Self-assembly via anisotropic interactions

Modeling association kinetics of patchy particle systems and self-assembly induced by critical Casimir forces

Newton, A.C.

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3 Modeling critical Casimir force induced self-assembly experiments on colloidal dumbbells

Colloidal particles suspended in a binary liquid mixture can interact via solvent mediated interactions, known as critical Casimir forces. For anisotropic colloids this interaction becomes directional, which leads to rich phase behavior. While experimental imaging and particle tracking techniques allow determination of isotropic interaction effective potentials via Boltzmann inversion, the modeling of effective interaction in anisotropic systems is non-trivial precisely because of this directionality. In this work we provide a framework for extracting effective interaction potentials for non-spherical dumbbell particles from observed radial and angular distributions, by employing Reference Interaction Site Model (RISM) theory and direct Monte Carlo simulations. For colloidal dumbbell particles dispersed in a binary liquid mixture and interacting via induced critical Casimir forces, we determine the effective site-site potentials for a range of experimental temperatures. Using these potentials to simulate the system for strong Casimir forces, we reproduce the experimentally observed collapse, and provide a qualitative explanation for this behavior.
3.1 Introduction

Colloidal particles suspended in a binary liquid mixture of water and picoline (3-methylpyridine) experience an effective attraction when the temperature is raised from below towards the coexistence line of the binary mixture. As this universal attraction between colloids occurs close to the critical point of the binary liquid, it is commonly referred to as the critical Casimir force \[28, 32\]. The solvent mediated interaction is highly dependent on temperature, with the range of the attraction increasing as the temperature approaches the critical point. In contrast to more common colloidal interactions such as electrostatic or depletion interactions, this temperature dependence gives precise control over the interactions between colloids. Previous work employing critical Casimir forces showed that spherical colloids can spontaneously phase separate into different colloidal phases over a small range of temperature \[34-36\].

Recent breakthroughs have made it possible to synthesize anisotropic colloids \[4, 5, 16, 111\] and study their behavior in binary liquids. These particles have an anisotropic shape, and/or interact via directional potentials. Particles of the latter category, known as ”patchy particles”, are able to form colloidal molecules \[16\], and open crystal structures \[4\]. Suspensions of anisotropic colloidal particles have, therefore, great potential for the assembly of novel nano and micron-scale structures. In a recent paper we showed that the critical Casimir force can induce directional interactions between anisotropic dumbbell colloids \[112\]. Controlling the temperature leads to different structural morphologies, including small clusters, strings, and aggregates. At temperatures very close to the binary liquid coexistence line, a sudden collapse transition was observed \[112\]. The aim of this work is to provide an effective pair potential that is able to describe the behavior of the dumbbell system.

Modeling colloidal systems via effective pair potentials has a long history. A famous example is the DLVO theory that describes the effective interaction in colloidal suspensions as a combination of electrostatic repulsion and van der Waals attraction \[113, 114\]. More recent examples include the depletion potential, induced by non-adsorbing polymers, and the critical Casimir force itself \[35, 115\]. These potentials are fundamentally isotropic in nature, allowing a description of the interaction as a potential acting on the centers of mass of the two particles. This symmetry allows extracting the effective pair potential by Boltzmann inversion of the radial distribution function obtained from experiments via advanced optical imaging and particle tracking techniques. The situation is more complex for anisotropically interacting particles where such symmetry does not exist. One choice is to make the potential angular dependent, which is for example done in models such as the Kern-Frenkel model \[116\]. Another option, which we follow here, is to view the anisotropic particle as a rigid construction consisting of several particles that each interact via an isotropic potential. This is essentially a molecular viewpoint, where the constituents of the molecule are isotropic spheres, glued together to form a rigid anisotropic colloidal building block. This viewpoint is suitable for the dumbbell system that we consider here. We develop a simple
model for the dumbbell interactions based on an isotropic form of the effective critical Casimir potential, which we then optimize, employing both Reference Interaction Site Model (RISM) theory \cite{117,119} and direct Monte Carlo simulations, in order to reproduce variants of experimental radial and angular distribution functions. The obtained potential reproduces the different morphologies observed far from the critical point remarkably well. In addition, the optimized potential gives an explanation for the structural collapse observed in the experiments when the temperature approaches the coexistence line of the binary fluid.

The remainder of the chapter is as follows. In section 3.2 we explain the experimental setup, introduce the model and theoretical and simulation methods. In Section 3.3 we present and discuss the results. We end with concluding remarks.

3.2 Methods

Experiments

The colloidal patchy dumbbell particles, composed of sterically stabilized PMMA spheres with a core fluorescently labelled with NBD-MAEM and a non-fluorescent shell, were prepared following the procedure laid out in Ref. \cite{112}. The particles were suspended in a binary liquid mixture of heavy water and picoline (3-methylpyridine, 3MP), with a weight fraction \( c_{3MP} = 0.25 \), below the critical composition, \( c_c = 0.28 \) \cite{120}. The hydrophobic spherical ends prefer 3MP, while the hydrophilic shells prefer the water component. Glass capillaries were filled with suspensions at colloid volume fraction of 0.2\%, and flame sealed to prevent any composition change due to evaporation. Critical Casimir interactions were induced by heating the suspensions to temperatures \( \Delta T = T_{CX} - T \) below the coexistence temperature \( T_{CX} = 38.55^\circ C \) where the two solvent components 3MP and water still form a homogeneous mixture. To minimize equilibration times, we first kept the suspension at \( \Delta T = 5^\circ C \), where critical Casimir interactions are negligible and the particles do not aggregate. As the suspension is not density matched, particles sediment to the bottom of the capillary resulting in a quasi-2D system.

We follow particle aggregation directly in real space by imaging individual particles in an area of \( 104 \mu m \times 104 \mu m \) using confocal microscopy. For each measurement, a series of at least 3000 images was recorded for sufficient statistics. To ensure the same initial conditions (no clusters formed inside the capillary) for all measurements, we always equilibrated the system at \( \Delta T = 5^\circ C \) for at least 15 minutes before raising the temperature to the final desired value close to \( T_c \). The images were analyzed using the particle tracking software IDL \cite{121} and the positions of the centers of the fluorescently labelled spherical ends are determined with an accuracy of 0.03\( \mu m \) in the horizontal, and 0.05\( \mu m \) in the vertical direction. These data sets underwent an identical analysis as the data obtained from simulations, for consistency. The colloidal surface charge and Debye length for the prepared suspension were determined using electrophoresis and conductivity.
Dumbbell model and interaction potentials

Previous work has demonstrated that the phase behavior of spherical colloids in near critical binary liquids can be modeled via a superposition of the Casimir attraction and an electrostatic repulsion \[34, 35\]. We extend this model towards dumbbells by modeling the particles as two touching fused hard spheres with radius \( R = 1.15 \mu m \). The distance between the centers of mass of the spheres is thus equal to \( 2R \). Every pair of spheres not on the same dumbbell interacts via a simple potential:

\[
    u(r) = u_{\text{rep}}(r) + u_{\text{att}}(r),
\]

where \( r = r_{i\alpha} - r_{j\gamma} \) is the center-center distance between two spheres not belonging to the same dumbbell: sphere \( \alpha = 1, 2 \) of dumbbell \( i \) and sphere \( \gamma = 1, 2 \) of dumbbell \( j \). We assume that the repulsion between particles is dominated by electrostatic repulsion and a hard-sphere mechanical repulsion, so that \( u_{\text{rep}}(r) = u_{HS}(r) + u_{\text{el}}(r) \), with the hard sphere \( u_{HS}(r) \) potential defined as

\[
    u_{HS}(r) = \begin{cases} 
        0 & \text{if } r > 2R \\
        \infty & \text{if } r \leq 2R,
    \end{cases}
\]

and the electrostatic repulsion as \[122\]:

\[
    u_{\text{el}}(r) = \frac{2\pi R \sigma^2 l_D^2}{k_B T \epsilon \epsilon_0} e^{- (r - 2R)/l_D},
\]

where \( \sigma \) is the surface charge density, \( l_D \) is the Debye length, \( \epsilon \) is the dielectric constant of the solvent (\( \epsilon = 69 \)), \( \epsilon_0 \) is the electric permittivity and the unit of energy is in \( k_B T \). The surface charge, \( \sigma \), and Debye length, \( l_{Deb} \), have been measured via electrophoretic experiments which yielded \( \sigma = -0.188 \mu C/cm^2 \), and \( l_D = 24.3 \text{nm} \). As the diameter of the particle is roughly \( 2.3 \mu m \), these numbers correspond to a high repulsion (\( \epsilon_{Deb} = \frac{2\pi R \sigma^2 l_D^2}{k_B T \epsilon \epsilon_0} = 6.9 \times 10^3 k_B T \)) that decays relatively quickly (\( l_D = 0.0211 R \)).

The attraction between two spherical particles is given by the temperature dependent Casimir interaction which at short distances is argued by Fisher and de Gennes to be of the form (using the Derjaguin approximation) \[32, 35\]:

\[
    u_{\text{att}}(r) = u_{Cas}(r) = -\frac{2\pi R}{\xi} e^{-(r - 2R)/\xi},
\]

where \( \xi \) is the correlation length of the fluctuations in composition of the near critical binary liquid. Note that the pre-factor is of the form \( \xi^{-1} \). A consequence of this is that the pre-factor diverges for small correlation lengths, which is slightly counter-intuitive as the general observation is that particles become more strongly aggregated close to the critical point (large \( \xi \)) suggesting a stronger attraction between particles. However, due to the strong electrostatic repulsion described
above only the long range effects of the Casimir attraction are important, which cancels the diverging part of the Casimir potential.

The correlation length close to the critical point of the binary liquid, \([\rho_C, T_C]\) scales with the temperature as follows [35]:

\[
\xi(\Delta T) = \xi_0 \left( \frac{\Delta T}{T_C} \right)^{-\nu},
\]

where \(\xi_0\) is the correlation length at \(T = 0\)K, \(T_C\) is the critical temperature, \(\Delta T = T_C - T\) is the distance between the experimental temperature and the critical temperature, and \(\nu = 0.63\) is the relevant critical exponent. Clearly, the correlation length diverges as the critical point is approached. Even when the binary liquid is prepared slightly off-critical, this scaling of the correlation length usually does approximate the behavior well [123]. For our system the coexistence temperature \(T_{CX} = 38.55{\text{C}}\). Therefore, our simple model potential is completely defined by the parameters \(R, \sigma, l_D, \Delta T\) and \(\xi_0\). The value of \(\xi_0\) is not known from experiments, and we therefore fit this value in order to describe how the potential develops when approaching the coexistence temperature.

Note that we do not claim that this potential form is the best way to describe the critical Casimir forces. Especially when the binary liquid is prepared off-critical, the scaling of the correlation length is also dependent on the distance to the critical composition [40, 46, 47]. Here, we do not take this into account as we do not aim to have a complete descriptions of the Casimir forces, but a sufficient one to describe the overall aggregation behavior.

Due to the size of the particles and because the system is not density matched, the particles easily sediment to the bottom of the sample. To mimic this situation we added a gravitational potential in the simulations

\[
u_{grav}(r) = r_z/l_{grav},
\]

with \(r_z\) the vertical height above the bottom of the box and \(l_{grav} = k_B T/\Delta \rho V_{db} g\) with \(\Delta \rho = 0.19\text{gcm}^{-3}\) for PMMA in water/3MP mixture, \(V_{db} = \frac{8}{3} \pi R^3\) and \(g = 9.81 ms^{-2}\). Based on the buoyancy of the particles, we estimated the gravitational length \(l_{grav} \approx 0.15R\). Periodic boundaries were only applied in the \(x\) and \(y\) directions, so that particles cannot sediment below \(z = 0\). In addition, in the experiments the glass surface can also induce critical Casimir forces and can restrain particles to the surface [28] . In this way, the system becomes effectively quasi two dimensional, as is observed in the experiments. To model this effect we added a square well potential

\[
u_{surf}(r) = \begin{cases} 
0 & \text{if } r_z > \Delta \\
-\epsilon_{surf} & \text{if } r_z \leq \Delta,
\end{cases}
\]

with the range \(\Delta = 1.7R\) and depth \(\epsilon_{surf} = 10k_B T\). This choice of parameters roughly reproduced the observed average number of dumbbells sticking out of the plane. Moreover, if a weaker wall interaction is used spurious peaks arise in
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the $\theta$-$\phi$-distributions explained in Eq. 3.12 below, which are not present in the experimental distributions.

For the Monte Carlo simulations the total potential energy of the dumbbell system is thus given by

$$U_{tot} = \sum_{j=1}^{N} \sum_{i<j}^{N} \sum_{\alpha,\gamma=1}^{2} u_{rep}(r_{i\alpha,j\gamma}) + u_{att}(r_{i\alpha,j\gamma})$$

$$+ \sum_{i=1}^{N} \sum_{\alpha=1}^{2} u_{grav}(r_{i\alpha}) + u_{surf}(r_{i\alpha}), \quad (3.8)$$

where $r_{i\alpha,j\gamma} = r_{i\alpha} - r_{j\gamma}$ is the center-center distance between two spheres not belonging to the same dumbbell.

**Potential optimization**

Although the parameters of the potential are connected to physical properties of the system as indicated in Eqs. 3.3 and 3.4, the system is not solely determined by these properties. Additional effects such as van der Waals forces and polymer repulsion could also play a role in the interaction of colloids, especially since these dumbbell particles are not synthesized to minimize these effects. Previously in Refs. [34] and [36] the potential for spherical particles was obtained via fitting the potential of mean force obtained via inversion of the radial distribution function $g(r)$. At low density this inversion is simply $u(r) = -k_{B}T \ln g(r)$. However, several problems arise for anisotropic particles. While the one-to-one mapping between radial distribution function and the effective pair potential still holds [119, 124], the simple inversion of the radial distribution function is not valid anymore. Additional complications arise due to the fact that not all particles are accounted for, because the visualization via the microscope is limited to a plane. Moreover, the intrinsic error of the tracking of the particles causes an error in the particle positions. Finally, the polydispersity of the spheres and the variation in the distance between spheres of the dumbbell, play a role. Clearly, we can not use a direct fitting procedure to obtain the anisotropic potential. However, we can try to predict the radial distribution function for anisotropic particles by simulation or theory, and compare these predicted distributions to the experimental one, and determine which potential parameters give the most optimal match.

For this purpose we propose several distribution functions to compare between simulations and experiment. From the experimental imaging techniques we determine the 2D site-site radial distribution $g_{\alpha\gamma}(r)$ between sphere $\alpha = 1,2$ on dumbbell $i$ and sphere $\gamma = 1,2$ on a different dumbbell $j$, defined as

$$g_{\alpha\gamma}(r) = \rho^{-2} \langle N(N-1)\delta(r_{i\alpha})\delta(r_{j\gamma} - r) \rangle, \quad (3.9)$$

where $\delta(r)$ denotes the Dirac delta function, $\rho$ is the 2D particle density (the number of particles per area), and the angular brackets denote an ensemble average over all configurations. The probability to find a site $\gamma$ a distance $r$ away from site
\( \alpha \) (with \( \alpha \) and \( \gamma \) on different molecules) is thus \( 2\pi r \rho g_{\alpha \gamma}(r) \). This distribution can be connected with the well-known reference interaction site model (RISM) integral equation theory for molecular fluids \[119, 125, 126\]. This distribution is estimated from the experimental data by evaluating

\[
g_{\alpha \gamma}(r) \approx \frac{1}{n_f} \sum_{k} \frac{1}{N_k (N_k - 1)} \sum_{\alpha, \gamma = 1}^{N_k} \sum_{i < j}^2 \frac{\delta(r_{i\alpha,j\gamma} - r)}{f(r_{i\alpha}, r_{j\gamma})},
\]

with \( n_f \) the number of frames, \( N_k \) the number of dumbbells in frame \( k \), \( f(r_{i\alpha}, r_{j\gamma}) \) denotes the fraction of the circle centered at \( (r_{i\alpha}) \) and goes through \( r_{j\gamma} \) that falls inside the microscope image. This fraction corrects for the fact that particles outside the image do not contribute.

In a similar way we also measure the minimum distance radial distribution, \( g_{md}(r) \), where only the minimum distance between all dumbbell pairs is counted. This distribution is estimated from the experimental data by evaluating

\[
g_{md}(r) \approx \frac{1}{n_f} \sum_{k} \sum_{i < j} \frac{\delta(\min(r_{i1,j1}, r_{i1,j2}, r_{i2,j1}, r_{i2,j2}) - r)}{N_k (N_k - 1) f(r_{i\alpha}, r_{j\gamma})},
\]

where the \( \min() \) function returns the lower of its arguments. These versions of the radial distribution minimize the effect of the trivial neighbor.

We can also use a slightly different approach and focus solely on the orientations the particles have with respect to each other when they bind, by measuring the bond-angle distributions, which should be less dependent on the standard error of determining distances given by the system. For neighboring dumbbells we define two different bond angles, \( \phi_{ij} = \arccos(p_i \cdot v_{ij}) \) and \( \theta_{ij} = \arccos(p_i \cdot p_j) \) where \( v_{ij} \) is the vector between the center of mass of the spheres (on different dumbbells) closest to each other, so that \( |v_{ij}| = \min(r_{i1,j1}, r_{i1,j2}, r_{i2,j1}, r_{i2,j2}) \), and \( p_i \) is the dumbbell vector of which the direction is given by the sphere that defines \( v_{ij} \) (see Fig. 3.1). Through these angles different particle orientations can be discerned

![Cartoon explanation of the angles \( \phi \) and \( \theta \) used to discern configurations between dumbbells.](image)

Figure 3.1: Cartoon explanation of the angles \( \phi \) and \( \theta \) used to discern configurations between dumbbells.

and analyzed. The angular distribution distribution is given by

\[
p(\theta, \phi) = \frac{1}{n_f} \sum_{k} \sum_{i < j \in nn} \delta(\theta_{ij} - \theta) \delta(\phi_{ij} - \phi),
\]

(3.12)
where the second sum is over the bonded neighbors only.

In contrast to the radial distribution function of spherical particles in a dilute suspension, none of the three distributions Eqs. 3.10–3.12 are directly related to the effective pair potential. Therefore, we perform many Monte Carlo simulations with a predefined set of potential parameters, \( \{ \xi_0 \} \), and subsequently find the distribution which fits best with the appropriate experimental distribution. To obtain a degree of similarity between two distributions we use the Jensen-Shannon divergence:

\[
d_{JS} = \sum_i P(i) \log \frac{P(i)}{M(i)} + \sum_i Q(i) \log \frac{Q(i)}{M(i)},
\]  

(3.13)

where \( \sum_i \) is the sum over every bin \( i \), \( P(i) \) and \( Q(i) \) are the distributions from simulations and experiments respectively, and \( M(i) = \frac{1}{2}(P(i) + Q(i)) \). The potential parameters that give the smallest \( D_{JS} = \sum \Delta T d_{JS}(\Delta T) \) (where the sum is over all temperatures measured experimentally), determine the optimized pair-potential in Eq. 3.1, where the sum goes over the set of temperatures used in experiment. Note that \( g_{md}(r) \) and \( g_s(r) \) are not normalized, so that the value for \( d_{JS} \) is not bound by \( \ln 2 \).

RISM theory

We employed the RISM theory as a first approximation to match the observed site-site radial distribution functions to an underlying effective potential between the dumbbell particles. In this approach we followed Talbot and Tildesley, who applied the RISM theory to 2D dumbbell systems \[126\]. Since the experimental system is only quasi 2D we do expect some differences.

The 2D site-site correlation function is given by

\[
g_{\alpha \gamma}(r) = \rho^{-2} \langle N(N - 1) \delta(r_{1\alpha}) \delta(r_{2\gamma} - r) \rangle,
\]  

(3.14)

where \( \delta(r) \) denotes the Dirac delta function, \( \rho \) is the 2D particle density (the number of particles per area), and the angular brackets denote an ensemble average over all configurations. The probability to find a site \( \gamma \) a distance \( r \) away from site \( \alpha \) (with \( \alpha \) and \( \gamma \) on different molecules) is thus \( 2\pi \rho g_{\alpha \gamma}(r) \).

Setting the total correlation function \( h_{\alpha \gamma}(r) = g_{\alpha \gamma}(r) - 1 \), the RISM theory defines the direct correlation function \( c_{\alpha \gamma}(r) \) by a (2x2) Ornstein-Zernike matrix equation

\[
\hat{h}(k) = \hat{\omega}(k) \hat{c}(k) \hat{\omega}(k) + \rho \hat{\omega}(k) \hat{c}(k) \hat{h}(k),
\]  

(3.15)

where the hats denote 2D Fourier transforms, also known as Hankel transforms,

\[
\hat{f}(k) = 2\pi \int_0^{\infty} f(r) J_0(kr) r dr
\]  

(3.16)

and

\[
f(r) = \frac{1}{2\pi} \int_0^{\infty} \hat{f}(k) J_0(kr) k dk
\]  

(3.17)
with \( J_0(x) \) denoting the zeroth order Bessel function. The elements of the \( \omega \) matrix are
\[
\omega_{\alpha\gamma}(k) = \delta_{\alpha\gamma} + (1 - \delta_{\alpha\gamma}) J_0(k l),
\]
with \( l \) the intramolecular distance between the centers of mass of particles in one dumbbell. Because dumbbells are homo dimers all site-site correlations are identical and the RISM equation reduces to a single scalar equation:
\[
\hat{h}(k) = \hat{\omega}(k)\hat{c}(k)\hat{\omega}(k) + 2\rho \hat{\omega}(k)\hat{c}(k)\hat{h}(k),
\]
where \( \hat{\omega}(k) = 1 + J_0(k l) \) and the density is now the sphere density rather than the dumbbell density. Rearrangement leads to an expression for the direct correlation function
\[
\hat{c}(k) = \frac{\hat{h}(k)}{\hat{\omega}(k)^2 + 2\rho \hat{\omega}(k)\hat{h}(k)}.
\]
Like in any integral equation approach this equation needs a closure relation. Since we consider particles with long range interactions (relative to the hard sphere interaction), a reasonably good closure is the hypernetted-chain (HNC) approximation [127]
\[
g(r) = h(r) - 1 = e^{-\beta u(r)} + h(r) - c(r).
\]
Eq. 3.20 and 3.21 form a closed set, and allow the computation of the \( g(r) \) from a given \( u(r) \). The solution is obtained numerically, by iteration, mixing in the previous solutions of \( h(r) \) at each iteration step. The \( u(r) \) is optimized using the Jensen-Shannon divergence of the computed final \( g(r) \) and the experimental \( g(r) \). For comparison of the computed and experimental distributions, the computed \( g(r) \) is convoluted with a Gaussian function of width \( w \), to mimic the experimental error. During the optimization \( \xi_0 \) as well as the width \( w \) were varied.

Simulation details

Optimization potential via MC

For the optimization via Monte Carlo simulations, we placed \( N = 100 \) dumbbell particles in a cubic box and applied periodic boundaries in the \( x-y \) direction. The number of particles was chosen to correspond roughly to the experimentally observed number of dumbbells. The gravitational and square well potential acted in the \( z \)-direction, as described above. The size of the box was set to \( L = 64R \), chosen such that the number density of the cubic box is \( \rho = 0.0004 R^{-3} \), and the 2D number density \( \rho = 0.025 R^{-2} = 0.02 \mu m^{-2} \). In order to minimize hysteresis during aggregation we employed an annealing procedure. Starting far from \( T_C \), at \( \Delta T = 1.6K \) where the attraction is very shallow, we performed \( 10^6 \) equilibration and \( 10^6 \) production cycles, where a cycle consists of moving each particle once on average, before increasing the temperature with 0.05K. This procedure was repeated until \( \Delta T = 0.85K \), corresponding to a strong Casimir attraction. The Monte Carlo moves were comprised of single particle translation and/or rotation.
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moves, augmented with cluster moves \[128\]. A MC cycle consists of \(N\) particle rotations or translations, and 1 cluster move. Cluster moves were performed using the algorithm in Ref. \[90\]. The maximum translation and rotation were optimized to achieve an acceptance ratio between 20\% and 70\%. We performed this scheme for values of the zero temperature correlation length \(\xi_0 = 9.2 \times 10^{-4}\mu m\) to \(\xi_0 = 20.7 \times 10^{-4}\mu m\) with increments \(\Delta \xi_0 = 1.15 \times 10^{-5}\mu m\).

Modeling the network collapse

For the diffusion limited aggregation (DLA) simulations to study the collapse transition from a network structure, we first start with cluster moves only, so that clusters do not relax internally. A particle is considered part of a cluster if it is within \(0.23\mu m\) within any of the particles of a cluster. We then relaxed the obtained DLA network structure using single particle moves and rotations with very small maximal translation and rotation displacements, until the local energy minimum was reached.

3.3 Results and Discussion

Potential optimization

RISM Approach

As an initial step we used the RISM approach to optimize the potential, using the Jensen-Shannon divergence between the experimental and predicted \(g_{\alpha\gamma}(r)\). Note that in order to properly compare experimental distribution to either theoretical predictions or simulations, the experimental error needs to be taken into account. This experimental error arises from uncertainty in measuring the positions of the center of the spheres, polydispersity in particle size and variation in the intramolecular distance between the dumbbell spheres. As the size of the particles is around \(2.3\mu m\), the expected range of the attraction far from the coexistence temperature (\(\Delta T > 1K\), is small relative to the size of the particle. In contrast, the broad first neighbor shell peak in the experimental \(g_{md}(r)\) and \(g_{\alpha\gamma}(r)\) would suggest a larger attractive range. However, the observed fluctuations in bond distance of two bound dumbbells in the experimental image sequence are commensurate with the expected width of the potential, and not with the broad first peak in the radial distribution. This suggests that the broadness of the peak is introduced by the polydispersity in particle size and shape, and the measurement error. To mimic this error, the computed \(g_{md}(r)\) and \(g_{\alpha\gamma}(r)\) is convoluted with a Gaussian function of width \(w_c\). The number density in the plane is set to \(\rho = 0.025\mu m^{-2}\).

The results of the RISM optimization are shown in Fig. 3.2a. Fig. 3.2c shows the Jensen-Shannon divergence for the different \(\xi_0\) and \(w\) values. The global minimum is obtained around \(\xi_0 = 16.3 \times 10^{-4}\mu m\) and \(w = 0.16R\). The potentials corresponding to the minimum in \(D_{JS}\) are shown in Fig. 3.2a. Note that the potentials
are relatively short ranged compared to the particle size. Far from the coexistence temperature $\Delta T = 1.55K$ the attraction has a minimum of about $0.05k_BT$. As the temperature increases, the potential gradually deepens and widens. The predicted and broadened $g_{\alpha\gamma}(r)$s are shown in Fig. 3.2b together with the experimental measurements. There are some differences with the experimental rdfs, e.g. in the height of the first peak, and some of the more detailed features. However, the location of the peaks and the qualitative behavior is in agreement. Note that the fit is global, and optimizes all potentials simultaneously.

Figure 3.2: (a) optimized potentials obtained from the measured $g_{\alpha\gamma}(r)$ using RISM. (b) comparison of predicted with experimental $g_{\alpha\gamma}(r)$. (c) Jensen-Shannon divergence for different $\xi_0$ and $w$ values. Note that the $w$ values are in units of diameter of the particle.

Simulation approach

Next, we used direct Monte Carlo simulations to globally fit the potentials to the entire set of measured distributions for the minimum distance radial distribution function $g_m d(r)$ as well as the site-site radial distribution function $g_{\alpha\gamma}(r)$. These simulations are expected to be more accurate compared to the RISM results, as they are performed in 3D, and mimic the experimental situations to a much better degree. Again the predicted radial distribution functions were convoluted with a
Figure 3.3: (a) Optimized potential for 5 values of $\Delta T$ for $\xi_0 = 16.5 \times 10^{-4} \mu m$. As the critical point is approached, a minimum is developed. Note that the short ranged nature of the potential due to the relative size of the correlation length and the size of the particles. Inset shows the divergence of the correlation length close to $T_C$. (b) Sum over temperatures, $D_{JS}$, as a function of $\xi_0$ when fitting $g_{md}(r)$ demonstrating that the minimum is indeed at $\xi_0 = 16.5 \times 10^{-4} \mu m$ ($D_{JS}$ is not bounded by the usual value of $\ln 2$ due to the fact that the radial distributions are not normalized). The sharp increase at higher $\xi_0$ is due to the fact that complete aggregation occurs for these values. (c) Fitted $g_{md}(r)$ and (d) fitted $g_s(r)$ for $\xi_0 = 16.5 \times 10^{-4} \mu m$ demonstrating that for this value of $\xi_0$ simulations (lines) reproduce the main features and trend of the experimental distributions (points) very well. Note that the $w$ values are in units of diameter of the particle.

Gaussian of width $w$ to take into account the effect of the experimental measurement errors.

In Fig. 3.3b the $D_{JS}$ values found for various $\xi_0$ and $w$ are plotted when using $g_{md}(r)$ to optimize which demonstrates that $\xi_0 = 16.5 \times 10^{-4} \mu m = 1.65 \text{nm}$ and $w = 0.18R$ yields the best fit. This value defines the effective pair sphere-sphere potential given by Eq. 3.1 over the entire temperature range. Fitting to $g_{\alpha\gamma}(r)$ also yields a fitted value of $\xi_0 = 16.5 \times 10^{-4} \mu m$. The value of $\xi_0$ is on the same order as has been found in previous work \cite{31}. The site-site effective pair potentials $u_{ij}(r)$ are plotted in Fig. 3.3a clearly showing the weak interaction at low temperature $\Delta T = 1.55K$ which deepens and develops a longer range when the temperature is
Figure 3.4: (a) Experimental and (b) simulation $\theta$-$\phi$ angle probability distributions for from left to right $\Delta T = 1.55K, 1.15K, 0.95K$ (for experiment and simulation) and $0.05K$ (for experiments) and $0.85K$ (or simulations). Note that the optimized potential at $\Delta T = 0.05K$ also shows the same distribution. On the x-axis is $\theta$ angle and on the y-axis is $\phi$ angle. While there are differences in the angles sampled for experiments and simulation, the main features of the experimental distributions are clearly reproduced in simulations. Far from the critical point linear configurations dominate, indicated by the population $\theta = 180^\circ$ and $\phi = 180^\circ$. As $T_C$ is approached, the population shifts to $\theta = 0^\circ$ and $\phi = 70^\circ$ or $\phi = 110^\circ$. At high temperature experiment and simulation do show exactly the same features, demonstrating that for fully aggregated particles no distinction can be made between temperatures based on the $\theta$-$\phi$ distribution.

raised closer to the coexistence temperature.

The corresponding $g_{md}(r)$ and $g_{\alpha\gamma}(r)$ are presented in Fig. 3.3c and 3.3d. As in the case for the RISM optimization, a reasonable match is found for most temperatures. However, there are also differences with the RISM results, due to the approximations made in the theory. For instance, it seems that the optimized potential is too weak for $\Delta T = 1.55K$ and $\Delta T = 1.35K$. While a very good match is found for higher temperatures for both $g_{md}(r)$ and $g_{\alpha\gamma}(r)$, while in the RISM optimization it is the other way around. Also the second peak in $g_{md}(r)$ is well reproduced at high temperatures. Several features in $g_{\alpha\gamma}(r)$, e.g. near $r = 3.2\mu m$ and $r = 3.9\mu m$, are not well reproduced, possibly because the model potential, although capable of describing the main features of the dumbbell particles, can not account for every signature in the radial distributions as the particle shape can deviate from the simple modeled one. Moreover, the experimental data set itself is of limited size.
Validation of the optimized potential

To validate the optimized potential, we compare experimental and simulation snapshots as well as the simulation predictions of the angular distributions with experimental ones, and compute the location of the condensation transition with the second virial coefficient approach.

In Fig. 3.4 the angular distributions are shown. The features of the distributions significantly change with temperature. At low temperature, $T = 37.00^\circ C$, where the attraction is minimal, the majority of the population is in the top right corner at high $\theta$ and high $\phi$, which corresponds to bonds being formed in a linear orientation. As temperature increases, the degree of aggregation also increases and the population shifts from high $\theta$ and high $\phi$, to two peaks at $\theta = 0^\circ$ and $\phi = 70^\circ$ or $\phi = 110^\circ$, which corresponds to a more closed packed bond formation. The corresponding optimized angular distributions obtained via simulation are also presented. The simulated distributions show the same trend as the experiments, i.e. the population shifts from the linear orientation towards more close packed configurations. The two most right pictures differ in temperature for experiment ($\Delta T = 0.05K$) and simulation ($\Delta T = 0.85K$), but do show exactly the same features. This demonstrates that when the particles are fully aggregated, no distinction can be made between temperatures based on the $\theta$-$\phi$ distribution.

Images from experiments in Fig. 3.5, showing the aggregation of particles at several temperatures, are qualitatively well reproduced by simulation. While no aggregation is observed for temperatures far from $T_C$, particles start to aggregate into clusters as the temperature is increased toward the binary liquid coexistence line. The experimental aggregation temperature is found to be around $\Delta T = 0.95K$, something that is reproduced in the simulations.

Since the optimized potential is relatively short ranged, it is not so easy to predict this onset of aggregation. A simple but effective predictive measure for aggregation is the second virial coefficient, $B_2$ [50, 129]:

$$B_2 = \frac{1}{2} \int dr \int d\Omega (1 - e^{-\beta u_{eff}(r, \Omega)}), \quad (3.22)$$

where $r$ is now the inter particle vector between centers of mass of two dumbbells, $d\Omega$ denotes the relative orientation of the dumbbells in 3D, and the inter-molecular potential is $u_{db}(r, \Omega) = \sum_{\alpha, \gamma=1}^2 u(r_{\alpha\gamma}(r, \Omega))$, with $u(r_{\alpha\gamma})$ the effective site-site pair potential, and $r_{\alpha\gamma}$ the distance between the centers of mass of the dumbbell spheres $\alpha$ and $\gamma$ each on different dumbbells. Positioning one of the particles in the origin with its intramolecular vector along the z-axis, the integration is thus over all positions of orientations of the second dumbbell. Of special importance is the reduced second virial coefficient, $B_2^* = B_2 / B_{2D}^{HDB}$ where $B_{2D}^{HDB}$ is the hard dumbbell fluid which is known exactly [126]. This reduced second virial coefficient provides a rough indication of the aggregation behavior. When $B_2^*$ becomes negative, particles begin to attract each other. When $B_2^* < -1.5$ it indicates a transition to a condensed phase [50, 129]. In Fig. 3.6 the numerically integrated $B_2^*$ for the optimized potential is shown. $B_2^*$ becomes negative around $\Delta T = 1.0K$
and smaller than $-1.5$ below $\Delta T = 0.95K$ which is indeed the aggregation temperature in experiments. Further decrease of $\Delta T$ causes a fast drop of the $B^*_2$ indicating that the system is undergoing a condensation/aggregation transition in this temperature region.

![Figure 3.5: Snapshots of (a) the experiment and (b) simulation for from left to right $\Delta T = 1.55, 1.15, 0.95$ and 0.55K, demonstrating that the correct morphology for every temperature is obtained.](image)

![Figure 3.6: Numerical calculation of $B^*_2 = B_2/B_{2\text{HSD}}$ for the optimized potential. The $B^*_2$ becomes negative around $\Delta T = 0.95K$ which is also the aggregation temperature in experiments. Further decrease of $\Delta T$ causes a fast drop of the $B^*_2$ indicating that the experiments are very close to the fluid transition in this region.](image)

**Collapse from network to compact state**

Critical Casimir forces can clearly induce aggregation between anisotropically shaped colloids. Although this aggregation is in principle reversible with temper-
Figure 3.7: (a) Optimized potential for $\Delta T$ close to $T_C$, $\Delta T = 0.2K$ (blue), 0.05K (yellow), 0.03K (red), 0.01K (purple), showing that due to the pre-factor in Eq. 3.4 the potential becomes very long ranged and flatter for small $\Delta T$, leading to the particles becoming more motile. Inset shows how the potential minimum increases close to $T_C$. (b) Relaxation of the total energy divided by minimum of attractive well over time for $\Delta T = 0.01K$ (red), 0.02K (orange), 0.04K (cyan) and 0.3K (blue) starting from five different trapped network structures. (c) Sudden increase close to $T_C$ in average $E_{tot}(U_{min}N)^{-1}$ at the final time-step for each $\Delta T$ which is a measure for the number of interactions per dumbbell. (d) Slope of $E_{tot}$ divided by $U_{min}$ over time demonstrating that relaxation of energy is significantly higher close to the critical point.

Ature, the morphology of the final structure still highly depends on the protocol of the experiment. When a temperature ramp is used that increases the temperature from $\Delta T = 5.0K$ in a short time-frame to $\Delta T = 0.5K$, thus inducing a strong attraction, the resulting structure can become (partially) kinetically trapped in a metastable state from which it is usually very difficult to escape. In general one can anneal such a trapped state by weakening the attraction again (assuming the attraction is reversible in practice) so that the particles unbind again and the system can escape from the metastable trapped state.

While the range of the Casimir attraction monotonically increases upon approaching the coexistence temperature, due to the functional form of Eq. 3.4 the minimum of the potential does not behave monotonically with temperature, and in fact reaches a maximum depth before becoming more shallow again (see the inset of Fig. 3.7a). We argue that this particular feature of the potential leads to
Figure 3.8: (a) Series of snapshots for a network-like structure close to the critical point. From left to right, we can see the structure relaxing towards a more compact structure facilitated by the long range nature of the Casimir force. (b) Series of snapshots for a network-like structure from simulations at $\Delta T = 0.01K$ modelling the collapse seen in experiments. Note that in experiments the collapse is observed at $0.05K$. However, the temperature sensitivity is also on this order. Clearly, the structure fully collapses when the correlation length diverges at $\Delta T = 0.01K$. At this point the range of the Casimir attraction is long enough such that the particles globally find their minimum. If the correlation length remains small, the relaxation is not observed on this time-scale.

The observed experimental behavior of a structural collapse for temperatures close to the coexistence line. In Fig. 3.8 a sequence of snapshots is shown of such a collapse transition, from an extended network to a more compact structure. The system relaxes over several minutes, where the initial configuration on the left is stuck in a metastable state with more linear chain-like structures. For temperatures very close to $T_c$, ($\Delta T \approx 0.05K$), the structure collapses towards a more compact structure as shown on the right in Fig. 3.8.

We can model this collapse transition by preparing a non-equilibrium network like structure using a diffusion limited aggregation scheme (see Methods), in which we only perform MC cluster moves which are always accepted provided there is no hard core overlap. A cluster is defined as a set of contiguous particles, where we consider two dumbbells to be contiguous when any two spheres of the dumbbell are closer than $0.2R$. Starting from a random gas-like configuration, this procedure quickly results in a network structure in which the particles have not been allowed to equilibrate due to the fact that only cluster moves are used. Subsequently, this network structure is quenched into a local energy minimum dictated by the
optimized pair potential at $\Delta T = 0.5K$, employing only local single particle MC moves with small translation and rotation step sizes, such that the system becomes truly trapped in this network structure (see Fig. 3.8). Repeating this procedure five times generates five independent initial structures which are then relaxed via single particle translation and rotation MC moves with small step sizes ($\delta_t = 0.02R$, $\delta_r = 0.03 \text{ rad}$) for $10^7$ MC cycles, where every MC cycle has $N_{\text{part}}$ translation and rotation moves. This roughly corresponds to an experimental relaxation of several minutes [94]. Snapshots of the resulting collapse structures are shown in Fig. 3.8.

The analysis of these simulations is summarized in Fig. 3.7. Fig. 3.7b. shows the relaxation of the total energy versus simulation time for several values of $\Delta T$. It is clear that when the attraction is still short ranged, the potential does not allow equilibration of this structure to a more compact configuration, because the dumbbells only interact with their local neighborhood. However, as the correlation length quickly increases at very small $\Delta T$, the pair interaction also becomes longer ranged. Therefore, the particles have more ‘wiggle’ room within the potential well, allowing the Casimir force to induce a full collapse of the structure, thereby lowering the energy of the system significantly. The energy per particle normalized to the minimum ($E_{\text{tot}}(U_{\text{min}}N)^{-1}$), is plotted in Fig. 3.7c and clearly shows that the structure collapses only for low $\Delta T$, and thus for longer ranged attractions at small $\Delta T$, a particle thus effectively interacts with more neighbors. The relaxation of the potential energy over time is shown in Fig. 3.7d, also demonstrating that indeed the energy relaxes faster for small $\Delta T$.

### 3.4 Conclusions

We have demonstrated that the experimentally observed Casimir induced self-assembly of colloidal dumbbells [112] can be modeled with a relatively simple potential form. We optimized this potential to reproduce both the minimum distance and site-site radial distribution function. The good agreement between simulation and experimentally observed radial and angular distributions and structures suggests that the effective pair potential sufficiently accurately describes the interaction between colloidal dumbbells, at least for short-ranged potentials. For temperatures very close to the coexistence line, where the correlation length increases drastically, probably an effective pair potential is insufficient to describe the interaction as many body effects become important. Additionally, we have shown that the divergence of the correlation length, together with the weakening of the potential depth is able to explain the experimentally observed collapse of locally stuck network structures into more compact configurations. These results are quite robust as in fact it only requires that the attractive force becomes shallower when the range of interaction increases, which makes the finding more general. The universal nature of the Casimir force offers opportunities for other anisotropic colloidal systems. Future prospects entail the further modification of the particle shape and physio-chemical surface properties to induce more complex structure formation.