $q^2$ and linearly extrapolated to $q^2 = 0$ using the linear fitting function $h(q^2)$ (dotted line). To determine $\Delta S(0)$, the third-degree polynomial fitting of $\log(S) - h(q^2)$ is extrapolated to $q^2 = 0$. [51]
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$S(0) = 1$, typical for a colloidal gas, to $S(0) = 0$ at time $t_c$, when the material is no longer compressible (Figure 3.6b). The compressibility vanishes at $\phi \approx 55\%$, the hard sphere melting transition, where the fluid-crystal coexistence ends and the material has completely converted into the crystal phase. This happens consistently for all quench rates. Furthermore, $t_c$ coincides with the inflection point in the $\phi(t)$ curves, i.e. $t_c \approx t_x$, indicating that further increase of the volume fraction can only occur by compression of the crystal lattice. We further determine the virial coefficient $B_2$, a widely used measure of the thermodynamic state of attractive particles describing the balance of repulsive and attractive particle interactions. [91] Experimentally, the second virial coefficient $B_2$ is determined from the deviation $\Delta S(0)$ in the low-q limit (Figure 3.6f) according to

$$
\Delta S(0) = S(0) - cB_2,
$$

where $c$ is a positive constant.

This virial coefficient is related to the effective pair potential $U(r)$ of the QDs via

$$
B_2(T) = -2\pi \int_0^{+\infty} [\exp (-U(r)/k_B T) - 1]r^2 dr
$$

as shown in Figure 3.6f. In the case of $\Delta S > 0$ ($B_2 < 0$), the dominant particle interactions are attractive, while for $\Delta S < 0$ ($B_2 > 0$), the dominant interactions are repulsive. Initially, $\Delta S = 0$ as expected for a colloidal gas of non-interacting particles. In contrast, at later times $t > t_c$, when the crystal lattice becomes compressed, $\Delta S(0)$ saturates at positive values, indicating attractive particle interactions. Interestingly, for the slowest quench, the particles become repulsive at intermediate times, possibly due to a slow spatial redistribution of sterically repulsive ligands bound to the QD.

3.3.3 Modeling of interparticle potential

We can understand the change from repulsive to attractive interactions from the compression-induced change in effective length of the stabilizing ligands. Using standard bond lengths and angles, an oleate ligand molecule can be approximated as a cylinder of length $\ell = 1.9\,\text{nm}$. [93] However at late stages, we measure $d_{FCC} \approx 2\,\text{nm} \equiv 2\ell$; therefore as the volume fraction increases during the evaporation of emulsion droplets, the effective length of the ligand chain must decrease. The effective ligand length can decrease either through ligand density redistribution around a QD, or interpenetration of ligand chains bound to neighboring particles. [77,78] To elucidate these changes of particle interactions quantitatively, [33,38] we model the effective pair potential $U(d)$ as a superposition of a repulsive steric component $U_{\text{steric}}$, [94] and a short-ranged, attractive van der Waals component $U_{\text{vdW}}$. [34] The resulting potential, $U = U_{\text{steric}} + U_{\text{vdW}}$, as a function of ligand length $\ell$ for 5.4nm spherical QDs and a ligand surface coverage of $3\,\text{nm}^{-2}$. [40] shows a shallow attractive secondary minimum arising when the ligand length $\ell$ becomes smaller than 2nm (Figure 3.7f). This secondary minimum deepens as the ligand length decreases, until the steric repul-
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Figure 3.7: Modeled thermodynamic parameters. (a) Modeling of the pair potential $U(d)$ of the 5.4nm spherical quantum dots subjected to van der Waals attraction and steric repulsion for various ligand length, $\ell$, decreasing from 5 to 0.5nm in steps of 0.5nm from right to left. (b) Comparison of measured and modeled second virial coefficient as a function of surface-to-surface distance between quantum dots.

sion becomes insufficient and the potential is dominated by the primary van der Waals minimum. This is indeed in general agreement with the excellent colloidal stability of QDs stabilised with long oleate ligands, and their limited stability when stabilized with shorter ligands. The measured surface-to-surface distance $d_{FCC}$ decreases until $d_{FCC} \approx 2nm$ at late times, implying $\ell \approx 1nm$. This causes QDs to be gently but progressively destabilized, and subjected to increasingly attractive interactions that are initially small enough to allow an equilibrium crystalline phase to form, but later lead to permanent assembly. [95] A quantitative comparison of predicted and measured second virial coefficient $B_2$ for the slow quench (Figure 3.7b) shows good agreement for short surface-to-surface distances, while deviating at larger particle separations, likely due to additional repulsive components such as electrostatic interactions that are not included in the model. This agreement at short distances indeed supports the idea that when compressed, the QDs exhibit attractive van der Waals forces that eventually arrest them into stable supercrystals.

3.3.4 PbS QD Supercrystals

We finally investigate the generality of this assembly approach by using PbS QDs passivated with the same oleate ligands (Figure 3.8). We synthesize $\sigma_{QD} = 6.3nm$ PbS QDs with a polydispersity of 3% following a reported procedure (Figure 3.8a,b). By driving the assembly of PbS QDs into supercrystals, we find great similarity
with the results relative to CdSe dots illustrated above, indicating that these results are general and not limited to a particular QD core material. In particular, PbS crystallize in a FCC lattice with final effective volume fraction consistent with close packing at the end of the experiment (Figure 3.8c,d). Interestingly, for the same assembly conditions, the detectable onset of supercrystal nucleation takes place much earlier in time with PbS QDs, $t \approx 50$ minutes, respective to CdSe dots, $t \approx 100$ minutes (Figure 3.6a, green curve). We attribute this effect to the polydispersity difference between the two species of QDs: higher polydispersity results in delayed nucleation.

### 3.4 Conclusions

Small angle X-ray scattering proves to be an extremely sensitive technique to monitor the crystallization kinetics and energetics of colloidal QDs during the emulsion templated process. The transitioning from a colloidal gaseous to a solid phase at an effective volume fraction of 55% is compatible with an effective hard sphere model, including the volume occupied by the ligands. Grown supercrystals at the end of the assembly exhibit close to 74% effective volume fraction and 85% face-centered-cubic packing, expected to ripen to 100% in roughly 24 hours, while late stages are governed by increasing van der Waals attraction. This novel assembly approach yields spherical and crystalline superstructures approaching single-crystal quality and of sizes up to one micrometer in a matter of minutes. The rapid and facile production shown here is therefore encouraging for the large-scale realization of bottom-up QD-based artificial solids. Additionally, through droplet microfluidics the emulsion polydispersity can be narrowed to such a degree that the resulting supercrystals may be packed into hypercrystals, ordered on three distinct length scales. The hypercrystalline order will lie in the range of the visible spectrum, enabling interesting photonic applications based on all-QD devices. Furthermore, the prospect of exchanging insulating oleates for conductive ligands while preserving the long-range order within supercrystals will facilitate coherent electronic transport over large distances. We expect this combination of order with transport to substantially improve quantum dot devices such as solar cells and switches.
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Figure 3.8: PbS QD supercrystals. (a) STEM micrograph of PbS QDs deposited on a carbon-coated copper grid from hexane. (b) Azimuthally averaged SAXS pattern of a dilute 5mg/mL dispersion of the same PbS QDs in hexane. The pattern is fit to a spherical form factor accounting for particle polydispersity. (c) Effective structure factor of PbS QDs dispersed in hexane droplets at a concentration of 5mg/mL and 60°C, during crystallization. (d) Effective FCC volume fraction in time for PbS QDs crystallizing into a supercrystal. Inset: STEM micrograph of the resulting supercrystals.