The phase behavior of a weakly attractive colloidal system
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4.1 Introduction

The structure and dynamics of colloidal systems interacting via a (weakly) attractive potential is a current topic of high interest. Theory and simulations point to phase behavior not encountered in atomic or molecular systems. Examples are the predicted existence of critical points in the solid phase \(^{87}\), and the existence of low- and high-density glasses separated by a phase line ending in a critical point\(^ {88–90}\). On the other hand, they may show phase behavior similar to what is observed in molecular systems, a liquid phase in equilibrium with a gas phase. It all depends on the strength and range of the attraction. However, experiments are scarce \(^ {90, 91}\). The lack of a continuous control parameter together with the influence of gravity are two, amongst others that slacken the pace of the experimentalist to verify the predicted phenomena of the simulators and theorists. An attractive interaction can be induced in several different ways, most notably by adding a non-adsorbing polymer to a hard-sphere repulsive colloidal system\(^ {16}\). Size and concentration of the polymer determine the range and strength of the interaction. The addition of polymer cannot be considered as a continuously controllable parameter. Another scenario for an attractive interaction is offered by charge stabilized colloidal particles in a binary liquid mixture. More than twenty years ago, Beysens and Esteve\(^ {92}\) observed the reversible “aggregation” of colloids near the phase-separation temperature \(T_{cs}\) of the suspending binary liquid, still in the one-phase region. The aggregation was obvi-
ously induced by an attraction that could be controlled by the temperature. Reversing the temperature away from the phase-separation line, the aggregate was resuspended to its original state. Gravity prevented an assessment of the state the particles condensed into. At first, the authors contributed the phenomenon to the adsorption layers formed on the colloidal particles when the phase separation line of the binary mixture was approached. Provided one could density match the colloid with the binary liquid, this system promised a continuous control over the potential with a reduced influence of gravity. We found this system in charge-stabilized polystyrene particles suspended in the quasi-binary mixture of 3-methylpyridine/\(H_2O/D_2O\).

Figure 4.1: Schematic representation of the scenario leading to aggregation at \(T_a\) and subsequent phase separation of the binary mixture at \(T_{cx}\). For the polystyrene in the quasi-binary mixture of 3-methylpyridine/\(H_2O/D_2O\), 3-methylpyridine (dark shade) adsorbs preferentially onto the polystyrene and prefers the 3-methylpyridine-rich phase after phase separation. 3MP and water are labelled black and white, respectively. \(T_a\) and \(T_{cx}\) are the aggregation temperature and coexistence temperature of binary liquid mixture, respectively.

The first paper of Beysens evoked a discussion about the nature of the attraction leading to the aggregation phenomenon. Many papers followed, experimental and theoretical, to elucidate the process or establish the parameters determining the process e.g\([92, 35, 66, 68, 93, 94, 69, 95–99]\). Beysens and others reported observations of aggregation phenomena in systems of colloidal silica dispersed in mixtures of 2,6-lutidine and water in the one-phase region. They showed that aggregation was related to the affinity of the colloidal surfaces for one of the solvent components. They did measurements in a temperature range near the critical temperature in the two-phase region of the mixture. They related the aggregation to the prewetting transition expected near the critical point of the binary-liquid mixture. An alternative approach was to consider the aggregation as a phase separation in a three-component system\([94]\). In this explanation, the main role of the colloids is to couple to the degrees of freedom of the host liquid by preferring one of the liquid species and thereby decreasing the local chemical potential. In the interface potential
approach, Yeomans and coworkers considered the capillary condensation and the subsequent bridging between the spheres as a possible mechanism for the wetting-induced colloidal aggregation[100]. This mechanism of capillary condensation was beautifully demonstrated by the experiments of Cannel et al. Recently, the initial interactions in a stable suspension were modelled in terms of an improved DLVO potential with the attractive dispersion interaction described by the Dzyaloshinskii-Lifshitz-Pitaevskii (DLP) potential[92, 66]. In this model, the authors take into account the presence of an adsorbed layer to calculate the Van der Waals interaction and the screened electrostatic potential. The result showed that the dominant factor that modifies colloidal stability in the presence of an adsorbed wetting layer is the change of the Debye screening length within the adsorption layer, which is different from that in the bulk. This screening potential progressively weakens the repulsive contribution to the DLVO potential as the thickness of the adsorption layer increases. The model was applied to typical dilute suspensions of silica in 2,6-lutidine/water mixtures. The aggregation sets in when the adsorbed layer thickness is about 12nm. The particles can overcome the barrier, and the adsorbed layers of the two particles merge. The inter-particle medium becomes lutidine-rich and the resulting interaction potential has a high repulsive barrier which prevents the particles from coming into direct contact with each other. The model is essentially an adaptation of the classical description of the destabilization of a colloidal suspension by adding salt. Here it is not the salt, but the dielectric constant of the adsorbed layer that determines the path of the flocculation. Most of the models neglected the proposal of Fisher and De Gennes in 1978[78] that the overlap of the adsorption layers leads to a lowering of the free energy or an effective attractive potential. The solvent-mediated interaction to describe “flocculation” of colloids in binary mixtures was part of a general description of the interaction between interfaces in a medium close to a critical point. The interaction results from the enhancement of order parameter fluctuations near the critical point. The local perturbation caused by a particle is not screened completely after a few atomic layers, but influences the system over an appreciable distance, i.e. the correlation length. The original proposal was worked out in more detail by, amongst others, Krech and Dietrich[101, 38]. During this process, the phenomenon lost its name, solvent-mediated interaction, and became known as the critical Casimir effect. Experimentally, the effect has been observed by Rafai in flat geometries. Dietricht and Hertlein[102] reported the direct measurement of a critical Casimir force between a silica particle and a flat surface in a 2,6-lutidine/water mixture. We will show in this chapter that the solvent-mediated interaction, or critical Casimir effect, is the driving force in the observed phenomenon. Ideally one would use a system where the normal Van der Waals attraction is absent. We found a sys-
tem in fluorinated particles, with a high surface charge density, which are wetted by water. The index of refraction is matched with the suspending fluid, their density, alas, is not.

This chapter focuses on the systematic experimental study of the colloidal phase behavior in the one-phase region $T < T_{cx}$. We show that the "aggregation" observed by Beysens and coworkers is in reality a reversible phase transition for the colloidal system. Density matching between the particles and the suspending medium enables us to observe stable gas-liquid and gas-solid equilibria. In a density matched system the nuclei can - in principle - grow to macroscopic dimensions, while in a non-density matched system gravity perturbs this growth process at a very early stage, as observed in the measurement by Narayanan[103]. The phases are characterized by synchrotron Small-Angle X-ray Scattering (SAXS). The complementary techniques of visual observation (backscattering), laser-transmission measurement (forward scattering), and microscopy are used to substantiate our findings from the SAXS measurements. Measurements on the index matched system indicate that the driving force of the condensation transitions is the critical Casimir effect.

4.2 Experimental Techniques

Experiments were carried out using two different charged colloidal particles: polystyrene and silica particles, suspended in a quasi-binary liquid mixture of 3-methylpyridine/$H_2O/D_2O$. The composition of the binary mixture is $C_{3MP} = 0.25$, $C_{H2O} = 0.5625$, $C_{D2O} = 0.1875$. For this liquid mixture without colloids, $T_{cx}$ is around $65^\circ C$. The water-to-heavy water ratio is chosen such that the density of the liquid mixture closely matches that of the particles in the temperature region where the transition occurs. On the other hand, this composition is far from the critical concentration of the binary mixture ($C_{3MP} = 0.32$) thus avoiding effects of solvent critical scattering.

At the same time, this concentration allows studies in the region of the phase diagram where the colloidal condensation region is expected to be at its widest, where the difference between the condensation temperature $T_a$ and the demixing temperature of the solvent $T_{cx}$ is largest (refer to the schematic phase diagram in Fig 4.1). The particles have a diameter of 105nm with a polydispersity of 2.3%, determined from the scattering form factor, and an effective surface-charge density of $0.4 \mu C/cm^2$, measured by electrophoresis. The 3-methylpyridine and heavy water were purchased from Aldrich chemicals. The water is deionized Millipore water (MilliQ). Six samples were prepared with particle volume fractions of $\phi = 0.0025$, 0.0050, 0.0100, 0.0150 and 0.0500, and a reference sample without any colloidal particles at all. The samples were put in flat borosilicate capillaries with an optical path length
of 0.5mm, which were flame sealed to avoid solvent evaporation. The glass surfaces were thoroughly cleaned with chromic acid and rinsed with Millipore water to guarantee a clean OH surface and to avoid contaminations that might influence the phase behavior. The samples were studied by small-angle x-ray scattering (SAXS) at the beamline ID02 of the European Synchrotron facility (ESRF). A thermostatted oven, available at the beamline, ensured a temperature stability better than 2mK. We raised the temperature in steps of 0.05K, waited for 5 min after each temperature increment to let the system equilibrate, and recorded the scattered intensity. This corresponds to an average heating rate of $10^{-4}K/s$. The measured 2-dimensional SAXS patterns were normalized and azimuthally averaged to obtain the intensity $I(q)$ as a function of the amplitude of the scattering vector $q = (4\pi/\lambda) \sin(\theta/2)$ with $\theta$ the scattering angle and $\lambda = 1\AA$ the wavelength of incident X-rays. Transition temperatures were also verified by measurement of the sample turbidity. For direct visualized observation the samples were placed in a thermostatted water bath, and pictures of the samples were taken using a CCD camera.

### 4.3 Results

#### 4.3.1 Two characteristic temperatures: $T_a$ and $T_{cx}$

The aggregation temperature of the colloidal particles, $T_a$, and the phase separation temperature, $T_{cx}$ (subscript $cx$ denoting the coexistence of 3MP-rich and 3MP-poor phases), of the mixture were determined for each sample by both visual observation and turbidity measurements. Fig. 4.2 shows the typical evolution of the transmitted laser intensity as a function of temperature at $C_{3MP} = 0.25$. The first sharp decrease in transmission (Fig. 4.2 curve b) indicates the condensation temperature. The following increase results from sedimentation of the particles. Finally, the second sharp decrease at $T_{cx}$ results from the solvent demixing. Curve a is the transmission of the pure binary mixture. The samples were then placed in a water bath to observe the macroscopic phase behavior by using the CCD camera.

The photographs in Fig. 4.3 qualitatively illustrate the macroscopic state of the suspension in the characteristic regions. At low temperature, the particles are homogenously distributed in the binary mixture (a). As the temperature increases, the homogenous colloidal system separates into a dense (particle-rich) phase in the upper and a rare (particle-poor) phase in the lower sector of the sample cell (b). The particle-rich phase starts to grow from the liquid-vapor interface downwards. Above $T=56.9^\circ C$, the particle rich phase becomes unstable with respect to gravity and falls down to the bottom of the sample cell (b’). When we increase the temperature further
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Figure 4.2: (A) Examples of laser transmission measurements. The temperature scan on both binary mixture (curve a) and colloidal suspension in a binary mixture independently (curve b). (B) The schematic phase diagram of polystyrene particles in the mixture 3-methylpyridine/\(H_2O/D_2O\). \(T_a\) and \(T_{cx}\) are the aggregation temperature and coexistence temperature of binary liquid mixture, respectively.

Figure 4.3: A series of photographs representing the characteristic state of polystyrene particles in the mixture 3-methylpyridine/\(H_2O/D_2O\) at ratio \(X=0.25\) and the volume fraction \(\phi=0.01\).

to \(T_{cx}\), the binary suspending liquid finally separates into a 3MP-rich and a water-rich phase with a sharp interface (c). Most of the particles assemble in the lighter 3MP-rich phase.

A small amount stays at the bottom as a dense phase. Upon shaking, practically all colloidal particles are assembled into the upper 3MP-rich phase. The observed phase behavior of the samples combined with turbidity measurements are collected in a diagram (Fig.4.4), where the characteristic temperatures are plotted as a function of volume fraction. The remarkable feature of this diagram is the large separation
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Figure 4.4: Temperature-dependent phase behavior as a function of volume fraction based on both visual observation and turbidity measurements. The lower set of points are the condensation temperatures $T_a$, the upper set the demixing temperatures $T_{cx}$. The temperature difference between $T_{cx}$ and $T_a$ is much larger than the one degree reported earlier. Here, the difference between $T_a$ and $T_{cx}$ is approximately 6.5 degrees at a volume fraction of 0.015. The large temperature gap rules out a possible relation between aggregation and the prewetting transition, or capillary condensation.

4.3.2 Influence of gravity on the condensed state

The density of the suspending liquid can be tuned by the ratio heavy water to water, $X$. Fig.4.5 shows the density of binary liquid mixture at different values of $X$. The result is only applied at room temperature due to the different thermal expansion of each component, however, we could estimate the density matched point at the aggregation temperature directly by measurement. We studied three samples with different ratios, $X$, keeping the concentration of particles constant at $\phi = 0.01$. Table 2.3 gives the details of the sample preparation for the system polystyrene spheres in the mixture of 3-methylpyridine/$H_2O/D_2O$.

In Figs 4.6-4.10, we demonstrate all types of colloidal phase behavior by macroscopic observation. We were able to do this only with the samples where the ratio $X = 0.5$. In Fig.4.6, a colloidal-rich phase is formed in the middle of the capillary. This phase remained stable for hours, no drift upwards or downwards was observed. Hence, with this ratio the density of the fluid can be considered to match
Figure 4.5: Density of binary liquid mixture at the different ratio heavy water and water. The result is from the calculation at room temperature. The thick solid line represents the density of polystyrene.

Figure 4.6: The photographs are taken at different temperatures of time for polystyrene particles in mixture 3-methylpyridine/H₂O/D₂O. The colloidal-rich phase is formed in the middle of capillary at $X = 0.5$. Left: T=49.5°C; Middle: T=50°C; Right: T=50°C, after 4 hours respect to state in the middle.

the density of the particles with their adsorption layers at $T_{ex}$. After four hours, the macroscopic smooth appearance of the dense phase began to coarsen. A sponge-like structure developed, as illustrated in Fig. 4.7. The image was magnified ×100. In order to characterize the sponge-like structure, we calculated the static intensity correlation function, shown in fig. 5.4. The two static intensity correlations at different times show that the size of the denser regions, as well as the darker, less dense
regions, increases with time. At a slightly higher temperature the coarsening developed to form the structures shown in fig. 4.9. At the beginning, it is a connected branch structure. Chains of irregular beads, with a high density of colloidal particles, are seen in a colloid-poor background. The beads coalesce to eventually form droplets. The pattern is consistent with simulation result reported by Tanaka[104]. These droplets then remained stable for hours, not moving up or down. The droplets have the signature of a liquid. Macroscopically this looks like the spinodal decomposition into the liquid phase. What happens when these droplets move and collide with each other can be seen in Fig. 4.10. At the ratio $X = 0.25$, the particles firstly condensed at the upper part of capillary. With time, the dense phase will settle down
Figure 4.9: Structure evolution of polystyrene particles in the mixture 3-methylpyridine/$H_2O/D_2O$ at temperature close to $T_{c,x}$ and ratio $X=0.5$. (a) sponge-like structure, (b) loosely connected branch structure, (c) droplet.

Figure 4.10: The state of polystyrene particles in a binary mixture at $T=63^\circ C$ and $X=0.25$. (a) The colloid-rich droplet on the top of colloid solid (pillar shape). (b) Two colloid-rich drops contact. (c) Two droplets start to merge.

because the colloidal-rich phase is heavier than the surrounding liquid at this ratio. The corresponding states are displayed in Fig.4.3. Due to the slight mismatch in density, we observe an interesting phenomenon at the low part of the capillary. One free colloidal-rich droplet is merging with another droplet which is positioned on top of a solid pillar. Fig.4.10 shows the sequence of coalescence of the two drops. From the coalescence event we can determine the interfacial tension between the colloidal-rich liquid and the colloidal-poor gas phase. A detailed description of the coalescence events will be reported in chapter 7. We obtained an interfacial tension of around $2.7 \times 10^{-7} N/m$. This ultra-low interfacial tension verifies the coexistence of a colloid-gas and colloid-liquid equilibrium. Apparently we have chosen the parameters such that we are at the triple point of our colloidal system. Since gravity is acting now we can not be sure if this is the true equilibrium triple point. The compressed solid pillar may be a glass. The structure factor measurement by X-ray should give
an answer to clarify. For the ratio $X = 0.75$, the particles condensed at the upper part of the capillary and remained at the top. It is essential to study the equilibrium phase behavior without sedimentation disturbing the process. Compared with the previous works by Beysen[35], the similar phenomena which they defined as the aggregation of the silica particles in a lutidine and water mixture barely identify the true nature of "aggregation" because of the limited time to investigate the equilibrium phase before the aggregates dropped out the sight.

We mainly focus on the condensation of colloidal dispersion at the one-phase region of binary mixture, however, the phenomena about the colloidal phase behavior in the two-phase region of binary mixture is also worthwhile to explore. We observed the partitioning of the particles into a preferred phase when the temperature is quenched deeper into the two-phase region. Partitioning particles into preferred phase is a technique which is used for the separation of polymers and biological macromolecules[105, 106]. From the visual observation, we found that polystyrene particles will partition into 3MP phase. The liquid-like structure of colloid is observed in the 3MP-rich region after phase separation.

4.3.3 Evolution of the microstructure

We qualitatively studied the macroscopic condensed phase by the backscattering and forward scattering in the previous section on a scale large in comparison with the building blocks. Now we quantitatively characterize the phase by the structure factor using the small-angle x-ray scattering. Typical SAXS intensity profiles of the sample with volume fraction $\phi = 0.015$ at temperatures around the condensation temperature are shown in Fig.4.12. They are representative of the scattering profiles of all the samples that form a colloidal solid from gas phase. Curve D is the scattering intensity profile of a dilute sample with volume fraction 0.0005 at $T = 25^\circ\text{C}$. We consider this to be the form factor of the particles. The examples shown are taken from a run where we increase the temperature from room temperature to $T_{cx}$. We observe that the form factor changes as temperature increases close to the coexistence temperature of the binary mixture. The structure factor, obtained from intensity profile by division with the measured form factor at the different temperature appears the artificial peak at the $q$ value where is the minimum of form factor. The form factor has to be adapted at the different temperatures. The slight shift of the form factor may result from the adsorption layer on the particle when the temperature approaches the coexistence temperature of binary mixture. Due to the low electron-density contrast between polystyrene and the binary mixture, we could not qualitatively determine the thickness of the adsorption layer as a function of temperature. A few degrees before $T_a$, determined by the turbidity measurement, we let the system equilibrate
for 5 minutes. We then increase the temperature in increments of 0.05°C, wait for 120 seconds, and take a spectrum with an exposure time of 60 seconds. We repeat this procedure until we reach $T_{cx}$. This amounts to an average rate of change of the temperature of $10^{-4}$°C/s. The spectrum $A$ taken at $T = 51.6$°C equals 1 after dividing the form factor. It shows the features typical to a dilute gas phase. Within 0.3 degrees of $T_{cx}$ we observe the appearance of pronounced peaks, indicating a phase transition from gas to solid (B). We obtain the structure factor of the solid phase by dividing the scattering function $B$ by the measured form factor (Fig.4.12). We observe peaks characteristic of a crystalline solid. Firstly, the height of the first maximum of $S(q)$ is above the static freezing criterion ($\sim 2.85$)[107]. The peaks are located at $q$-values in the ratios $\sqrt{3} : \sqrt{4} : \sqrt{8} : \sqrt{11} : [\sqrt{16} : [\sqrt{19} : \sqrt{20} : \sqrt{24}$. The bracket means these orders are not present here. These peak positions are characteristic of the face centered cubic (fcc) lattice. From the absolute values of $q$ (indicated by ticks in Fig.4.12b) we calculate the lattice spacing to be 184nm. Fitting the peaks with Gaussian functions with a full width at half maximum of $\Delta q = 0.005$nm$^{-1}$. We calculate a size of the crystalline domains ($l_c$) to be $l_c \approx \frac{2\pi}{\Delta q} = 1250$nm. The hexagonal symmetry of the diffraction peaks in the two-dimensional SAXS pattern (in Fig.4.11) indicates that the fcc crystals are preferentially oriented with their hexagonal close-packed planes parallel to the glass wall of the capillary [108].

Figure 4.11: 2D images of the scattered intensity. Several rings with the mixture of speckles and spot with hexagonal symmetry.

With a particle radius of 52.5 nm, and a lattice spacing of 184nm, we calculate a volume fraction of $\phi = 0.38$ for the fcc crystal. For a hard sphere fcc solid, the volume fraction has a value of 0.54 at the melting point. From which we calculate an equivalent hard sphere radius of 59 nm for our charged particles. In the crystal, we determine the free space between the surfaces of the particles to be 22 nm[58]. This is
Figure 4.12: (a) SAXS intensity profiles at the characteristic temperature for the volume fraction of particle 0.015. Curve D represents the fitted form factor based on the measurement of intensity at volume fraction $\phi=0.0005$. The intensity profile is shifted for the sake of clarity. (b) The corresponding structure factor for curve B. The vertical ticks under the Bragg peaks indicate the expected positions of the lattice spacing $s$ of an fcc powder with a lattice parameter $a$ of 184 nm.

Figure 4.13: The development of $S(q_m)$ and $q_m$ as function of temperature at the volume fraction $\phi = 0.01$.

an order of magnitude larger than the thickness of the adsorption layer, which is approximately equal to the bulk correlation length. When the temperature approaches $T_{cx}$, the adsorption layers could overlap, but the colloidal particles with their adsorption layers are still suspended in the same homogeneous liquid as the particles in the gas phase from which the solid crystallized. However, the global composition of the
suspending liquid inside the crystal is different from the gas phase, due to an at least two orders of magnitude higher volume fraction of the particles. The suspending liquid contains more 3-methylpyridine, still less than in the 3-methylpyridine-rich phase, that is formed at a higher temperature when the suspending liquid phase separates. We can sublimize the crystal when we decrease the temperature back to \( T = 51.6 \degree C \) (line C). We can repeat this whole process several times. The transition is reversible. Furthermore, we do not see any hysteresis, provided the temperature is changed slowly. A peak in \( S(q) \) results from correlations in the positions of neighboring particles, and its location provides a rough measure of the mean interparticle distance. Fig. 4.13 shows that the peak moves to low \( q \) and grows in height. The \( q_m \) shift to low \( q \) value and the amplitude increase of the peaks suggested crystal growth. The time scale on which we change the temperature, should be compared with the nucleation- and growth-rate of the crystal. The crystallization process will be discussed in chapter 6 in detail.

Figure 4.14: 3D plot of intensity profile and structure factor as function of \( q \) vector and temperature for the particle with the volume fraction \( \phi = 0.05 \).

For the sample with a volume fraction 0.05, the colloidal phase behavior is different from the low density samples. Fig. 4.14 shows a 3D plot for the intensity profile and structure factor as a function of temperature to show the characteristics of evolution of structure. For the sake of clarity, some intensity profiles are shifted at the characteristic temperature. In Fig. 4.15 presents the evolution of \( SAXS \) intensity for the sample of volume fraction 0.05, as the temperature was raised from room temperature until \( T = 57.3 \degree C \). The intensity profile (curve I) is similar to that of the form factor, which was determined from a very dilute sample with volume fraction
Figure 4.15: (a) SAXS intensity profiles in the vicinity of $T_a$. Curves I-IV present the characteristic temperature intensity profile respectively. The curves have been displaced along the intensity axis for the sake of clarity. The inset shows the 2-D scattering pattern corresponding to curve III. (b) Structure factors corresponding to the intensity profiles $I(q)$ in Fig.4.15(a). These demonstrate the transition from gas (I) to liquid (II), and solid (III). The ticks at the bottom in (III) indicate the peak positions for an $fcc$ crystal with lattice constant $d=181$ nm. The solid line indicates the structure factor calculated for $fcc$ crystals of size $\sim 900$ nm.

0.0005. After subtraction of the background scattering due to the suspending fluid and division by the form factor, we obtained the corresponding structure factor depicted in Fig.4.15(I). The structure factor is essentially 1 over the whole wave vector range. When we raised the temperature by 0.2 °C, we observed the appearance of a pronounced peak (curve II) as shown by the structure factor in Fig.4.15(II). This structure factor is typical for a liquid or a dense fluid phase. With increasing temperature, the height of the peak increased continuously until $T = 59.5$ °C (curve III), where it suddenly jumped to a value above 2.85, the freezing criterion[68]. We also observed that the peak narrows and higher order reflections appear: the liquid has turned into a solid. When we lowered the temperature back to 57.3 °C, we obtained spectrum IV which is indistinguishable from I: the solid melts and the suspension is back in the gas phase. This whole process can be repeated several times. The transition is reversible and we do not see any appreciable hysteresis. The peaks in the structure factor of the solid phase in Fig.4.15 b are located at $q$-values in the ratio $\sqrt{3} : \sqrt{4} : \sqrt{8} : \sqrt{11} : \sqrt{12}$. These peak positions are characteristic of the face cen-
tered cubic (fcc) lattice. The observed peaks correspond to (111): (200): (220): (311): (222). From the absolute values of \( q \) indicated by ticks in Fig. 4.15b (III) we calculated the cubic crystal lattice constant to be 181 nm. Using this lattice parameter and the radius of the particle known from the form factor, \( R = 52.5 \) nm, we determined the volume fraction of particles \( \phi_{fc} = 0.406 \). The peaks in Fig. 4.15b (III) can be fitted with Gaussian functions with a full width at half maximum of \( \Delta q = 0.007 \text{nm}^{-1} \) which is significantly larger than the instrument resolution \( \approx 0.003 \text{nm}^{-1} \). The fitted width corresponds to an average crystallites size of \( l_c \approx 2\pi/\Delta q \approx 900 \) nm.

The \( q = 0 \) limit of the structure factor is related to the isothermal osmotic compressibility. The \( S(0) \) and \( S(q_m) \) (in Fig. 4.16) defines the value of \( S(q) \) at \( q = 0 \) and the first maximum. They are extracted from the structure factors in Fig. 4.14. Although we observe the changes of slope in both two curves, the continuity in \( S(0) \) and \( S(q) \) suggest the phase transition does not have the character of the first-order phase transition. However, in terms of slopes changes, it suggests the occurrence of a second order transition. This may result from a too rapid increase of temperature during the measurement.

One feature to be mentioned in Fig. 4.17 is the presence of an isoscattering point at \( q \approx 0.05 \) during the early stage of the phase transition, when the attraction is already active but a static liquid peak has still not developed. Around this \( q \)-value the scattered intensity is independent of temperature. This onset of phase transition can be distinguished from sudden deviation from this isoscattering point.

This system also offers the opportunity to study the melting process because the
transition process is reversible. Fig. 4.18a shows that the intensity profile changes when we decrease the temperature. The amplitude of peaks decreases and $q_m$ shifts to low $q$ (Fig. 4.18b). There are less correlated particles and the mean interparticle distance gets larger. They are signature that big colloidal crystallites become smaller. This melting process can be controlled by temperature directly.

4.3.4 Phase diagram of colloidal dispersions in a binary mixture

The phase behavior that we observe with SAXS, turbidity measurement and visual observation, is summarized in a tentative phase diagram for the colloidal system in Fig. 4.19, where we plot $\Delta T = T_{c3} - T_a$ versus the reduced volume fraction $\phi^*$.

From all the data obtained for colloids in binary liquid mixtures, it is clear that this temperature difference is the experimentally relevant parameter to describe the state of the colloidal system. At low volume fractions, the colloidal system shows two stable phases: fluid and crystal. At higher volume fractions, we observe equilibria of gas and liquid, and liquid and solid.

We determine the volume fractions at the transitions in the following way. The volume fraction of particles in the gas phase is set to the initial volume fractions of the samples we prepared. The volume fraction in the solid phase is determined from the crystal lattice constant and particle radius as described above. For the volume fraction of the liquid, we fit the structure factor to an effective hard-sphere model[109]. As a reference state we take the liquid in equilibrium with the solid un-
under the assumption that the liquid-solid gap is the same as that of hard spheres[58].
With this reasonable assumption we came to the volume fraction of liquid and indicated them by close circles in Fig.4.19. The similarity of the diagram presented in Fig.4.19 with the diagrams suggested by Frenkel[87] for attractive colloidal systems is striking. The existence of a gas-liquid coexistence region before the liquid-solid coexistence proves that there is an attractive potential with a relatively long range. Another observation for colloid-gas and colloidal-liquid coexistence is the ultra-low interfacial tension between the colloid-rich and colloid-poor phases. We present one example of coalescence events when two colloid-rich droplets merge in Fig.7.9. Following the width of the liquid bridge as function of time, we could determine the interfacial tension between colloid-rich and colloidal-poor, the detailed mechanism of which will be presented in chapter 7. The $1.1 \times 10^{-7}$ N/m interfacial tension strongly verifies the colloidal-gas and colloidal-liquid equilibrium. Our experimental phase diagram sheds a new light on weakly attractive colloidal systems.

4.3.5 The two length scales

From the model we proposed in chapter 3, two length scales play a crucial role to explain the interaction. The repulsive part is from Coulombic double-layer interaction, which is characterized by the Debye screening length; the attractive part results from either the solvent mediated interaction or the Van der Waals interaction. The
Figure 4.19: Phase diagram of polystyrene spheres in the quasi-binary mixture 3-methylpyridine/H$_2$O/D$_2$O. Triangles, solid circles and squares mark the temperatures $\Delta T = T_{cx} - T_a$ versus volume fraction $\Phi$ for solid, liquid and gas phases.

solvent mediated interaction is characterized by the correlation length. Both light scattering and X-ray small-angle scattering measurement are carried out to determine the correlation length independently. In the X-ray measurement, we measured the binary liquid mixture without colloids and the same liquid mixture with colloids. The Ornstein-Zernike relation predicts linear variation of the reciprocal of the scattered intensity with the square of the scattering vector. This behavior is clearly observed from sample of binary liquid mixture without colloids in Fig. 4.20. The correlation length $\xi$ was determined by the intercept and slope of Fig.4.20b at each $(T_{cx} - T)/T_{cx}$. We can determine the correlation length of binary liquid mixture with colloids corresponding to the value of binary mixture at the same reduced temperature to $T_{cx}$. In chapter 3, we mainly use this measured correlation length to calculate the interaction.

$$\frac{1}{I_q} = \frac{1}{I_0} (1 + (q\xi)^2),$$  \hspace{1cm} (4.1)

where $q = (4\pi n/\lambda) \sin(\theta/2)$, $\lambda$ the wavelength of light, $n$ the refractive index, $I_0$ the intensity scattered at $q = 0$, and $\xi$ the correlation length.

From dynamic light scattering measurement, we observed the double-exponential correlation functions in the binary mixture with colloids. Fig.4.21 shows the normalized $g^{(2)} - 1$ (intermediate function) for different temperatures. A feature of our data is the presence of two relaxation process at all temperatures. Especially the shape of double-exponential decay is more pronounced when the temperature approaches to
Figure 4.20: (a) The reciprocal of the scattered intensity $I$ as a function of the square of the scattering vector amplitude $q$ for binary mixture without colloids when the temperature approaches to coexistence temperature of binary mixture. $C_{3MP} = 0.25$. (b) The measured correlation length as function of the reduced temperature.

The coexistence temperature of binary mixture. These curves can be fitted with two exponential as suggested by Hair[110]. This expression also arises in a way from the theoretical treatment of Anisimov[111].

$$g^2(t) - 1 = A_{fast} \exp[-(\Gamma_{fast} t)] + A_{slow} \exp[-(\Gamma_{slow} t)], \quad (4.2)$$

The fast mode can be illustrated by the composition fluctuation of solvent; the slow mode should represent the mutual diffusion of colloids. The composition fluctuation decay rate: $\Gamma_c = D_c q^2$ gives value of the coefficient $D_c$ that when reduced by the Kawasaki-Stokes form, $D_c = k_B T / 6 \pi \eta \xi^*$, yielded a dynamic correlation length $\xi^*$ in qualitative agreement with the behavior expected for the static correlation length $\xi$. $\eta$ is the viscosity of solvent. From the independent measurements with the same condition of binary mixture, we measure the viscosity in the rheometer at each corresponding temperature. Thus, the correlation length ($\xi$) of local concentration fluctuations (in fast mode) can be determined. The correlation length obtained from the dynamic light scattering is shown in Fig.4.22. The correlation length at reduced temperature with respect to $T_{cx}$ is well determined. It means the correlation length at the aggregation temperature is well defined.

In Fig.4.4, we observe the polystyrene particles shift down the demixing temperature of binary mixture. In order to estimate salt content of colloids in a binary mixture, we put the salt with known concentration to binary liquid mixture. From the equivalent of shift of $T_{cx}$, we can determine the salt content of colloids in a binary
Figure 4.21: Temperature dependence of the correlation function for polystyrene particle in 3MP/water/heavy water mixture. Notice that with a single-exponential decay is found at the temperature far away from $T_{cx}$.

Figure 4.22: Correlation length as function of deduced temperature for the polystyrene particle in binary mixture by means of dynamic light scattering measurement.

mixture. Fig. 4.23 showed the shift of $T_{cx}$ as function of the salt concentration. From this way, we can determine the salt content with this internal calibration. Thus, the Debye screening length of binary mixture is determined by the salt concentration. To accurately derive the $\lambda_d$, we have to take the different dielectron constant corresponding to the solvent composition. The Debye screening length are derived at the four different composition for our experimental purpose (Fig. 4.23b). The pure wa-
ter and 3MP are two reference state. The screening length at $C_{3MP} = 0.25$ and 0.40 are estimated because our polystyrene particle and fluorinate particle measurement mainly fixed the $C_{3MP} = 0.25$ and $C_{3MP} = 0.4$ respectively.

Now we can define the Debye screening length and correlation length for each colloids in a binary mixture. These two length scaled were essential to understand the origin of attraction, especially for quantitative calculation in chapter 3.

![Figure 4.23](image)

**Figure 4.23:** (a) The temperature difference between $T_{cx}$ and $T_{cx}$ as function of salt concentration. The content of salt of colloids in a binary mixture are estimated by the calibration of same shift $T_{cx}$. (b) The Debye screening length as function of salt concentration with different composition of 3MP.

### 4.3.6 Investigation around the critical point

The reentrant phase transitions in binary mixtures provide rich information because they permit a multitude of paths by which a critical point can be approached.

A wide variety of phases become accessible in these systems by mere variation of temperature, pressure, an additional component, isotope substitution, etc[86]. The unique feature of the mixture 3-methylpyridine, water and heavy water is that the loop of phase diagram $\Delta T$ can be tuned by controlling the quantity $X$ (the weight of heavy water divided by the weight of water+heavy water). The critical ratio $X = 0.17$ could shrink $\Delta T$ to 0.25K[52], we probe the colloidal behavior in large one phase region of binary mixture (in Fig.4.24a). The arrow indicates the measurement path. Fig.4.25 shows the evolution of the transmitted laser intensity as a function of temperature for the composition of solvent at $C_{3MP} = 0.25$, $X = 0.17$. The colloidal condensation temperature $T_a$ is determined by the sharp jump at the transmission.
The schematic representation of phase diagram of binary mixture changes with $X$. (a) critical ratio $X=0.17$, shrink the loop to reach the double critical point. (b) $X=0.25$, $C_{3MP}=0.32$, critical consolute point.

The volume fraction of particles in the initial fluid was 0.01. The transmitted laser intensity for the pure solvent is shown in curve B as a reference. The temperature difference $T_{cx} - T_a$ is 12°C. The value is 6°C larger than the that of the same concentration of particles at $X=0.25$. Fig. 4.26 presents the SAXS results for this composition. The temperature-dependent structure factor is depicted in Fig. 4.26a, we observe that structure factor changes from flat to one with higher-order peaks. But the temperature difference $T_{cx} - T_a$ is 12°C. The reason is that the correlation length at the critical point is much larger than when off-critical. From the Ornstein-zernike plot (Fig. d), we could calculate the correlation length to be around 38nm at the transition temperature $T_a = 55$°C. However, the crystal does not grow continuously. At high temperature and longer time, we observe that the position of the peak shifts to low $q$, and the height of peak smears out (Fig. 4.26c). The $q_m$ as function of temperature is shown in Fig. 4.26b. The $q_m$ shifts to low $q$, the mean interparticle distance is larger, the colloid-rich phase expands gradually. It suggested the position at ratio $X = 0.17$ is far away from the density matching condition. This observation again proves the necessity for the density matching to observe the equilibrium states.
Now we probe the critical consolute point in Fig.4.24 b. The sample is made by the 
$C_{\text{AMP}} = 0.32$, $X=0.25$, concentration of particle $\phi=0.01$. At this critical composition, 
the correlation length is diverged close to the critical temperature. This can give rise 
to a long-ranged interaction between the particles in analogy with Casimir effect. 
In the spherical surface, few experiments were accessible to investigate the critical 
behavior. The new result about the direct measurement of critical Casimir force was 
presented recently[102]. Fig.4.27a illustrated the temperature-dependent intensity 
profile for the sample at the critical consolute point. The evolution of microstructure 
is illustrated by the structure factor in Figure4.27b, is obtained from the measured 
intensity by dividing by the form factor. We only observe the liquid-like structure at 
the temperature 4 degree below the $T_{\text{cx}}$. The peaks develops with the temperature, 
the amplitude of peaks remains below 2.78. No crystal was observed. In fact, it 
conflicted the observation from Beysens. They reported no “aggregation”observed 
at the critical point, the aggregation line is closed at the critical point. From our 
observation, particles are still condensed when temperature approaches $T_c$.

4.3.7 Generality of the condensation phenomenon

The colloidal phase behavior in a binary mixture has been investigated in a variety 
of particles and different liquid mixtures. The general features have been ob-
Figure 4.26: (a) Evolution of the structure factor as a function of temperature. (b) $q_m$ changes as function of temperature. (c). 3D plot of intensity profile as function q vector and temperature. (d) Ornstein-zernike plot at T=55 °C The ratio $X = 0.176$, $\phi = 0.01$.

served in silica particles in 3-methylpyridine, water and heavy water[52]; Lutidine and water[92], and surfactant 2-butoxyethanol ($C_4E_1$) and water[93]. The ideal system should match the refractive index and density of particles with that of solvent to avoid the sedimentation and multiple scattering side effect from an experimental point of view. We have recently found that fluorinated particles in 3MP and water provide a closely index-matched suspension with a tunable solvent-mediated interaction (in chapter 5).

We now illustrate some observations concerning the condensation of silica particles in a liquid mixture of 3-methylpyridine/water/heavy water. The mean radius of the particles was 110 nm with a polydispersity of 6%. The volume fraction of particles presented here is 0.023. Fig.4.28a shows the typical intensity profile before and after the condensation. The detector was focused on the upper part of capillary. The intensity dramatically dropped down when the dense phase formed due to the gravity. In the meantime, the pronounced peak appears at $q = 0.05$, the peak position slightly shifts to the low $q$ value. Again, in the highly mismatched den-
sity condition, although we could observe the aggregation, but we are never able to reach the equilibrium state. The gravity immediately disturbs the process of phase transition.

4.4 Conclusion

In this chapter we have derived a colloidal phase diagram for a system of polystyrene spheres in a binary liquid mixture of 3-methylpyridine, water and heavy water from the measurements of the structure factor. We observed colloidal gas, colloidal liquid and colloidal solid phases. In these experiments we varied the volume fraction of the colloids and the Debye screening length. Essential point is also that we could derive from the same experiment the Debye screening length at the temperature where the transitions in the colloidal system took place, together with the other important length scale, the correlation length. The first condensation occurs at a ratio of the correlation length to the Debye screening length of \( \sim 2 \). Furthermore we observed

Figure 4.27: (a) SAXS intensity profile as function of temperature at the critical consolute. (b) The structure factor corresponding to the intensity profile in (a). \( C_{3MP}=0.32, \phi=0.01 \).
gas-liquid equilibrium. This is considerable proof of an attractive potential of a relatively long range, longer than the Debye screening length. The screened Coulomb potential is still there to prevent the colloidal system to collapse and flocculate. In the solid phase the distance of closest approach between the surfaces of the particles is 25 nm, significantly larger than the correlation length of 8 nm and a Debye screening length of 6 nm. Capillary condensation or bridging between wetting layers can be ruled out. In both cases the particles would be found in an environment that is rich in 3-methylpyridine, would have a shorter Debye length and hence a much smaller distance of closest approach. Moreover the interfacial tension of the condensed unit is then that of the interface between a 3-methylpyridine-rich and a water-rich phase with a much higher value than we found from the coalescence.

We are the first to observe the stable liquid and solid phases. Why did we succeed where others groups failed? Measurements by other groups observe a condensation very closer to the demixing line of the suspending binary liquid, and hence a larger ratio of correlation versus Debye screening length. Is this the same transition we observe at the large gap to $T_{cx}$? We can not give a definite answer to that based on our result. There are no measurements to characterize the colloidal phase these systems condensed into, only generally define as aggregation. The mismatch in density between colloids and suspending liquid was always large, the units formed
dropped out of sight. The condensate at the bottom of the cell could not be con-
sidered to form an equilibrium state. Density matching is an absolute necessity to
observe equilibrium phases and their transition temperatures. Our measurements
closer to the critical point make that clear. They proved to be unstable as soon as
they were formed, even with a density mismatch much smaller than in the systems
used by other groups. The condensation close to the phase separation line may be
due to capillary condensation. Experiments aboard the international space station
should give a definite answer to all these still open questions. Down on earth, not
all conditions can be satisfied simultaneously.

What is the origin of this attractive potential? According to Fisher and De Gennes[11]
the preferable adsorption of one of the liquids onto the surface of the colloidal parti-
cles close to phase separation of the binary liquid leads to a reduction of the free en-
ergy resulting from the overlap of the adsorption layers. This is the solvent-mediated
interaction, later coined “critical Casimir effect”. The range of the attraction in this
model is then determined by the thickness of the adsorption layer which is of the
order of the correlation length of the binary solvent. In chapter 3 we performed the
calculations with this model for the systems discussed in this chapter. This model,
without any adjustable parameters, is able to describe qualitatively the observed
phenomena: the change in condensation temperature with a change in the Debye
screening length, the possible existence of liquid and solid phases, the relatively large
distance of closest approach. Quantitatively there are large differences. It does not
contain the Van der Waals interaction, which should be taken into account here.

Beysens and coworkers[66] took the Van der Waals interaction into account, but
not the critical Casimir effect. They suggested another explanation of the adsorption
induced aggregation. They used a model, where the Debye screening length of the
screened Coulomb repulsion is shortened by the change in dielectric constant of the
adsorption layer. Thus the stabilizing repulsive barrier is reduced, the Van der Waals
attraction takes over and the particles contract into the primary minimum in a 3-
methylpyridine rich environment. They calculate that an adsorption layer of 12nm
thick is enough to destabilize the suspension and hence lead to particle aggregation.
The model is a variation upon the classical theme of flocculation. It cannot explain
the large interparticle separation in the solid phase observed by us. It is also unable
to explain the phenomenon of aggregation if the particles are preferentially wetted
by water. Then no aggregation should take place. This model is not able to even
qualitatively describe the observed phenomena. On the basis of our experiments we
conclude that the critical Casimir effect is the primary force that drives the observed
transitions.

Whether Van der Waals forces play a major role in the condensation remains to
be determined experimentally. A way to investigate this is to use colloidal particles, which refractive indexes match that of the solvent. The suspensions of fluorinated particles in 3MP and water provide a closely index-matched system. We observe the qualitatively similar colloidal phase behavior. The details will be discussed in chapter 5.