Chapter 7

Out-of-equilibrium assembly by critical Casimir forces

Active control over the aggregation of particles has important applications for the design of new nanostructured materials. In the two preceding chapters we have investigated phase equilibria due to critical Casimir forces. Here, we explore structures formed out-of-equilibrium by quenching the particles into a strongly attractive state. We demonstrate that via active control of the particle pair potential, we can quench the particles into well-defined aggregate structures with direct control of their morphology. By imaging the morphology in three dimensions, we show that the resulting structures are fractals, with a fractal dimension that is controlled precisely by the temperature quench. We use Monte Carlo simulations of diffusion-limited aggregation to relate the aggregate morphology to the particle pair potential. These results open a new route of control in the assembly of colloidal and nano-scale structures.
7.1 Introduction

Controlling the structure of aggregates is important for applications as diverse as filters, catalyzers, and electronic devices. The functionality of devices requires aggregate structures with specifically designed surface to volume ratio, morphology, and characteristic structural length scales. However, achieving specific aggregate structures by design is a difficult task, and there is no general framework to achieve active control over the aggregation process. In fact, usually such aggregation processes are irreversible with very little control over the resulting structures. Because of its importance, colloidal aggregation has been investigated intensely. The important low-density regimes of diffusion-limited aggregation (DLA) and reaction-limited aggregation (RLA) [1], where the particles stick irreversibly due to strong attractive interactions, have been much investigated in simulations and shown to exhibit universal features with well-defined fractal dimensions. In experiments, it is rather diffusion and reaction limited cluster aggregation that is observed [2, 3]. In this case, it is the growing fractal clusters that get attached to each other rather than single particles. This leads to lower fractal dimensions compared to DLA. Much more relevant for applications, however, is the regime of lower attractive potential, where because of particle detachment denser structures can form; this regime is much less explored [4, 5]. Consequently much less is known about the structures formed, and their dependence on the attractive potential. The reversible control of particle attraction by critical Casimir forces offers new opportunities to explore this regime, and to control the morphology and fractal dimension of colloidal aggregates by design.

In this chapter, we investigate the morphology of fractal structures that form when particles can detach from the growing aggregate with a finite probability. We combine experimental- and simulation studies of colloidal aggregation: In the experiment, we use critical Casimir forces to quench the particles in a state of well-defined attraction. We follow the diffusion-limited cluster aggregation as a function of the quench depth. We find that we can assemble the particles into aggregates with well-defined morphology and fractal dimension. We elucidate the relation between their fractal dimension, characteristic cluster length scale, and the depth of temperature quench by imaging the resulting structures at the particle scale. In the simulation, we use Monte Carlo simulations of diffusion-limited aggregation (DLA) with finite particle dissociation probability to model the aggregation process. This allows us to link the change of morphology and fractal
dimension directly to the attractive potential strength. We show that even at finite attractive potential, the aggregation exhibits universal properties: the change of fractal dimension with particle pair potential appears to be independent of the nature of the interaction, the type of aggregation, and the dimensionality.

7.2 Experimental control of the aggregate morphology with critical Casimir forces

The temperature dependence of the critical Casimir force allows us to explore out-of-equilibrium behavior by actively quenching the particles into states of different attractive strength. To do so, we use pNipam colloids suspended in a binary solvent consisting of 28 %wt 3mp (see chapter 5), and we employ a special heating setup consisting of two independent water circles to quench the system quickly and reliably to a temperature $\Delta T$ below the phase separation temperature $T_{cx}$. We first equilibrate the suspension at $\Delta T = 0.7^\circ C$, where critical Casimir forces are still negligible. Then, by switching the water cycle, we jump to the desired final temperature to achieve a well-defined attractive critical

![Figure 7.1: Tuning the morphology of colloidal aggregates by critical Casimir forces. Confocal microscope images and three-dimensional reconstruction of aggregates resulting from temperature quenches to $\Delta T = 0.12^\circ C$ (a, d), $0.14^\circ C$ (b, e), and $0.2^\circ C$ (c, f) below the phase separation temperature of the binary solvent.](image)

Casimir potential. After an hour, we image the resulting structures with confocal microscopy and obtain 3D reconstructions of the aggregate structures. The controlled temperature quench allows us to form aggregates with well-defined morphologies. This is demonstrated in Fig. 7.1, where we show confocal microscope images and three-dimensional reconstructions of typical aggregates obtained at various $\Delta T$. With increasing $\Delta T$, the structure of the aggregate changes from open, ramified (Fig. 7.1a, d) to dense and compact (Fig. 7.1c, f). These morphologies remain essentially unchanged over several hours as long as we hold the temperature fixed. We characterize the compactness of the structures by determining the number $N$ of particles within a distance $r$ to the cluster center. The data in Fig. 7.2a shows that, in good approximation, $N \sim r^{d_f}$, indicating that the structures are fractals on intermediate length scales. We conclude that even when the morphology becomes more compact, the fractal structure persists. We find, however, that the fractal dimension increases with $\Delta T$ as shown by the increasing slopes in Fig. 7.2a. This is confirmed when we analyze many more clusters, and plot the fractal dimension as a function of $\Delta T$ in Fig. 7.2. The fractal dimension increases continuously from $d_f \sim 2.1$, at small $\Delta T$ to $d_f \sim 3$ at larger $\Delta T$, confirming that the structures become more dense as the attractive strength decreases. These results demonstrate that by controlling the temperature quench, we can assemble structures with well-defined morphology and fractal dimension. By varying the temperature quench, we can continuously tune the morphology and structural properties of the aggregates.

![Figure 7.2](image)

**Figure 7.2:** (a) Scaling of the number of particles $N(r)$ with distance $r/r_0$ from the cluster center for selected temperatures: $\Delta T = 0.12 \, ^\circ\text{C}$ (circles), $0.14 \, ^\circ\text{C}$ (diamonds), and $0.2 \, ^\circ\text{C}$ (hexagons). (b) Fractal dimension as a function of temperature $\Delta T$, determined from the slopes in (a). A continuous increase of the fractal dimension towards the spatial dimension $D = 3$ is observed.
7.3 Monte Carlo simulation study of the fractal morphology

To elucidate how the change in morphology is related to the particle attractions, we perform Monte Carlo simulations of diffusion-limited particle aggregation. We carry out simulations in two and three dimensions, and model finite bond energies by a finite dissociation probability $\alpha$ with which particles can detach from the growing cluster. The particles move on two and three-dimensional square lattices following a random walk, until they get attached to the cluster. Singly bonded particles can dissociate from the cluster with probability $\alpha$, and the detached particle then diffuses until it sticks to the cluster again. This procedure is repeated until there is a collection of $10^4$ particles in the cluster. We first generate clusters, using 2D simulations, for a wide range of dissociation probabilities; different dissociation probabilities lead indeed to very different morphologies, as shown by the renderings of the final clusters in Fig. 7.3. Clear changes in the cluster morphology from a highly ramified fractal structure at $\alpha = 0$ to increasingly compact structures at higher $\alpha$ are observed. We measure the fractal dimension as before from the scaling of the number of particles as a function of distance from the cluster center. Two examples are shown in Fig. 7.4a. Indeed, $N(R) \sim R^{d_f}$ over almost the entire range of $R$, in agreement with our experimental observations. The resultant fractal dimension is shown as a function of $\alpha$ in Fig. 7.4b; it increases continuously from the DLA limit $d_f^{\text{DLA}} = 1.66$ [6] to the dimension of space $D = 2$, see Fig. 7.4b, main panel. We plot $D - d_f$ as a function of $\alpha$ in Fig. 7.4b (inset). Interestingly, for sufficiently large $\alpha$ the

![Figure 7.3](image-url): Diffusion limited aggregate cluster generated for various values of rate of dissociation $\alpha$. 

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fractal dimension is well described by $D - d_f \propto \alpha^{-\mu}$, where the exponent $\mu = 0.65 \pm 0.01$ (solid line in Fig. 4b). At lower $\alpha$, this power-law relation no longer holds, possibly because at small $\alpha$, the structure does no longer adjust on the simulation timescale.

The changing morphology leads to a dramatic change in the number $N_p$ of particles at the perimeter of the cluster, see Fig. 7.5. In the highly ramified structures ($\alpha \sim 0$), most of the particles sit at the perimeter of the structure, while with increasing $\alpha$, the number of perimeter particles drops rapidly, in agreement with the decreasing surface to volume ratio observed in the experiments. This change in the number of perimeter particles provides a

**Figure. 7.4:** 2D Monte Carlo simulations of cluster. (a) Representative graphs of $N(R)$ versus $R$ on log-log scale for the DLA cluster for $\alpha = 0.005$ and 0.5. (b) Plot of variation of fractal dimensions $d_f$ versus rate of dissociation $\alpha$. Inset graph shows variation of $(D-d_f)$ versus $\alpha$ on log-log scale, with linear fit in the region from $\alpha = 0.03$ to 1.

**Figure 7.5:** 2D Monte Carlo simulations results of the number of particles at the perimeter of the structure as a function of dissociation probability $\alpha$ demonstrates dramatic change of the cluster morphology. The low dissociation probability is directly reflected in the large number of particles at the perimeter.
crucial link between $\alpha$ and the changing fractal structure. At small dissociation probability, many more particles sit at the perimeter where they are relatively stable and dissociate only slowly. At higher dissociation probability, fewer particles sit at the perimeter, as a result of the higher dissociation rate that allows for structural rearrangement. The final aggregate structure results from the balance of morphology-dependent dissociation and restructuring due to re-attachment of particles. We perform similar simulations on a three-dimensional lattice. We find that, similarly, a relation of the form $D - d_f \propto \alpha^{-\mu}$ holds, where $D = 3$ (see figure 7.6). However, the value of exponent in this case is found to be $\mu = 0.53 \pm 0.01$.

7.4 Discussion

To compare quantitatively the cluster morphology change observed in the experiments and simulations, we relate the dissociation probability to the particle pair potential. Assuming thermally activated dissociation of particles, we can link the dissociation probability $\alpha$ in the simulations directly to an effective pair potential $V(r)$, using $\alpha \propto e^{-V_0/kT}$, where, the energy barrier $V_0$ is associated with depth of the potential $V(r)$. This effective pair potential can be extrapolated from direct measurement: as shown in chapter 5, at low attraction, the
Potential can be measured from the pair distribution function in dilute systems. Here, we use these measurements to extrapolate the potential depth to somewhat stronger attraction. We show the potential depth $-V_0$ as a function of $\Delta T$ in Fig. 7.7. Filled symbols indicate the experimental measurements. To extrapolate to stronger attraction, we follow the observation of Bechinger et al [7] that the potential depth increases exponentially with $\Delta T$. We fit the experimental data points with an exponential function, and extrapolate to lower $\Delta T$, see the solid line in Fig. 7.7. The exponential function does indeed fit the measurements well. The resulting extrapolated potential depths, which correspond to the temperature quenches used in this chapter, are shown as open symbols in Fig. 7.7.

We can now compare the experimental and simulated aggregate structures; we do this by plotting the variation of the fractal dimensions $(D-d_i)$ as a function of $\alpha$ for both experiments and 2D and 3D simulations in Fig. 7.8. Two crucial points can be noticed: first, by choosing $b$, we can collapse the two- and three-dimensional simulations and the experiments, indicating a common underlying mechanism. Second, for large $\alpha$, a linear relation between $(D-d_i)$ and $\alpha$ is observed, indicating that the aggregate structure changes continuously, and in a surprisingly linear way with the attractive potential. These observations highlight a general feature of the aggregation: although the different mechanism of aggregation, DLA in the simulations and DLCA in the experiment, results in different values of the fractal dimension, the relative changes of the fractal dimension are similar. Moreover, simulations by Shih et al [8] on a reversible growth model for

![Figure 7.7: Experimental potential depth $-V_0$ as a function of $\Delta T$: solid circles are measured values, open squares are extrapolated values, line is an exponential fit.](image)
cluster-cluster aggregation and experiments by Pusey et al [9] for a system of colloid-polymer mixtures, have reported that the fractal dimension is almost constant at large attraction energy $E$, but it increases drastically with decreasing $E$ when $E \leq 3k_BT$. In both cases, they observed fractal dimensions from $d_f = 1.9$ to $d_f = 3$ which is in good agreement with our experiments as well as simulations. Our direct comparison of experiments, and 2 and 3D simulations demonstrates that the morphology change exhibits universal properties, being independent of dimensionality, nature of the underlying lattice and the specific aggregation process.

### 7.5 Conclusions

In conclusion, we have shown that we can tune the morphology of colloidal aggregates continuously with exquisite control over their fractal dimension by combining critical Casimir forces with controlled temperature quenches. The controlled temperature quench forces the system in a state of well-defined attraction, allowing us to elucidate the formation of out-of-equilibrium structures. Comparison with simulations of diffusion-limited aggregation in two and three dimensions demonstrates that the underlying relation
between fractal dimension and attractive particle potential exhibits universal properties. Direct potential control such as that afforded by the critical Casimir effect can thus be used to precisely tune the average architecture of such out-of-equilibrium structures to yield specific branch thickness, surface-to-volume ratio, and fractal dimension. Such direct morphology control offers new opportunities for applications as for example to design specific structures required to reach specific functionality in devices.

Bibliography


