The phase behavior of a weakly attractive colloidal system

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In this chapter, we mainly present three experimental techniques for this study: Small Angle X-ray Scattering, Dynamic Light scattering and Confocal Microscopy.

### 2.1 Small Angle X-ray Scattering

The fundamental mechanism behind X-ray scattering from materials is Thomson scattering of X-ray photons from electrons\[44\]. The scattered intensity \(I_e\) is independent of the wavelength of the X-rays (except near atomic absorption edges) and is given by:

\[
I_e = I_0 \frac{r_e^2}{a^2} \left( 1 + \cos^2 \theta \right),
\]

(2.1)

where \(r_e = 2.818 \times 10^{-15}\) m is the classical electron radius, \(I_0\) is the incident beam intensity per unit cross-section, \(a\) is the distance between the scattering electron and the observation point, and \(\theta\) is the scattering angle\[45\]. For small angles, equation 2.1 is simplified to \(I_e = I_0 (r_e^2/a^2)\), which shows that the SAXS intensity is simply related to the electron density of the sample.

Fig.2.1 depicts the scattering geometry of a typical SAXS setup. A highly collimated and monochromatic X-ray beam with wave length \(\lambda\), impinges on a sample and the scattered intensity in the forward direction is recorded by a two-dimensional detector. The scattering is fully elastic because of the high energy of the radiation as compared to typical excitations in the sample. Therefore, the magnitudes of the inci-
Figure 2.1: (a) Schematic plot of x-ray scattering geometry. $K_i$ and $K_s$ are the wave vector of incident and scattered radiation, respectively. $\theta$ is the scattering angle, and $q = K_s - K_i$ the scattering vector. (b) example of SAXS 2-D image.

dent and scattered wave vectors are equal,

$$|k_i| = |k_s| = \frac{2\pi}{\lambda}, \quad (2.2)$$

and the refractive index is close to unity. The momentum transfer or scattering vector is

$$q = k_s - k_i, \quad (2.3)$$

and its magnitude is

$$|q| = \frac{4\pi}{\lambda} \sin(\theta/2). \quad (2.4)$$

The total scattering amplitude is the sum over all electrons with their corresponding phase shifts, $\exp(-i q \cdot r)$. It is the Fourier integral over the scattering volume $V$:

$$A(q) = \int_V \rho(r) e^{-i q \cdot r} d^3r, \quad (2.5)$$

where $\rho(r)$ is the electron density at position $r$ in the sample. SAXS originates from spatial inhomogeneities of the electron density. The total scattered intensity is the square of the modulus of the total scattering amplitude. The experimental investigation presented in this thesis was carried out using spherical particle in a solvent. In this case, the intensity scattered by the particles can be written as[46, 47]:

$$I(q) = |A(q)|^2 = N_p (\rho_r^* - \rho_m^*)^2 V_p^2 F(q) S(q). \quad (2.6)$$

Therefore, the scattered intensity is proportional to the number of colloidal particles per unit volume $N_p$. It is also proportional to the square of the contrast $\Delta \rho^* = \rho_r^* - \rho_m^*$. 

$$\Delta \rho^* = \rho_r^* - \rho_m^*$$
Table 2.1: X-ray scattering length densities for typical materials studied in this thesis.

<table>
<thead>
<tr>
<th>Material</th>
<th>Formula</th>
<th>M</th>
<th>$d$ (g/cm$^3$)</th>
<th>$\rho^*$($10^{-10}$ cm$^{-2}$)</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>silica</td>
<td>SiO$_2$</td>
<td>60.08</td>
<td>1.9-2.0</td>
<td>15</td>
<td>1.47</td>
</tr>
<tr>
<td>polystyrene latex</td>
<td>C$_8$H$_8$</td>
<td>104</td>
<td>1.00-1.05</td>
<td>9.3</td>
<td>1.55</td>
</tr>
<tr>
<td>3-methylpyridine</td>
<td>C$_6$H$_7$N</td>
<td>93</td>
<td>0.96</td>
<td>8.84</td>
<td>1.50</td>
</tr>
<tr>
<td>water</td>
<td>H$_2$O</td>
<td>1.8</td>
<td>18</td>
<td>9.4</td>
<td>1.33</td>
</tr>
</tbody>
</table>

$(\rho_p^* - \rho_m^*)$, where $\rho_p^*$ and $\rho_m^*$ are the X-ray scattering density for the particle and suspending medium, respectively. $\rho^*$ can be calculated from

$$\rho^* = \frac{n_e d N}{M},$$  \hfill (2.7)

where $n_e$ is the number of electrons per molecule, $d$ is the mass density of the material, $N$ is Avogadro’s number and $M$ is the molar mass. The values of $\rho^*$ for the materials used in this thesis are given in table 2.1.

For a dilute system, the interparticle correlations can be neglected. The structure factor $S(q)$ represents the correlations and equal 1 in the dilute limit. Then $I(q)$ depends only on the shape and size of particles described by the form factor $F(q)$. In the mathematical terms, $F(q)$ is an integral of the phase shift factor $\exp(-i q \cdot r)$ over the volume of the particles. For a uniform spherical particle of radius $R$ and volume $V$

$$F(q, R) = \left[ \frac{3 \sin(qR) - qR \cos(qR)}{(qR)^3} \right]^2. $$  \hfill (2.8)

In more concentrated system, the interparticle correlations should be taken into account. The interparticle correlations are described by the pair correlation function $g(r)$, defined as:

$$g(r) = \langle \hat{\rho}(r) \hat{\rho}(r') \rangle_N = \left\langle \sum_{i,j} \delta(r - r_i) \delta(r' - r_j) \right\rangle_N, $$  \hfill (2.9)

where $\langle \hat{\rho} \rangle$ is the deviation of the density from its canonical average. In scattering experiments we observe the phase shifts caused by the scattering particles integrated over the scattering volume. Thus the structure factor is given by:

$$S(q) = \frac{1}{N} \left\langle \sum_{i,j} e^{i q (r_i - r_j)} \right\rangle_N, $$  \hfill (2.10)

where $r_i$ and $r_j$ are the positions of particles $i$ and $j$. From Eq.(2.9) and (2.10) it is clear that the pair correlation functions are related by a Fourier transform. After
some algebraic manipulations, the relation between the two functions can be written as:

\[ S(q) = 1 + 4\pi N \int_0^\infty (g(r) - 1) \frac{\sin(qr)}{qr} r^2 dr. \]  

(2.11)

The \( q = 0 \) limit of the structure factor is related to the isothermal compressibility \( \chi_T \), as \( S(0) = Nk_bT\chi_T \)[16]. Experimentally \( S(0) \) can be obtained from linearly extrapolating the structure factor to \( q = 0 \) on a plot of \( S(q) \) versus \( q^2 \), since it can be shown that \( S(q) = S(0) + O(q^2) \). According to the Ornstein-Zernike behavior[48], the correlation length can be derived directly from \( S(0) \). In the chapter 4, we employed this experimental technique to study the colloidal phase behavior in a binary mixture.

Figure 2.2 is a schematic layout of the high-brilliance beamline ID02 at the European Synchrotron Radiation Facility (ESRF) and a picture of sample position in the hutch.

![Figure 2.2: (a): Schematic layout of the SAXS beamline ID02 at the ESRF. (b) A picture of sample position in the measurement.](image)

### 2.2 Dynamic light scattering

Electromagnetic radiation impinging on a sample is scattered by spatial inhomogeneities of the refractive index, such as a random assembly of colloidal particles suspended in a fluid. The electric field amplitudes scattered by different regions in the sample interfere and thus create an intensity distribution of dark and bright regions in the far field, called a speckle pattern. The speckle pattern reflects the instantaneous configuration of the scatterers. If the scatterer moves, for example as a result of Brownian motion, the speckle pattern will change in time such that initially dark regions become bright and vice versa. If one places a detector of the size of a typical speckle spot at a particular point in the far field, the intensity measured at
this point will fluctuate in time according to the movement of the scatterers. The fluctuations are quantified by the intensity autocorrelation function\cite{49, 50}:

$$\langle I(q, t)I(q, 0) \rangle = \lim_{T \to \infty} \frac{1}{T} \int_{0}^{T} I(q, \tau)I(q, \tau + t)d\tau, \quad (2.12)$$

where $I(q, t)$ is the scattered intensity. For an ergodic system, the time average implied by the bracket is equivalent to an ensemble average. In a photon correlation spectroscopy experiment, a fluctuating signal proportional to $I(q, t)$ is sent into a correlator that calculates the normalized intensity correlation function in real time:

$$g^2(q, t) = \frac{\langle I(q, 0)I(q, t) \rangle}{\langle I(q) \rangle^2}. \quad (2.13)$$

Under the condition that the electric field amplitude $E(q, t)$ is a zero-mean complex Gaussian variable, $g(q, t)$ is given by

$$g^2(q, t) = 1 + \beta^2 \frac{\langle E^*(q, t)E(q, 0) \rangle^2}{\langle I(q) \rangle^2} = 1 + \beta^2 |F(q, t)|^2, \quad (2.14)$$

where $F(q, t)$ is the normalized intermediate scattering function. It gives the correlation of the density fluctuations in space and time. At zero time difference it is equal to the static structure factor defined above. The contrast $\beta^2$ depends on the coherence of the beam, the coherence preserving properties of the optical elements in the setup, and the number of coherence areas observed at the detector.

In a dynamic light scattering experiment, one is interested in the wave-vector dependent decay of the normalized intermediate scattering function. In particular, the initial decay of $F(q, t)$ gives the collective short time diffusion coefficient $D(q)$ of the colloidal suspension\cite{16}, according to

$$\lim_{t \to 0} \frac{d \ln F(q, t)}{dt} = -D(q)q^2. \quad (2.15)$$

In a dilute system, the diffusion coefficient does not depend on $q$ and the normalized intermediate scattering function becomes single exponential,

$$F(q, t) = e^{-D_0q^2t}, \quad (2.16)$$

where $D_0$ is the diffusion coefficient at infinite dilution.

The experimental setup and optical geometry for dynamic light scattering is shown in figure 2.3.

In the experiments, we study the colloidal phase behavior in a binary mixture. There are three components in the system. In the table 2.1, we see that the components of the sample have quite different refractive indices. Multiple light scattering
may come up in a scattering experiment and spoil the direct connection with structure factor or intermediate scattering function. The theory we mentioned above only holds in the single scattering limit. The condition for this to hold is:

\[ l_s \gg L, \]  

(2.17)

where \( l_s \) is the mean distance between two scattering events and \( L \) the sample size. In the dilute limit, the scattering mean free path is given by

\[ l_s = \frac{1}{N\sigma}, \]  

(2.18)

where \( N \) is the number density of colloids and \( \sigma \) the scattering cross section

\[ \sigma \propto \pi R^2 |n_1/n_0 - 1|^2. \]  

(2.19)

In these expression, \( R \) is the radius of the scatterers, \( n_1 \) their refractive index, \( n_0 \) is medium refractive index. The single scattering limit can be achieved by using dilute sample or when refractive index of scatterers is nearly matched to that of the surrounding medium. In the interesting case of high particle concentration or high contrast between particle and suspending fluid, where \( l_s \ll L \), multiple scattering will arise. Then we use X-ray scattering to study this opaque system thus overcoming multiple scattering. In x-ray scattering measurement, the interference pattern is mainly from the electron density correlation.
Using very dilute samples of silica particles suspended in lutidine/water mixtures we observe two contributions to the light scattering. Some examples of the intensity correlation functions displayed in figure 2.4 show a double exponential decay. A correlation function of silica in pure water, that shows single exponential decay, is added as a reference. The amplitude of the second exponent increases gradually by increasing the lutidine concentration to the critical concentration. Two exponential decay is attributed to the diffusion of colloidal particles and fluctuation of solvent composition respectively.

### 2.3 Laser scanning confocal microscopy

To study the colloidal phase behavior in the real space we use the laser scanning confocal microscopy (LSCM). The image can be captured with rate of 120 frames per second with a resolution of 512 by 512 pixels. A schematic setup of confocal microscopy is shown in Fig.2.5. In contrast to conventional microscopy, where typically light is collected from a thick section of the sample, the confocal microscopy can use the pinhole in front of the detector to block most of the out-of-focus signal. The sample is scanned point by point. Fluorescent samples, further, give better contrast because a filter can block out everything except the fluorescent wavelength[51].
2.4 Sample preparation and characterization

In the experiments we used 3-methylpyridine (3MP), water and heavy water as solvent mixture. 3-methylpyridine is a clear organic liquid. It can be used as a solvent, and is completely miscible with water at room temperature. The chemical formula is \( C_6H_7N \). Both 3MP and heavy water were purchased from Aldrich Chemicals. The water is deionized Millipore water (MilliQ). Three different charged colloidal particles were probed: polystyrene latex spheres, silica spheres and fluorinated spheres. Table 2.1 shows the physical properties of the different particles we will refer to in the thesis. We mainly fixed the composition of the binary mixture at \( C_{3MP} = 0.25 \) by weight fraction, because it is far from the critical composition \( C_{3MP} = 0.32 \)\[^{[52, 53]} \], the interference of density fluctuation close to critical point can be diminished. During the measurement, we prepared samples with different volume fractions of particles. Originally the particles were suspended in water. High volume fractions of particles were obtained by centrifuging the initial stock suspension, removing the supernatant, and adding the proper portion solvent. Then the concentrated sample was systematically diluted to get the range of volume fractions. The samples were contained in flat borosilicate capillaries with an optical path length of 0.5 mm, 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 contamination that might influence the phase behavior. The capillary sample cell can be seen in Fig.2.6.

The size and polydispersity of the particles was determined by measuring the particle form factor with small angle X-ray scattering (SAXS) at the ESRF. SAXS is an idea tool for the characterization of colloidal particles. Fig.2.7 shows the intensity profile for a dilute sample (\( \phi = 0.0005 \)) in water. The data are fitted to the form fac-
tor expression for spherical particle (Eq. 2.8). The expression was convoluted with a Schulz distribution for the particle radius to account for polydispersity [54]. From the data shown in Fig. 2.7, we can determine the radius $R = 52.5$ nm with a good fit. The polydispersity can be estimated around 2.1%, which is very monodisperse.

Electrophoresis was performed to estimate the surface charge density. Generally, electrophoresis is the motion of dispersed particles relative to a fluid under the influence of an electric field. Electrophoresis occurs because particles dispersed in a fluid almost always carry an electric surface charge. An electric field exerts electrostatic Coulomb force on the particles through these charges. We could measure the elec-
Table 2.2: Radius($R$), inverse of Debye screening length ($\kappa$), electrophoretic potential ($\zeta$), surface charge density per particle ($\sigma$).

<table>
<thead>
<tr>
<th>Material</th>
<th>$R$ (nm)</th>
<th>$\kappa R$</th>
<th>$\zeta$ (mV))</th>
<th>$\sigma$ ($\mu C/cm^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>52.5</td>
<td>5.5</td>
<td>-53</td>
<td>0.4</td>
</tr>
</tbody>
</table>

trophoretic mobility of particles directly in the experiment. From the mobility data, the zeta potential of the particle can be estimated. Electrophoresis gives you the zeta potential ($\zeta$) and the so-called electrokinetic charge density. This is not the same as the total charge density, however we can qualitatively determine the order of magnitude of the surface charge density. We employ the following formula derived by Ohshima et al.[55]:

$$\sigma = \frac{e kT}{e} \left[ \exp \left( \frac{e \zeta}{2kT} \right) - \exp \left( - \frac{e \zeta}{2kT} \right) + \frac{4}{\kappa R \exp(e \zeta/2kT)} - 1 \right].$$

(2.20)

The results are summarized in table 2.2.

We used the 3-methylpyridine, heavy water/water as the binary liquid mixture. A close-loop coexistence curve for this two-component solution exemplifies the reentrant miscibility as shown in Fig 2.8. The system is homogeneous outside the loop and partially miscible inside the loop. The upper and lower extremals of this curve signify the upper and lower consolute points ($T_U$ and $T_L$). In contrast to binary liquid mixtures which display an upper consolute point ($T_U$), there are very few mixtures that have a $T_L$. Indeed, there are even fewer systems which possess both $T_L$ and $T_U$ before boiling or freezing transitions hide them. A simple energetic and entropic criterion cannot describe the reentrant miscibility. Due to the apparent increase in entropy as a result of mixing, the lower miscible or mixed state implies higher configurational entropy. This issue was successfully resolved by Hirschfelder et al. employing the notion of hydrogen bonding between unlike molecular species[56, 57]. The strong directional nature of hydrogen bonding hinders many rotational and vibrational degrees of freedom. The orientational entropy lost in this way is greater than the compositional entropy gained by mixing. In addition, strong hydrogen bonding lowers the total energy of the system, which has a major role in reducing the free energy of the system and establishing the thermodynamic stability of the mixed state at lower temperatures[52]. The loop size is given by the difference $\Delta T$ between upper and lower consolute points. The limit when $\Delta T = 0$ marks a double critical point. The advantage of using reentrant liquid mixtures to probe colloidal phase behavior in a binary mixture is that tuning the ratio of heavy water and water (and therefore the strength of the hydrogen bond) can tune the size of the loop, the colloidal phase behavior can be studied even in the non-phase-separating mixtures.
Table 2.3: Details of the sample preparation for system 3MP + water + heavy water. $C_{3MP}$ is weight fraction of 3MP. $X$ is weight fraction heavy water in the water/heavy water mixture, $T_L(\circ C)$ is low consolute temperature. The critical composition of 3MP is 0.32.

<table>
<thead>
<tr>
<th>No.</th>
<th>$C_{3MP}$</th>
<th>$X$</th>
<th>$T_L(\circ C)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLS1</td>
<td>0.25</td>
<td>0.17</td>
<td>68</td>
</tr>
<tr>
<td>PLS2</td>
<td>0.25</td>
<td>0.25</td>
<td>64.5</td>
</tr>
<tr>
<td>PLS3</td>
<td>0.25</td>
<td>0.5</td>
<td>53.5</td>
</tr>
<tr>
<td>PLS4</td>
<td>0.25</td>
<td>0.75</td>
<td>43</td>
</tr>
<tr>
<td>PLS5</td>
<td>0.32</td>
<td>0.25</td>
<td>61</td>
</tr>
</tbody>
</table>

and thereby eliminating the interfaces of bulk phase separation. There are several accessible paths to approach the critical point for the critical behavior study. On the other hand, by tuning the ratio of heavy water and water, the system benefits from the density match between particle and binary liquid mixture, the true equilibrium phase can be studied without the influences of gravity to disturb the phase formation.

Figure 2.8: General phase diagram illustrating how the phase diagrams of binary liquid mixtures depend on the ratio heavy water and water $X$. Every slice through the general phase diagram represents the phase diagram of a mixture that has particular $X$ which we used in our measurement.

Appropriate amounts of 3MP, water and heavy water were used to obtain the system by controlling the quantity $X$ (the weight fraction heavy water in the water/heavy water mixture). Table 2.3 gives the details of the sample preparation for
Three different particles are studied in the same binary liquid solvent (3MP/water/-heavy water): Polystyrene latex spheres (PS), silica spheres (Sil) and fluorinated latex particles (FL). Polystyrene and silica spheres were purchased from the Polyscience. The fluorinated latex particles with a teflon core were acquired from Utrecht group. The basic physical properties of the three particles are listed in table 2.4.

<table>
<thead>
<tr>
<th>Suspension</th>
<th>Radius (nm)</th>
<th>density (g/ml)</th>
<th>refractive index</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>1000</td>
<td>1.05</td>
<td>1.58</td>
</tr>
<tr>
<td>Sil</td>
<td>500</td>
<td>1.93</td>
<td>1.47</td>
</tr>
<tr>
<td>FL</td>
<td>200</td>
<td>1.6</td>
<td>1.37</td>
</tr>
</tbody>
</table>

Table 2.4: Summary of the physical properties of the particles