Phase transitions and interfaces in temperature-sensitive colloidal systems
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Chapter 5

Colloidal phase transitions induced by critical Casimir forces

The critical Casimir effect is a thermodynamic analogue of the well-known quantum mechanical Casimir effect. It acts between two surfaces immersed in a critical binary liquid mixture, and results from the confinement of concentration fluctuations of the liquid. Unlike the quantum mechanical effect, the magnitude and range of this attraction can be adjusted with temperature via the solvent correlation length, thus offering new opportunities for the assembly of nano and micron-scale structures. In this chapter, we demonstrate the active assembly control of equilibrium phases using critical Casimir forces. We guide colloidal particles into analogues of molecular liquid and solid phases via exquisite control over the particle interactions. We measure the critical Casimir pair potential of the particles directly by following density fluctuations in the colloidal gas. This allows us to elucidate the applicability of continuum models to the colloidal assembly process. We apply the Van der Waals model of molecular liquefaction to show that the colloidal gas-liquid condensation is accurately described by the Van der Waals theory, even on the scale of a few particles. We then use the experimentally measured particle pair potentials as input to Monte Carlo simulations to map out the entire phase diagram of
colloids interacting via critical Casimir forces. The calculated phase diagram agrees well with measurements of the experimental system, indicating that many body effects are limited. This phase diagram is qualitatively similar to those of molecular system. These results open up new possibilities in the active assembly of micro and nanostructures.

5.1 Introduction

The critical Casimir effect provides an interesting analogue of the quantum mechanical Casimir effect [1-4]. Close to the critical point of a binary liquid, concentration fluctuations become long-range, and the confinement of these long-range fluctuations between two surfaces gives rise to critical Casimir interactions. This offers new opportunities to achieve active control over the assembly of colloidal particles [5-8]. At close distance, solvent fluctuations confined between the particle surfaces lead to an effective attraction that adjusts with temperature on a molecular time scale. Because the correlation length depends on temperature, temperature provides a unique control parameter to control the range and strength of this interaction [1]. The advantage of this effect is its universality: as other critical phenomena, the scaling functions depend only on the symmetries of the system and are independent of material properties, allowing similar interaction control for a wide range of colloidal particles [9]. Such assembly control would have important applications for the design of structures at the micrometer and nanometer scale. In principle, by tuning critical Casimir interactions with temperature, analogues of molecular liquid and solid phases should be directly observable, and such direct control would offer new opportunities to actively guide the assembly of particles into nanostructures.

In this chapter, we demonstrate the direct control of equilibrium phase transitions with critical Casimir forces. Through exquisite control of the particle pair potential with temperature, we assemble colloidal particles into phases that are analogues of molecular liquid and solid phases, and we visualize these phases in three dimensions and on the single particle level. The direct imaging allows for direct measurement of the critical Casimir pair potential, and we elucidate the relation between critical Casimir attraction and gas-liquid condensation, a crucial step in the equilibrium assembly process. Gas-liquid condensation reflects the competition between the energy cost for compression of the particles against their entropic pressure, and the energy gain from the condensation of the
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Attractive particles. At some critical attraction, the energy released by condensation exceeds the energy needed for compression, and the system can lower its free energy by condensation into the liquid phase, thereby reducing the pressure of the remaining gas. As the attraction increases, an increasing portion of the gas condenses.

We measure important parameters of the condensation process: equilibrium densities of liquid and gas phases, and relative amount of gas and liquid. These microscopic observations provide a unique opportunity to test the applicability of mean field models of liquefaction. We find that the widely used Van der Waals model of molecular liquefaction also describes the particle condensation in our colloidal system remarkably well, even on the scale of a few particles, indicating that this mean-field model applies also to describe the condensation of nanoparticles in the formation of nanostructures.

We also combine the experimentally measured potential and Monte Carlo simulation to investigate phase equilibria due to critical Casimir forces. We locate colloidal gas, liquid and solid phases as a function of temperature and colloidal volume fraction. The resulting colloidal phase diagram agrees well with experiment, indicating that many body interactions play a secondary role and that pair potentials describe the experimental system well. The phase diagram has the characteristic topology of the molecular systems similar to that obtained with the Lennard-Jones potential, but occurs over a very narrow temperature range due to the strong temperature-dependence of the critical Casimir interactions.

5.2 Gas-liquid transition in the van der Waals model

In 1873, to describe attractive molecules of finite size, Johannes Diderik van der Waals modified the ideal gas equation of state \( pV = Nk_B T \) that relates the pressure \( p \), volume \( V \) and temperature \( T \) to \([10, 11, 12]\)

\[
(V - Nb) \left( P + \frac{N^2 a}{V^2} \right) = Nk_B T
\]

The attraction between molecules reduces the pressure by \( N^2 a/V^2 \), where \( a \) accounts for the attractive potential of a particle due to all other particles. The finite molecule size reduces the volume accessible to the molecules by \( Nb \), where \( b \) indicates the volume around a
particle which is inaccessible all other particles. If the number of molecules is fixed, molecular gases are condensed to liquid either by compression or by lowering the temperature, and by measuring \( P, V \) and \( T \), the parameters \( a \) and \( b \) can be determined. An example of van der Waals isotherms is sketched in Fig. 5.1a. At high temperature, the isotherms show a pure gas phase. While at low temperature, the double-loop of the isotherms indicates the characteristic gas – liquid coexistence: at equal pressure, a low density phase and high density phase coexist. By rewriting Eq. 5.1 to

\[
P V^3 - (bP + RT) V^2 + aV - ba = 0, \quad (5.2)
\]

we see that the pressure is a cubic polynomial in \( V \): There is a region in which the polynomial has three real roots. As we increase \( T \) these roots move closer together, and merge at the critical point (point \( C \) in Fig.5.1a) when \( T = T_c \), the critical temperature. At the critical point the gas and the liquid have equal density and specific entropy and the equation of state must be of the form

\[
(V - V_c)^3 = 0 \quad (5.3)
\]

where \( V_c \) is the critical volume. Combining Eq. 5.2 and Eq. 5.3 we obtain the critical pressure \( P_c \), the critical volume \( V_c \) and the critical temperature \( T_c \) as

\[
RT_c = \frac{8a}{27b} \quad (5.4)
\]

**Figure 5.1:** (a) van der Waals isotherms; at high temperature, the isotherms show a pure gas phase. At low temperature, the double-loop of the isotherms indicates the characteristic gas – liquid coexistence. The critical point is at \( C \). (b) Maxwell equal area rule; two hatched regions are equal. Gas and liquid coexist at specific volumes \( v_{\text{gas}} \) and \( v_{\text{liq}} \), respectively. \( \bar{v} \) is an average specific volume of the system.
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\[ P_c = \frac{a}{27b^2} \]  
\[ V_c = 3b \]

To understand the gas-liquid condensation in more detail, let us consider a single isotherm containing a double-loop, as shown in Fig 5.1b. Along the isotherm, there is a portion (from \( e \) to \( d \)) where a compression gives rise to decreasing pressure, which indicates a physically unstable situation. The van der Waals equation fails to describe real substance in this region because the equation always assumes the fluid to be uniform, while between \( a \) and \( c \) on the isotherm, the stable state of the system is a coexistence of low density gas and a denser liquid phase. Thus, in 1875 James Clerk Maxwell replaced the isotherm between \( a \) and \( c \) by a horizontal tie line positioned so that the areas of the two hatched regions are equal. He argued that the work done on the system in going from \( c \) to \( b \) should equal work released on going from \( a \) to \( b \). The flat line portion of the isotherm now corresponds to gas-liquid equilibrium [11, 13]. This tie line intersects the isotherm at \( v_{\text{liq}} \) and \( v_{\text{gas}} \), the specific volumes of coexisting liquid and gas phases, which bound the gas-liquid coexistence regime.

The model predicts that a system with an average specific volume \( \bar{v} \) inside the coexistence regime will separate into phases with specific volumes \( v_{\text{liq}} \) and \( v_{\text{gas}} \), and with relative fraction

\[ f_{\text{liq}} = \frac{v_{\text{gas}} - \bar{v}}{v_{\text{gas}} - v_{\text{liq}}} \]  
\[ f_{\text{gas}} = \frac{\bar{v} - v_{\text{liq}}}{v_{\text{gas}} - v_{\text{liq}}} \]

The Van der Waals equation provides a universal model for molecular gas-liquid condensation. However, most experimental confirmation comes from macroscopic measurement of pressure and volume; the parameters \( a \) and \( b \) are then fit parameters to the measured isotherms. The direct observation of colloidal gas-liquid transition presented in this chapter allows us to determine values of \( a \) and \( b \) from microscopic measurement. The parameters \( a \) and \( b \) are directly related to the attraction and microscopic volume of the particles as [10]

\[ a = -2\pi \int_{r_1}^{r_\infty} U(r)r^2dr \]
\[ b = \frac{1}{2} V_{\text{excl}} = \frac{4}{6} \pi (2r_0)^3 \]  

(5.10)

where \( r_0 \) is particle radius, \( U(r) \) is the particle pair potential and the lower limit of the integration \( r_1 \) is defined as the position where potential becomes negative.

### 5.3 Observation of colloidal phase transitions induced by critical Casimir forces.

We use colloidal pNipam particles suspended in the binary mixture of 3-mp and water (chapter 2.3). Sufficiently far below \( T_{\text{cx}} = 52.2 \, ^\circ\text{C} \), the phase separation temperature of the binary solvent, the particles are uniformly suspended and form a dilute gas phase (Fig. 5.2a). At \( \Delta T = 0.3^\circ\text{C} \) below \( T_{\text{cx}} \), the particles condense and form spherical aggregates that

![Confocal microscope images of colloidal gas-liquid transitions induced by critical Casimir forces](image1)

**Figure 5.2:** Confocal microscope images of colloidal gas-liquid transitions induced by critical Casimir forces: colloidal gas (a), and gas - liquid coexistence (b).

![Pair correlation function and mean-square displacement](image2)

**Figure 5.3:** (a) Pair correlation function of colloidal particles in aggregates, the dashed line indicates the nearest-neighbor separation. (b) Mean-square displacement of particles in the dilute phase (circles) and in the aggregates (dots). The linear fits to the data yields diffusion coefficients, \( D_{\text{gas}} \) and \( D_{\text{liq}} \) that differs by a factor of 10.
coexist with a low-density colloidal gas (Fig. 5.2b). Within the aggregates, particles show the characteristic short-range order of a liquid as shown by the pair correlation function in Fig. 5.3a. We further confirm the liquid nature of the aggregates by tracking the motion of the particles, and comparing their mean-square displacement with that of the particles in the dilute gas in Fig. 5.3b. The mean square displacement grows linearly with time, similar to that of the motion of molecules in liquids. Moreover, it is a factor of 10 slower than that of the gas particles, indicating the confinement of the particles in the dense liquid environment. When we raise the temperature further to $\Delta T = 0.2^\circ C$, the particles inside the aggregates form an ordered face-centered cubic lattice (Fig. 5.4): the colloidal liquid has frozen into a crystal. These observations appear as analogues of gas-liquid and liquid-solid transitions, driven by critical Casimir interactions. Because of the exquisite temperature dependence of critical Casimir interactions, these phase transitions occur with only small changes in temperature, and they are reversible: the crystals melt, and the liquid drops evaporate when the temperature is lowered below the characteristic thresholds. Such reversible control offers new opportunities for guiding the growth of perfect structures from colloidal building blocks [14]. The exquisite temperature dependence and reversibility allows precise control over the growth and annealing of perfect equilibrium structures, in analogy to the growth of atomic materials.

To elucidate the gas-liquid phase coexistence, we show three-dimensional reconstructions in Fig. 5.5. These reconstructions correspond to the confocal microscope images in Fig. 5.2. Red spheres indicate particles with more than 4 neighbors and small blue spheres

![Figure 5.4](image)

**Figure 5.4:** Confocal microscope image of colloidal crystal. Inset illustrates the relation between the imaged particle configuration and the structural motif of the face-centered cubic lattice.
indicate particles with a large and small number of nearest neighbors, respectively. Red particles demarcate density fluctuations in the colloidal gas (a) and colloidal liquid aggregates coexisting with the colloidal gas (b).

Interestingly, at $\Delta T=0.5^\circ C$, small clusters of red particles appear and disappear, indicating spontaneous fluctuations in the density of the colloidal gas (Fig. 5.5a). These density fluctuations become more pronounced as the temperature approaches $T_c$. Then, at $\Delta T=0.3^\circ C$, after 10 min, red spheres form stable connected clusters (Fig. 5.5b), indicating stable liquid nuclei that grow to become large drops. To determine gas and liquid equilibrium densities, after 30 min, we measure the density of particles in the liquid and gas phases from the number of red and blue particles per volume, and obtain $\rho_{\text{liq}}=3.0 \mu m^3$ and $\rho_{\text{gas}}=0.1 \mu m^3$, respectively.

### 5.4 Direct measurement of particle pair potential

We elucidate the mechanism that drives the condensation of particles by measuring the particle pair potential directly from the density fluctuations in the gas. The potential of mean force, $U_{mf}$, is related to the pair correlation function $g(r)$ which indicates the probability of finding two particles separated by $r$ as [15]

$$g(r) \sim \exp[-U_{mf}(r)/k_B T]$$

(5.11)

We acquire 3000 images of particle configurations of the colloidal gas to determine the average pair correlation function at different temperatures, which we show in Fig. 5.6a. An
increasing peak arises at $r \sim 2.7 r_0$, indicating increasing particle attraction as the temperature approaches $T_c$. For dilute suspensions, $U_{\text{inf}} \approx U$, and the pair potential is obtained directly from the measurement of $g(r)$ as
\[ U(r) / k_B T = -\ln g(r) \] (5.12)

**Figure 5.6:** Particle pair correlation function (a) and corresponding particle pair potential (b) measured at different temperatures. The symbols indicate room temperature (black circles), $\Delta T=0.5$ °C (red squares), 0.4 °C (green rhombi), 0.35 °C (blue hexagons) and 0.30 °C (magenta stars). The solid black line in (b) indicates the best fit with a screened electrostatic potential.

**Figure 5.7:** Attractive critical Casimir potentials extracted from the potential curves in (Fig. 5.6). Inset: range $l_{\text{attr}}$ (black filled square) and amplitude $A_{\text{attr}}$ (red open circle) of the critical Casimir potential as a function of $\Delta T$. Dashed lines are guides to the eye.
The resulting pair potentials at different temperatures are shown in Fig. 5.6b. An attractive minimum emerges as the temperature approaches $T_c$. This minimum reflects the competition between the critical Casimir attraction $U_{\text{attr}}$, and the screened electrostatic repulsion $U_{\text{rep}}$ of the charged particles. We consider the total pair potential as [7]

$$U = U_{\text{rep}} + U_{\text{attr}}$$  \hspace{1cm} (5.13)

where the screened electrostatic potential associated with the charged particles is described by [10]

$$U_{\text{rep}} (l) \approx A_{\text{rep}} \exp(-l/l_{\text{rep}})$$  \hspace{1cm} (5.14)

where $A_{\text{rep}} \sim 2\pi r_0 k_B T / l_{\text{rep}}$ is the amplitude, $l_{\text{rep}}$ is the Debye screening length and $l = r - 2r_0$ is the distance between particle surfaces. The attractive critical Casimir potential can be approximated by [7]

$$U_{\text{attr}} (l) \approx -A_{\text{attr}} \exp(-l/l_{\text{attr}}).$$  \hspace{1cm} (5.15)

Here $A_{\text{attr}} \sim 2\pi r_0 k_B T / l_{\text{attr}}$ and $l_{\text{attr}}$ are the amplitude and the range of the critical Casimir attraction, respectively. We determine $A_{\text{rep}}$ and $l_{\text{rep}}$ from the potential at room temperature, where critical Casimir interactions are negligible. Excellent agreement with the data is obtained for $A_{\text{rep}} = 4.3 k_B T$ and $l_{\text{rep}} = 0.36 r_0$ (black circles and solid line in Fig. 5.6a). The values of $A_{\text{attr}}$ and $l_{\text{attr}}$ are then determined from the best fit of $U$ to the measured potentials; these parameters are shown as a function of temperature in Fig. 5.7, inset. The data indicates that $l_{\text{attr}}$ grows linearly with temperature, while the amplitude $A_{\text{attr}} \sim 1/l_{\text{attr}}$, as expected for the critical Casimir force between two spheres [7]. We use these parameters to determine the critical Casimir component, $U_{\text{attr}}$, of the pair potential, which we plot in Fig. 5.7, main panel.

### 5.5 Experimental study of gas-liquid coexistence using the van der Waals model

The precision of these pair potential measurements allows us to make direct comparison with continuum models. We do this by applying the van der Waals equation of state to our attractive colloidal system. In contrast to molecular gases where values of $a$ and $b$ can only be inferred from macroscopic measurements, for our colloidal system, we can
determine the parameters $a$ and $b$ directly from the measured particle pair potential and particle size. Furthermore, while for molecular gases, the value of $a$ is temperature-independent, and the only change with temperature occurs in the thermal energy, $k_bT$, for our colloidal system, temperature changes directly the value of $a$ via the critical Casimir interactions. We determine values of $a$ by numerical integration of the measured pair potentials using Eq. 5.9 and $b$ from the measured particle radius using Eq. 5.10. The results are listed in Table 1. We plot the resultant $P$ as a function of $V/Nb$ in Fig. 5.8. The values of $a$ result in four isotherms; red and green curves show isotherms characteristic of a gas, while blue and pink curves show the double-loop characteristic of gas-liquid coexistence.

To test the van der Waals model, we determine the average volume per particle from the volume fraction using $\bar{\nu} = b/4\phi$, and indicate the resulting value $\bar{\nu} = 12.5b$ with a vertical dashed line. This line falls within the coexistence regime of only the pink isotherm, indicating that gas-liquid coexistence should occur only for $\Delta T = 0.30^\circ C$, in agreement with our direct observation (Fig. 5.2). Further confirmation of the model comes from comparison of the measured and predicted values of $v_{\text{liq}}$ and $v_{\text{gas}}$. We determine the specific volumes of gas and liquid particles from the measured volume fractions $\phi_{\text{liq}}=0.25$ and $\phi_{\text{gas}}=0.005$ and obtain $v_{\text{liq}}/b=1$ and $v_{\text{gas}}/b=50$, in good agreement with the predicted values $v_{\text{liq}}/b=1.25$ and $v_{\text{gas}}/b=43$ determined from Fig. 5.8.

Furthermore, the relative amount of liquid and gas is $f_{\text{liq}}=0.69$ and $f_{\text{gas}}=0.31$, again in very good agreement with the values $f_{\text{liq}}=0.72$ and $f_{\text{gas}}=0.28$ obtained using Eq. 5.7 and Eq. 5.8. These results indicate that the van der Waals model provides a quantitatively accurate description of the colloidal gas-liquid equilibrium.

<table>
<thead>
<tr>
<th>$T$ ($^\circ C$)</th>
<th>$\Delta T$ ($^\circ C$)</th>
<th>$a$ ($bk_bT$)</th>
</tr>
</thead>
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<tr>
<td>51.70</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>51.80</td>
<td>0.4</td>
<td>1.28</td>
</tr>
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<td>51.85</td>
<td>0.35</td>
<td>3.67</td>
</tr>
<tr>
<td>51.90</td>
<td>0.3</td>
<td>5.25</td>
</tr>
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</table>

Table 1: Temperature-dependent Van der Waals coefficient

Values of the Van der Waals coefficient, $a$, determined for several temperatures by integration of the measured particle pair potential (see Fig. 5.8, inset).
Molecular gas-liquid condensation typically entails measurement of the equilibrium vapor pressure, $P_{eq}(T)$. For our colloidal system, this pressure is small and difficult to measure. However, we can estimate $P_{eq}$ from the intersection of the horizontal tie line with the y-axis. From Fig. 5.9, we find $P_{eq} = 0.025(k_BT/b)$ yielding an equilibrium vapor pressure of $2 \times 10^{-4}$ Pa, $10^9$ times smaller than typical vapor pressures of molecular gases at room temperature, which are of the order of $\sim 10^5$ Pa, the atmospheric pressure. This difference reflects the $10^9$ times lower colloidal particle density associated with the $\sim 10^3$ times larger colloidal particle diameter. Therefore, the gas-liquid transitions in the colloidal and molecular systems are comparable. Vertical dashed black line indicates the average volume per particle, $\bar{v}$. Inset: Enlarged section of the particle pair potential at $\Delta T = 0.35 ^\circ C$ illustrates the determination of the Van der Waals parameter $a$ by integration. The lower integration boundary, $r_1$, is indicated by a dotted line.

**Figure 5.8: Van der Waals isotherms of the colloidal gas-liquid transition.**

Van der Waals isotherms of the colloidal system for $\Delta T = 0.5 ^\circ C$ (red), $0.4 ^\circ C$ (green), $0.35 ^\circ C$ (blue), and $0.3 ^\circ C$ (pink). A transition from a gas (green and red isotherms) to gas-liquid coexistence (blue and pink isotherms) is observed. Horizontal lines indicate tie lines, constructed following the Maxwell rule of equal chemical potential (equal areas included by the tie lines and isotherms). Intersections with the isotherms delineate the gas-liquid coexistence regimes.
5.6 Monte Carlo simulation study of colloidal phase behavior induced by critical Casimir forces

In this section, we use the experimentally measured particle pair potentials and Monte Carlo (MC) simulations to fully examine the phase behavior of colloids in binary liquid solvents. This combination allows us to simulate phase equilibria due to critical Casimir forces. We locate colloidal gas, liquid and solid phases as a function of temperature and colloid volume fraction. In contrast to standard MC simulations where the temperature $T$ only enters via the thermal energy, $\beta^{-1} = k_B T$, our simulations need to account explicitly for the temperature-dependent potential. The resulting colloidal phase diagram agrees well with experiment, indicating that many body interactions play a secondary role and that pair potentials describe the experimental system well. The phase diagram has the characteristic topology associated with molecular potentials like the Lennard-Jones potential, but occurs over a very narrow temperature range due to the strong temperature dependence of the critical Casimir interactions. These results highlight a novel way to control colloidal assembly by temperature-dependent critical Casimir interactions.

Simulating the phase behavior of the critical Casimir colloidal system requires a computationally efficient model. While in principle it is possible to compute the phase behavior from the ternary system of colloids in the liquid mixture, in practice this is prohibited by the large differences in length scales between the solvent molecules and the colloidal particles. We therefore model the colloidal system as particles interacting with effective potentials which implicitly account for solvent effects. We thereby assume that many-body effects are negligible and that interactions are well-described by pair potentials; this choice is validated by the close agreement between the simulated phase diagram and our experimental observations.

As discussed in section 5.4, we consider the measured potential to consist of a screened electrostatic repulsion $U_{\text{rep}}(r)$ and a critical Casimir attraction $U_{\text{attr}}(r;T)$. Assuming the critical Casimir attraction to be negligible at room temperature, and $U_{\text{rep}}(r)$ to be independent of temperature allows us to determine $A_{\text{rep}}$, $l_{\text{rep}}$, $A_{\text{attr}}$, and $l_{\text{attr}}$ directly from $U(r)$ according to equations (5.13)-(5.15). The results of those parameters were shown in Fig. 5.7, inset. Using those parameters we reproduce total pair potentials and overlay them onto the experimental data in Fig. 5.9. The observed difference between the reproduced and the measured potentials at short interparticle distances arises because the pNipam
particles are soft and thus easily compressed below their diameter at infinite dilution (note that the potentials shown in Fig. 5.9 are still finite at $r < 2r_0$), and the chosen potential form does not account for this effect. We show in the following that this apparent shortcoming of the chosen potential, however, introduces only a small error in the calculated phase diagram:

We confirm this by calculating the normalized second virial coefficients $B_2$ for both types of potentials. The second virial coefficient is a rough estimator of the phase behavior that should arise from a given potential [16]: a $B_2$ that is positive correlates with net repulsion between the particles, indicating that a phase transition should not occur; a strongly negative $B_2$ indicates the opposite. A $B_2$ that is close to zero indicates little net attraction or repulsion between the particles, so a phase transition is not expected. It follows that if the experimental and reproduced potentials at the same temperature lead to second virial coefficients of the same sign and comparable magnitude, the phase diagrams resulting from those potentials are expected to have the same topology and show only quantitative differences. We calculate $B_2$ according to [17]:

$$B_2 = -\frac{2\pi}{B_{2,HS}} \int_0^{r_0} r^2 \left[ \exp(-\beta U(r)) - 1 \right] dr$$

(5.16)

**Figure 5.9:** Experimental (circles) and fitted (lines) pair-potentials between colloids in a 3mp-water mixture at room temperature (green), $\Delta T = -0.4 \degree C$ (black), $\Delta T = -0.35 \degree C$ (red), and $\Delta T = -0.3 \degree C$ (blue). The green line effectively is the fitted electrostatic potential.
In this expression $B_{2,\text{HS}} = 2/3\sigma^3$ is the second virial coefficient for a system of hard spheres of diameter $\sigma$. For $0 < r \leq 1.5 \, r_0$ the potential is too repulsive to be accurately measured in experiment. To integrate Eq.5.16 we thus used $U(r) = \infty$ for $0 < r \leq 1.5 \, r_0$.

The upper integration boundary is set to $r = 7 \, r_0$ because all potentials are approximately zero. The resulting normalized second virial coefficients are given in Table 2. At the lowest temperature $|\Delta T| = 0.4^\circ\text{C}$, for which potential was measured experimentally, the calculated $B_2$ coefficients for the fitted and experimental potentials are close to zero, indicating that phase transitions should not yet occur. This result is in line with our experimental observation: at this temperature, phase transitions do not occur yet. At the two highest temperatures for which the potentials were measured experimentally ($|\Delta T| = 0.35^\circ\text{C}$ and $|\Delta T| = 0.30^\circ\text{C}$), the $B_2$ coefficients for both fitted and experimental potentials are negative, so we expect that the fitted potential will lead to the qualitatively correct phase behavior. Furthermore, at $|\Delta T| = 0.3^\circ\text{C}$, the $B_2$ corresponding to the experimental potential is almost identical to that for the fitted potential at $|\Delta T| = 0.35^\circ\text{C}$. These finding suggest that approximating the experimental potentials with the fitted ones will result in a calculated phase diagram with the correct topology, but shifted relative to the true one by no more than $0.05^\circ\text{C}$.

Obtaining a complete phase diagram from simulations requires more closely-spaced potentials in a wider temperature range than is possible to measure experimentally. We therefore interpolate the critical Casimir potentials using a linear fit of the parameter $\lambda_{\text{attr}}$ as a function of temperature and $A_{\text{attr}} \sim 1/\lambda_{\text{attr}}$. Using this linear fit, we also extrapolate the critical Casimir potentials at lower and higher temperatures. We apply these potentials in Gibbs Ensemble MC simulations to investigate the gas-liquid transition of the colloidal system. For each temperature, we determine the associated pair potential $U(r; T)$ and compute the equilibrium gas and liquid volume fractions. The resulting gas and liquid volume fractions bounding the gas-liquid coexistence region are shown in Fig. 5.10. Close to $T_{\text{ex}}$, e.g. at $|\Delta T| = 0.3^\circ\text{C}$, the critical Casimir potential induces a separation into a dilute

| $|\Delta T|$ (°C) | Experimental | Fitted |
|-----------------|--------------|--------|
| 0.4             | 0.28         | -0.48  |
| 0.35            | -1.0         | -2.4   |
| 0.30            | -2.5         | -3.9   |

Table 2: $B_2$ coefficients for the experimental and fitted potentials at three different temperatures.
gas phase and a dense liquid phase with volume fraction around $\phi = 0.004$ and $\phi = 0.45$, respectively. As the temperature decreases, the critical Casimir potential becomes weaker, and the gas-liquid coexistence region shrinks, until near $\Delta T = 0.336$ °C, the binodal curve ends in a critical point (determined as described below) with a volume fraction $\phi = 0.136$. For temperatures $|\Delta T| \geq 0.3$°C the particles stay homogeneously suspended. Very similar behavior is observed in the experiments described in section 5.3. At $|\Delta T| = 0.35$°C, the colloidal particles remain uniformly suspended, while at $|\Delta T| = 0.3$°C and $|\Delta T| = 0.25$°C, phase separation into gas and liquid was observed. The volume fractions of gas and liquid measured by confocal microscopy are in reasonable agreement with the simulated phase diagram given the large uncertainty in the determination of $\phi$ and $|\Delta T|$ (see Fig. 5.10). Note that as our simulations are based on effective pair potentials from dilute solution, the observed agreement between experiment and simulation indicates that many body effects are limited, even at high colloid volume fractions.

We further investigated the occurrence of crystal-liquid equilibria. As the Gibbs ensemble is not easily applied to solid-liquid coexistence, we instead employ Kofke’s Gibbs-Duhem integration technique [18]. Here the full coexistence curve is computed by numerically

**Figure 5.10: Colloidal phase diagram induced by the critical Casimir forces.**

The circles denote the gas-liquid coexistence curve. Blue- and red circles represent the gas phase (G) and the liquid (L) phase, respectively. The black star indicates the gas-liquid critical point. The blue and red squares denote the fluid-crystal (F-C) coexistence curve. The black squares and error bars are experimental coexistence points of gas-liquid ($\Delta T = -0.3, -0.25$ °C) and gas-crystal ($\Delta T = -0.20$ °C).
integrating the Gibbs-Duhem equation (or equivalently, the Clausius-Clapeyron equation) starting from a known reference coexistence point. For our system, the relevant reference point is the hard sphere system coexistence at a pressure of \( \beta P/\sigma^3 = 11.67 \) [19] and volume fractions \( \phi_l = 0.494 \) and \( \phi_s = 0.545 \), for the liquid and the face-centered cubic (fcc) crystal phase, respectively. The resulting fluid-solid coexistence curve is shown in Fig. 5.10. This coexistence curve connects well with the gas-liquid phase boundary: the two curves intersect at the temperature \( |\Delta T| = 0.22^\circ C \), the triple point, where the liquid-crystal coexistence pressure almost vanishes [20]. These observations are consistent with our experiments: at temperatures \( |\Delta T| \) between 0.25 and 0.20 \( ^\circ C \), face-centered cubic (fcc) crystals formed inside the liquid drops; at \( |\Delta T| = 0.20^\circ C \), they consisted entirely of fcc crystals (see Fig. 5.4), exhibiting a volume fraction of \( \phi \sim 0.5 \), in agreement with the simulations (see Fig. 5.10).

The phase diagram shown in Fig. 5.10 mirrors the well-known gas-liquid-solid phase diagram of Lennard-Jones systems [21, 22], lattice-based Ising models [23], and systems with square-well potentials [24, 25]. The diagram is inverted with respect to the known phase diagrams of Lennard-Jones systems, because \( \beta U \) becomes stronger as we approach the solvent phase separation from below, instead of \( \beta U \) becoming weaker with increasing temperature, as is the case in Lennard-Jones systems. Because for our system, the interparticle potential is explicitly strongly temperature dependent, the entire phase diagram extends only over a very small temperature range of \( \sim 0.3 \) \( ^\circ C \).

### 5.7 Influence of the solvent composition

In this section, we investigate the influence of the solvent composition on the range and amplitude of particle pair potential. To do this, we increase the mass fraction of 3mp, in the water-3mp mixture, from 0.25 to 0.28 and use equal amount of H\(_2\)O and D\(_2\)O. The increase of 3mp lowers the solvent phase separation temperature to \( T_{cx}=39.5 \) \( ^\circ C \). We measure the particle pair potential directly from the density fluctuations of the colloidal particles as described earlier. The resulting particle pair potential at different temperatures is shown in Fig. 5.11a. Similar to the system with 0.25 mass fraction of 3mp, the range and the amplitude of attraction increase when the temperature approaches the solvent phase separation temperature. We compare pair potentials of the two solvent
compositions, measured at the same $\Delta T$. We see that the range of attraction increases as the 3mp fraction approaches the critical composition. These observations are in good agreement with earlier experimental results [1, 9]. We used this system to investigate colloidal phase behavior as before. We found that the system exhibits the gas-liquid coexistence at a larger temperature difference of $\Delta T = 0.40$ °C to the critical temperature. These results suggest that as the range of attraction increases, the gas-liquid coexistence appears at lower attraction strength, as expected from the second virial coefficient. Therefore, solvent compositions closer to the critical point may be advantageous, since they allow investigation of colloidal phase behavior in a wider temperature-range.

Finally, we investigate the potential depth as a function of temperature by plotting potential depth as a function of $\Delta T$ in Fig. 5.11b. The results show that the potential depth increases strongly as the temperature approaches the solvent phase separation temperature. The data suggest an exponential relation between the potential depth and $\Delta T$. This exponential dependence is in good agreement with results of Bechinger et al. for critical Casimir force between a single colloid and a planar surface [1, 9].

![Figure 11: Critical Casimir attractions.
](image)

(a) Pair potentials at different temperatures of pNipam particles suspended in binary solvent consisting of 28 % 3mp. (b) Potential depth as a function of $\Delta T$ below the solvent separated temperature $T_{cx}$. The data points are the minima of the pair potentials in (a). Solid line indicates the best exponential fit to the data.
5.8 Conclusions

In this chapter, we have demonstrated the formation of equilibrium liquid and solid phases using critical Casimir forces. Using Monte Carlo simulations with experimentally determined pair particle potentials as input, we have completed the phase behavior numerically, and mapped out the corresponding phase diagram. This active and reversible control of colloidal gas-liquid and liquid-solid equilibria lays the groundwork for novel assembly techniques making use of critical Casimir forces by a unique procedure of precise temperature control. Because of the reversibility of the interactions, one can imagine using temperature gradient and zone melting techniques to grow perfect equilibrium structures, in analogy to atomic crystal growth. The presented close correspondence of the colloidal and the molecular gas-liquid transition suggests further studies of equilibrium and non-equilibrium phenomena using these colloidal systems as models with active potential control. The close agreement between the molecular Van der Waals theory and the colloidal phase separation that we observe on the scale of just a few particle diameters suggests that such mean field models may also be applied to describe the condensation of nano particles in the assembly of nanostructures. Moreover, the agreement between the simulation phase diagram and experimental data suggests that the critical Casimir interactions between colloids are sufficiently well described by two-body potentials. In contrast to other temperature-dependent colloid-colloid potentials, the critical Casimir effect allows temperature control of colloidal phases in a new, reversible and universal fashion. We foresee that more complex structures can be obtained by particle surface patterning to create anisotropic critical Casimir interactions. Together with the tunable solvent correlation length, such surface modification might allow mimicking “atomic orbitals” to assemble colloidal particles into structures similarly complex as those of molecules.
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Bibliography


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