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Critical Casimir Forces Tailor Conductivity of Quantum Dot Films through Engineered Fractal Morphology

We are all apprentices in a craft where no one ever becomes a master.

— Ernest Hemingway

The assembly of colloidal quantum dots (QDs) into dense superstructures holds great promise for the development of novel optoelectronic devices. While several assembly techniques have been explored, achieving direct and precise control over the interparticle potential has proven to be a challenge. In the previous chapter, we have shown that critical Casimir forces can drive the growth of QDs into superstructures. In this chapter, we show that the morphology of QD superstructures can be controlled by the exclusively temperature-dependent critical Casimir potential. By investigating the microscopic structural, optical and conductive properties of critical Casimir-grown QD superstructures, we find that the choice of the interparticle potential plays a central role in maximizing conductivity across QD thin films.
Chapter 8. Critical Casimir Forces Tailor Conductivity of Quantum Dot Films through Engineered Fractal Morphology

8.1 Introduction

At the nanoscale, quantum dots (QDs) act as building blocks in the development of a wide range of optoelectronic devices converting light into electric current, e.g. photodetectors and solar cells, or vice versa, LEDs and lasers. For a device to operate, current must flow through the QD active film provided the existence of percolative conductive paths. The threshold for percolation depends on how efficiently the QD superstructure spans space, or more specifically, on the number of conductive bonds a QD establishes with its neighbors. These bonds are enabled by quantum mechanical coupling, and can be, for instance, epitaxial, or mediated by conjugated ligands. Maximizing the number of bonds in QD superstructures represents a modern grand challenge that must be addressed by controlling the assembly of QDs into superstructures.

Colloidal building blocks interacting via an interparticle potential offer, in principle, a large degree of control in tuning their assembly. In equilibrium, the assembly is driven by the minimization of the free energy, giving rise to rich phase behavior. The interparticle potential is typically described by the superposition of repulsive and attractive components, the former preventing the building blocks from aggregating, and the latter driving the assembly to an energetically favorable state. However, commonly used thin film fabrication techniques such as spin coating that employ fast solvent evaporation offer - while being efficient - little control over the structure of QD films. The resulting amorphous films permit conduction but preclude faster charge transport mechanisms requiring long-range order. The short timescales imposed by spin coating do not allow for control of QD pair potential, limiting the fundamental understanding of QD interactions and device optimization.

Over the last decade, much progress has been made in colloidal science to tailor colloidal particle interactions by depletion, magnetic, or DNA-mediated interactions. However, the long length scales of these interactions make them incompatible with the assembly of nanometer-sized QDs into dense superstructures. In fact, most interactions do not offer the possibility of continuously tuning their magnitude without irreversibly altering the composition of the dispersion. There is, therefore, a widespread need for an easily controllable inter-particle interaction to drive the assembly of nanometer-sized colloidal building blocks into dense and reproducible superstructures. In the last few years, the critical Casimir effect has emerged as a novel temperature-tunable interaction to drive the assembly of micrometer-sized colloidal particles. The tunability of this interaction resides on the exquisite role of temperature setting the length scale of solvent fluctuations, enabling direct control over both the magnitude and length scale of the interparticle attraction. In the previous chapter, we have shown that critical Casimir forces can also drive the assembly of nanometer-sized QDs in solution.
8.2 Experimental details

In this chapter, we use critical Casimir forces to gain control over the assembly of QD thin films. We use the temperature-dependent solvent fluctuations to tune the particle interactions and control QD film morphology, and to study the influence of morphology on film conductivity. The advantage of the critical Casimir force is that the length scale of solvent fluctuations is most compatible with the small size of the quantum dots, enabling their interaction control over a wide range of temperatures. We find that, when subjected to critical Casimir forces, the charge-stabilized QDs assemble into superstructures and subsequently deposit onto substrates. We study the properties of the resulting QD superstructures by optical spectroscopy and conductivity techniques. We find that while short-range conductivity between QDs is unaffected by the morphology change, the macroscopic conductivity increases by two orders of magnitude for lower attraction, thus suggesting that weaker attractive potentials maximize the number of long-range percolative pathways in the plane of conduction. We present a qualitative pair potential model, in which superimposing attractive critical Casimir and van der Waals components with electrostatic repulsion leads to temperature-dependent aggregation, of both reversible and irreversible nature.

8.2 Experimental details

Hydrophobic CdSe QDs with diameter $\sigma_{QD} = 6.5 \text{nm}$ are synthesized according to reported procedures and dispersed in hexanes. The native oleate ligands passivating the QD surface are then exchanged with short thioctannate complexes $\left(\text{NH}_4\right)_4\text{Sn}_2\text{S}_6$, making QDs hydrophilic and allowing dispersion in the critical Casimir solvent. The critical Casimir effect relies on the use of a mixture of two solvents, here water and 2,6-lutidine (Lut). Similar to the water-3MP mixture used in the previous chapter, the solvent mixture mixes homogeneously for temperatures $T < T_s$, and phase-separates into water-rich and Lut-rich phases for $T > T_s$, where $T_s$ is the phase separation temperature (Figure 8.1a). Below and in proximity of the critical point of the dispersion, identified by phase diagram coordinates $c_{\text{Lut}} = c_c = 30.2 \text{v/v}\%$ and $T_c = 307K$, solvent density fluctuations arise. These fluctuations can be described as spontaneous compositional variations resulting in locally water-rich or Lut-rich regions of average size $\xi$, the solvent correlation length. The confinement of solvent density fluctuations between two walls or particle surfaces will result in a net attractive force, namely the critical Casimir force. The magnitude and length scale of this interaction strongly depends on the size of compositional fluctuations, controlled by the distance $\Delta T = T_c - T$ from the critical temperature $T_c$ according to $\xi(\Delta T) \sim \xi_0 \times (\Delta T/T_c)^{-0.63}$ at the critical composition. The magnitude of the critical Casimir force can also be controlled by the solvent composition; choosing $\Delta c = c_{\text{Lut}} - c_c < 0$ will result in Lut-rich fluctuations while $\Delta c > 0$ will result in water-rich fluctuations. The largest forces arise in solvents poor in the
Figure 8.1: Schematics of quantum dot assembly via Critical Casimir forces. (a) Schematic phase diagram of a binary mixture of water and 2,6-lutidine. The grey shaded area indicates the solution demixed state, while the colorful shaded areas indicate approximate compositions and temperatures at which lutidine-rich or water-rich solvent density fluctuations arise. The red line indicates the bulk phase separation temperature. The critical temperature, $T_c$, and composition, $c_c$, are also indicated. (b) QD assembly schematic. A dispersion of ligand-stabilized QDs in the binary mixture (left). Solvent density fluctuations, depicted as blue dots, arise by decreasing $\Delta T$, driving the assembly upon confinement between QDs’ surfaces (center). The assembled superstructures sediment on a prepared substrate (right).

component preferred by the particles. Indeed, in the previous chapter we have shown that hydrophilic QDs preferably assemble in water-poor solvents; due to the increased particle-fluctuation affinity; Therefore, also here, we choose to work in a lutidine-rich solvent, $c_{Lut} = 32\text{v/v}\% > c_c$.

Hydrophilic QDs dispersed in this binary mixture are therefore expected to experience an increasingly attractive force upon approaching $T_c$ (Figure 8.1b). Once the QD superstructures have sufficiently grown, the assemblies sediment and deposit on a substrate placed at the bottom of the vessel. The deposits retrieved after different growth times show indeed growing superstructures (Figure 8.2). Already after a few minutes of growth at $\Delta T = 7.8K$, critical Casimir-grown superstructures are visible on the TEM grid, ranging from tens to hundreds of nanometers in size.

8.3 Results and discussion

To harvest the kinetic details of QD assembly via critical Casimir forces, we record small-angle X-ray scattering (SAXS) patterns (Figure 8.3). As superstructures grow in time, the typical scattering pattern for spheres gradually changes to a power-law beh-
8.3. Results and discussion

Figure 8.2: Micrographs of Casimir-driven aggregates during growth. (Top) Bright-field STEM micrographs portraying a snapshot, in time, of the growing superstructures at $\Delta T = 7.8K$ after deposition on the TEM grid. As the assembly proceeds, left to right, QD superstructures grow further to reach the micrometer scale, and eventually sediment onto the substrate (Figure 8.1b). After 24 hours, the TEM grid appears completely covered with QD superstructures (bottom right). (Bottom) Higher and lower magnification micrographs. Individual QDs are clearly visible in the inset, $\sigma_{QD} = 6.5nm$ in diameter, and appear to assemble in a disordered fashion.

behavior, $I(q) \sim q^{-d_f}$ suggesting the fractal nature of growing QD superstructures with fractal dimension $d_f$. [156,187,188] Unfortunately, probably due to the intense scattering background of solvent density fluctuations (Figure 8.4), we can only observe fractal behavior in a very limited range of wave vectors, $q \sim 0.1nm^{-1}$, making further analysis challenging. Yet, as the assembly takes place, the measured nanoparticle density in solution decreases, indicating sedimentation. The extent of sedimentation can be quantified by studying the Kratky plot, shown in Figure 8.3b; in conditions of high sample dilution, the area under the curves is proportional to the concentration of scattering objects in solution: [189]

$$Q(t) = \int_0^{+\infty} q^2 \times I(q, t) dq \propto \phi$$  \hspace{1cm} (8.1)
Chapter 8. Critical Casimir Forces Tailor Conductivity of Quantum Dot Films through Engineered Fractal Morphology

**Figure 8.3:** In situ small-angle X-ray scattering (SAXS). (a) Form factor $P(q)$ for a dispersion of CdSe QDs ($\sigma_{QD} = 2.90 \text{nm}$) in hexane (black curve). Evolution in time of the structure factor $S(q)$ for a dispersion of the same dots in a critical Casimir solution, colored curves ($c_{Lut} = 30\%, \Delta T = 0.2K$). The structure factor decreases in intensity over time and changes in shape. (b) Evolution in time of the Kratky plot ($q^2 \times I(q)$ versus $q$). The area under the curve is proportional to the concentration of QDs in solution. The decrease in time indicates sedimentation. (c) Time evolution of the fractal dimension as extracted from the slope around $0.1 \text{nm}^{-1}$ in (a), circles. Time evolution of the concentration of QDs in solution as determined from (b) following equation [8.1] relatively to the first time point (squares).

where $\phi \ll 1$ is the particle volume fraction. By plotting the relative concentration of particles $Q(t)/Q(0)$ we conclude that superstructures begin to sediment at around 60 minutes, once reached a critical size (Figure 8.3c). Interestingly, as particles assemble into superstructures and sediment, the observed fractal dimension increases to peak at the end of the experiment around $d_f \approx 1.7$.

We observe a clear dependence of the aggregate morphology on the temperature of the Casimir-driven superstructures as shown in Figure 8.5 displaying superstructures grown at $\Delta T = 0.1, 1.8$ and $18.4K$ for 84 hours. While temperatures closer to $T_c$ induce the growth of larger, branched structures, temperatures further away induce the growth of smaller, globular structures. This suggests that the stronger critical Casimir attraction closer to $T_c$ causes a more ramified morphology, while the weaker attraction further away from $T_c$ allows more compact structures to form. These morphological differences may affect the optical and transport properties of the assembled QD superstructures.

We, therefore, investigate the deposited superstructures by optical spectroscopy. After growing and depositing QD superstructures on a quartz substrate, we measure their light absorption spectra as shown in Figure 8.6a. We also show as reference the spectrum of QDs dispersed in hexane stabilized by long, insulating oleate lig-
8.3. Results and discussion

Figure 8.4: Measured solvent correlation length $\xi$ as a function of the distance in temperature $T_s - T$ from the phase separation temperature $T_s$. $\xi$ is experimentally extracted from the azimuthally averaged scattering patterns $I(q)$ of a binary mixture recorded as a function of temperature and plotted against the square of the scattering vector $q$. The Ornstein-Zernike relation predicts a behaviour of the type $I(0)/I(q) = 1 + (q\xi)^2$. Inset: Raw data used to extract $\xi$ as a function of temperature.

ands. While the overall spectral shape and excitonic peak positions are unchanged for samples grown at different $\Delta T$ values, demonstrating that the average QD size is unaffected in agreement with X-ray scattering results (Figure 8.3a-b), the half-width at half-maximum of the excitonic peaks increases from 27 to 35 meV for QDs assembled into superstructures, see inset in Figure 8.6a. This broadening is particularly evident at wavelengths around 620 nm, where the first and second exciton peaks start merging and the prominence of the third peak almost vanishes. The effect appears to be stronger for larger $\Delta T$ corresponding to weaker Casimir attraction. The peak broadening is likely due to electronic coupling between neighboring QDs, as opposed to the case of dispersed QDs, suggesting the overlap of single QD electronic wave functions promoted by the sub-nanometer size of the thioannate ligands.

To investigate in more detail the interdot electronic coupling and its dependence on temperature, we measure the electronic transport of Casimir-driven QD thin films. The charge carrier mobility represents the figure of merit in this regard, providing further insight into the extent of electronic coupling (Figure 8.6b). We first investigate electronic coupling on a local scale by using time-resolved microwave conductivity
Chapter 8. Critical Casimir Forces Tailor Conductivity of Quantum Dot Films through Engineered Fractal Morphology

Figure 8.5: Quantum dot superstructures assembled via Critical Casimir forces for different interaction strengths. (Top) Bright-field STEM micrographs of QD superstructures assembled via critical Casimir forces at different $\Delta T$ values corresponding to different interaction strengths, and deposited on a TEM grid for the measurement. Assembly time: 84 hours. (Bottom) Higher magnification micrographs.

(TRMC), [191] a contact-less spectroscopic technique probing charge carrier transport on a length scale of $\delta_{TRMC} \approx 28 nm$ for CdSe (Figure 8.6b). [56] Specifically, the QD film is excited with a 630nm nanosecond laser pulse inside a resonant microwave cavity. The generation of charge carriers causes a loss in microwave power reflected by the cavity which is directly proportional to the mobility of charge carriers. Extrapolating the photoconductance of the sample to zero photon flux yields an estimate for the conductivity of the film. The mobility values lie in the range of $4 - 7 \times 10^{-2} cm^2 V^{-1} s^{-1}$, in good agreement with the literature, [123] and are rather insensitive to the strength of the attractive potential used to drive the assembly (Figure 8.6b). Charge transport on the length scale of a few QDs is thus unaffected by superstructure morphology. We also probe the electronic transport on longer, micrometer scales by employing Casimir-driven QD thin films in field-effect transistors (FETs, Figure 8.6b), with a channel length of $\delta_{FET} = 2.5 \mu m$. We find that the films behave as n-type semiconductors, consistent with CdSe QDs passivated by in-
8.3. Results and discussion

**Figure 8.6: Optical and electronic transport in critical Casimir assembled structures.** (a) Light absorption spectra for QDs passivated by oleate ligands and dispersed in hexane (black curve), and QDs passivated by thiostannate ligands, assembled by critical Casimir forces and sedimented on a quartz substrate (colored curves); curves have been shifted for clarity. Inset: Detail of the first exciton peak for the various samples. (b) Electron mobility values measured with TRMC and FET devices, as a function of $\Delta T$. Inset: transfer curves of representative devices prepared at different temperatures, measured at 25V channel bias. Right-hand side, top: Schematic for TRMC. Right-hand side, bottom: Schematic for a FET device. The QD thin film is deposited on silicon oxide-covered n-doped silicon substrate. Charge transport is measured in the channel separated by two gold fingers, 2.5$\mu$m apart, representing the drain and source electrodes, and using the silicon as gate electrode. (c-e) AFM height maps of critical Casimir driven aggregates measured in the channel of the FET devices. Note the difference in height range shown in the colormaps.

organic ligands, with onset voltage unaffected by $\Delta T$, indicating that the different deposition conditions do not influence the concentration of dopants, see inset in Figure 8.6b. Remarkably, the values for the electron mobility rise strongly with $\Delta T$, indicating that the global charge transport is strongly affected by the morphology change, in line with the gradual broadening of the absorption peak in Figure 8.6a. At
Chapter 8. Critical Casimir Forces Tailor Conductivity of Quantum Dot Films through Engineered Fractal Morphology

Figure 8.7: Critical Casimir force-dependent microstructure morphology and fractal dimension. (a) The box-counting method applied to a QD superstructure grown at $\Delta T = 7.8K$. The box count decreases with box size following a power law behavior, indicating $d_f = 1.73$. Inset: QD superstructure used for the box-counting. (b) Two-dimensional fractal dimension histograms extracted from analyzing between 100 and 1000 fractal aggregates for each $\Delta T$ value. (c) Pair-potential of $\sigma_{QD} = 6.5nm$ CdSe QDs in binary mixture calculated as a function of $\Delta T$.

the same time, these mobility values are orders of magnitude lower than those found with TRMC, again demonstrating the much longer length scales probed with the two techniques, together with the presence of electronic traps in the film. The increased trapping probability on longer length scales strongly reduces charge transport. In situ atomic force microscopy can investigate the origin of this conductivity increase by directly probing the QD film morphology in the FET channel (Figure 8.6c-e). We find a substantial decrease in film thickness and roughness with increasing $\Delta T$, supporting the view that weakly attractive QDs at high $\Delta T$ form more compact superstructures. These may even deform upon deposition on the substrate, yielding a more two-dimensional film morphology that likely explains the gradual increase of in-plane conductivity with $\Delta T$. While this superstructure morphology only weakly affects the charge carrier mobility values measured by TRMC on a mean path of $\delta_{TRMC}/\sigma_{QD} \approx 4$ QDs, the charge transport probed by FET over longer distances of $\delta_{FET}/\sigma_{QD} \approx 400$ QD diameters reflects the increase in the number of parallel percolative paths available in the plane of conduction.

These percolative paths result from the space-spanning properties of the aggregate. To study this in more detail, we employ the box-counting method to investigate the scaling of the cluster mass as a function of length, [192] see Figure 8.7. We
8.3. Results and discussion

Figure 8.8: Superstructures simulated via diffusion limited aggregation. Measured two-dimensional fractal dimension values of superstructures generated via diffusion limited aggregation as a function of the sticking probability, $p$. Inset: Simulated superstructures. As the sticking probability decreases, the structures assume more compact morphologies characterized by higher fractal dimension $d_f$.

find a power-law relation over the available three orders of magnitude in length scale, indicating the lack of a dominant length scale of the system and therefore a fractal structure. Fractals are characterized by a fractal dimension, $d_f$, describing their space filling properties; in two dimensions, $d_f$ varies between 1 and 2 to indicate, respectively, linear and space filling planar structures. The resultant fractal dimension, in this case, is $d_f = 1.73$, consistent with values found for structures grown with diffusion-limited aggregation with a low sticking probability (Figure 8.8). A low sticking probability implies that the growing aggregate will explore a large number of configurations tending to equilibrium structures, characterized by a high fractal dimension. [156]

Measuring hundreds of superstructures for each $\Delta T$ value, we build the histograms shown in Figure 8.7b, whose maximum is at around $d_f \sim 1.5$, corresponding to a high sticking probability of $\sim 1$, see Figure 8.8. Since the magnitude of the Casimir interaction varies with $\Delta T$, we expect a dependence of $d_f$ on $\Delta T$. [173] Contrary to expectations, however, the distribution of these two-dimensional fractal dimensions is fairly robust upon varying $\Delta T$. A comparison between grown and simulated superstructures reveals that while the branched structures grown at lower $\Delta T$ seem unaffected by deposition on the substrates, the globular structures grown at higher $\Delta T$ appear to deform upon sedimentation, yielding three-dimensional, thick cores surrounded by quasi two-dimensional shells (Figures 8.5 and 8.8). We attribute this to the softness of structures grown at higher $\Delta T$, deforming upon contact with the substrate. These morphological differences ultimately are at the origin of the different
optical and transport properties shown in Figure 8.6.

The question then is what causes the initially weak aggregation, and its transition to permanently assembled superstructures. The critical Casimir force is a solvent-based interaction: Grown superstructures should ideally dissolve once the solvent is removed. The observation of stable superstructures even after solvent removal suggests that eventually van der Waals forces act between the particles, binding them together irreversibly, while the temperature dependence of the grown QD superstructures and their deformation upon sedimentation indicate that weaker critical Casimir forces drive their initial growth. We hence hypothesize that the temperature-dependent critical Casimir forces control the initial reversible assembly, while van der Waals forces lead to their arrest at later stages and during drying, a mechanism we also observed in a recent emulsion-based assembly of QD supercrystals. To elucidate the transition from reversible Casimir to irreversible van der Waals interactions, we model the pair potential using DLVO theory, describing the balance of electrostatic repulsion and van der Waals attraction, and superimpose the temperature-dependent critical Casimir interaction. The latter is determined via explicit critical Casimir modeling on particles of identical sizes as in our studies and correlation lengths extracted from SAXS (Figure 8.4), while the electrostatic interaction is corrected tentatively for ion-solvent fluctuation coupling (Figure 8.7c). As $T_c$ is approached, the critical Casimir potential deepens, leading to a well-defined secondary minimum. Consistent with this simple model, we observe that at large $\Delta T$ QDs are weakly attractive but can eventually aggregate by overcoming the energy barrier to the primary minimum. This scenario gradually shifts at temperatures closer to $T_c$: QDs become more attractive and spend more time at short interparticle distances, while irreversible aggregation becomes more likely because of the decreased barrier height. This transition from weakly- to strongly-attractive QDs may qualitatively explain the experimentally observed marked morphological differences between superstructures grown at different $\Delta T$. The critical Casimir interactions thus allow to tailor the assembly of QDs from reversible to irreversible, providing ultimate control over the assembled structure.

### 8.4 Conclusion

We have shown that the critical Casimir interaction is a powerful tool to engineer the morphology of QD superstructures. By mildly adjusting the temperature of the solution, we can drive the assembly of QDs into superstructures that grow in time to reach sizes compatible with device application, where the superstructure morphology reflects the magnitude of the attractive potential. While higher temperatures induce the growth of branched superstructures, lower temperatures allow for softer denser and aggregates. Upon deposition on the substrate, these soft aggregates deform, increas-
8.4. Conclusion

ing the surface coverage and leading to enhanced electronic coupling. In turn, this results in more numerous percolative pathways for conduction, allowing for higher charge carrier mobilities. The choice of substrate can span virtually any solid-state substrate, allowing a full topographic, optical and electronic characterization of the critical Casimir-grown QD superstructures. We anticipate that by controlling not only the interparticle interaction, but also the QD-substrate interaction, critical Casimir forces should be able to drive strictly two-dimensional growth or QD epitaxy.