The phase behavior of a weakly attractive colloidal system
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1. General Introduction

1.1 Colloids

In 1861, Thomas Graham coined the term colloid (“glue” in Greek) to describe Selmi’s “pseudosolutions”[1]. Nowadays, colloid science is an interesting field with exciting developments all over the world. A colloidal suspension is a type of inhomogeneous mixture which consists of two separate phases: a dispersed phase and a continuous phase. In the mixture, the dispersed phase is made of tiny particles, droplets or bubbles that are distributed more or less evenly throughout the continuous phase. The size of the dispersed-phase particles range between 1nm and 1000nm in at least one dimension (i.e. in between the typical length scales of molecular systems and macroscopic bodies). There are many possibilities for the shape and constituent material of colloidal particles and their dispersive medium. These include the classic colloids, surfactant systems, block copolymers, etc. It is clear that colloid science deals with materials that are ubiquitous in our daily life. For example, yoghurt, paint, detergents, personal care products are related to colloidal dispersions. The following thesis presents model colloidal dispersions where interactions can be tuned by changing the thermodynamic state of the solvent.

1.2 Colloids as a model system

In science, the interest in these dispersions originates from the fact that they can simulate atomic fluids at larger scales of length and time[2, 3]. As in atomic systems, the interaction between the particles can be approximated by a potential of mean force or effective pair potential. These potentials can be related to microstruc-
ture and macroscopic thermodynamic properties using classical statistical mechanics. Depending on the volume fraction, the colloidal systems can be found either in the fluid, crystalline or glassy phases; or when an attractive interaction between the colloidal particles is present, in a liquid phase\cite{4,5}. Since interparticle interactions can be tuned, manipulated or modelled in several ways\cite{6}, transitions between different phases can be accessed experimentally more readily than in the case in atomic systems\cite{7}. The most apparent difference between atoms and colloids is their characteristic length scale, which is microscopic (0.1-0.2nm) for atomic systems and mesoscopic (1-10^4nm) for colloidal system. Hence light scattering is the most appropriate technique to study the colloidal system. However, a large majority of the common colloidal systems are opaque in the visible light range. Multiple scattering therefore hampers a straightforward measurement of the dynamic structure factor, that would yield the complete information about the system. The alternative is to use shorter wavelengths, where contrast between the components is reduced so far that multiple scattering is absent. The price to pay is a measurement of the scattered intensity at low angles, close to the main beam. With the advent of high brilliance X-ray sources at the synchrotron, small-angle X-ray scattering (SAXS) has become a standard technique. Our results stem mainly from SAXS measurements undertaken at the ESRF in Grenoble (chapter4). With this method we measured the structure factor of an ensemble of particles, that were density matched. Microscopy is used as a complementary experimental method. Using micron-sized particles, we can use confocal microscopy to follow particle motions in real-time, albeit of a restricted number of particles, index and not density matched with the suspending liquid. Normal microscopy is used to characterize phenomenologically the phases on a large scale with respect to the interparticle distances. Thus, we were able to observe the stability with respect to gravitational force, and for example the coalescence of droplets of a colloidal liquid in equilibrium with its gas phase. In this way we could characterize the different phases of a colloidal system, tune both the amplitude and range of attractive potentials by temperature alone.

### 1.3 Colloidal phase behavior

What do we expect for the phase behavior of attractive colloidal systems? Fig.1.1 illustrates three separate phase diagrams for the temperature-volume fraction plane for colloids\cite{8}. The first (Fig.1a) is a simple system of hard spheres. Entropy considerations predict that these systems will form crystals if the volume fraction is increased. Above the ‘freezing’ volume fraction, \( \phi_f = 0.494 \), it is entropically favorable if some spheres are in a crystalline geometry, but above the ‘melting’ volume
fraction, $\phi_{m} = 0.545$, all spheres should be in the crystalline phase (Fig.1.1a). Only the volume fraction controls the phase diagram. Introducing a long range attraction results in three-phase equilibria, with a triple point and phase line between liquid and gas ending in a critical point. This is the phase diagram we know from atomic and molecular systems (Fig.1.1b). With shorter-range attractions the gas-liquid (or fluid-fluid) equilibrium becomes metastable (Fig.1.1c). This type of phase diagram is encountered in protein systems[8, 9]. In this thesis, in chapter 4, we will show that our colloidal system has a phase diagram that belongs to class (b). It is a charge stabilized colloidal system suspended in a binary liquid mixture. In previous experiments on these systems it was observed that the colloidal particles aggregated when the binary solvent was brought close to the phase separation with the temperature as the controlling parameter, the term flocculation was adopted for this phenomenon. How can one distinguish aggregation or flocculation from a condensation into a stable liquid or solid state? What are the potentials that can induce flocculation and what the potentials result in an observed class-b phase diagram? Many questions are open in this weakly attractive colloidal system.

### 1.4 Interaction between colloidal particles

The forces that play a role in the interaction of colloidal particles are:

- **Excluded-volume repulsion and entropic forces**: These forces are always important, but in hard sphere systems these are the only forces that determine the phase behavior.

- **Screened Coulomb interaction**: Charges on the surface of the colloidal particles are the source of a Coulomb force around the particle, which is screened.
by counter-ions in the solvent. It is repulsive and is one of the important stabilizing forces of colloidal suspensions.

- **Van der Waals forces**: This is the force between interfaces that separate three dielectric media. It is repulsive in the asymmetric case, attractive in the symmetric case. The last case holds for colloidal suspensions.

- **Depletion forces**: This force acts between the colloidal particles in a suspension, when polymers are added to the suspending liquid.

- **Solvent-mediated force, or critical Casimir force**: It acts between surfaces immersed in a binary liquid mixture close to its critical point and arises from the confinement of concentration fluctuations within the thin film of fluid separating the surfaces[10, 11]. For the different boundary condition, it can be attractive (symmetric geometry) or repulsive (asymmetric geometry)[12, 13].

As for the stabilized colloidal system, we should consider the total interaction between the attraction and repulsion. The attractive Van der Waals interactions, also called London- dispersion forces, are always present between particles of the colloidal dispersion. This force originates when a spontaneously formed electric dipole on one molecule induces another dipole in a neighboring molecule which tends to align itself with the first dipole. Considering two large spheres of radius \( R \) at a center-to-center distance of \( r \), the total non-retarded interaction energy is the result of the integration over all possible pairs of constituent molecules and it is given by[14]:

\[
U_{VdW}(r) = -\frac{1}{6}A \left[ \frac{2R^2}{r^2} - 4 \ln \left( 1 - \frac{4R^2}{r^2} \right) \right],
\]

where \( A \) is the Hamaker constant which depends on the polarisabilities of both the particles and the medium, and it is of the order of \( 10^{-20} \sim 10^{-21} \) J. In practice, an estimate of the Hamaker constant is described by the formula[15]:

\[
A = \frac{3h\nu(n_1 + n_2)^2(n_1 - n_2)^2}{16\sqrt{2}(n_1^4 + n_2^4)^{3/2}},
\]

where \( h \) is Planck’s constant, \( \nu \) is the characteristic frequency and \( n_1 \) and \( n_2 \) are the optical refractive indices of the colloidal particles and the solvent, respectively. When the refractive index of the particles is closely matched with the solvent, \( n_1 \approx n_2 \), \( A \sim 0 \) and the Van der Waals attraction is strongly suppressed. However, the attraction does not completely disappear, because the matching is done in a certain wavelength.

The van der Waals attraction diverges as the gap between the surfaces tend to zero[16]

\[
\lim_{r \to 2R} U_{VdW}(r) = -\frac{A}{12} \frac{R}{r - 2R}.
\]
This negative potential has near contact a finite value, but much larger than the thermal energy $k_BT$, leading in general to an irreversible aggregation of the colloidal particles. The effect of the van der Waals forces is to create a primary minimum in the potential near $r=2R$. Thus one needs to introduce some mechanism providing a large positive potential barrier in order to prevent the particles from being trapped in the primary minimum.

In most colloidal systems, charged stabilization is the common mechanism to prevent flocculation. The Coulombic interaction between the charges acts as a repulsive barrier against dispersion forces thus avoiding the irreversible aggregation of colloids which occurs at the primary minimum. In reality, the strong electric potential resulting from the charge of the particles attracts free counterions, a fraction of which get absorbed onto the surface forming a layer of condensed counterions\cite{17}. The remaining free counterions form the so-called electrical double layer that screens the bare Coulomb repulsion between the charged colloidal particles and reduces its range. This leads to an interaction potential that does not scale as $1/r$, as for two charges in vacuum, but rather exhibits an exponential decay, the Yukawa-type form\cite{18, 19}

$$U_c(r) = \frac{(Z\tilde{e})^2 e^{\kappa r}}{4\pi\epsilon_0 \epsilon_r r},$$  \hspace{1cm} (1.4)

where $\epsilon_0$ is the permittivity of vacuum, $\epsilon$ is the dielectric constant of the medium and $\tilde{Z}$ is a charge incorporating the effect of the finite size of the colloidal particle:

$$\tilde{Z} = Z \frac{e^{\kappa R}}{1 + \kappa R},$$ \hspace{1cm} (1.5)

where $R$ is the radius of the particle. The inverse Debye screening length $\kappa$ is given by\cite{15}:

$$\kappa = \sqrt{\frac{\rho_c (q e)^2}{\epsilon_0 k_B T}},$$ \hspace{1cm} (1.6)

where $\rho_c$ is the density of the free counterions and $q$ their valence. Thus the screened Coulomb potential decays exponentially with the characteristic Debye length $\lambda_D$. The Debye length can be considered as the range of repulsive potential and corresponds approximately to the thickness of the diffuse electrical double layer. For the charged colloidal system, the total energy between charged colloids is the sum of the hard (Born) repulsion for $r < 2R$, the van der Waals attraction and the electrostatic repulsion. The Derjaguin-Landau-Verwey-Overbeek (DLVO) theory is a well-known model for describing the interactions in a colloidal system\cite{19}.
Fig. 1.2: The schematic description of the DLVO interaction potential. The two dashed lines indicate the separate contributions of van der Waals attraction and double-layer repulsion. The solid line represents the total potential energy.

1.4.1 Depletion attraction

A well known approach to inducing short-range attraction is by the addition of free random-coil polymers into colloidal systems[20]. When two colloidal particles come to close, polymers are expelled from the region in between. This is shown schematically in Fig. 1.3. The osmotic pressure due to polymers in the depletion region is lower than that in the outer regions. This imbalance of the osmotic pressure results in a an effective attractive interaction between the colloidal spheres. The range and strength of depletion attraction is controlled by the size of polymer and the concentration ratio between the colloid and polymer respectively. The phenomena of deple-
tion attraction is well established experimentally in model colloids and detailed, direct measurements exist of the potential of mean force for a variety of model systems [21–23]. Additionally, there have been many studies of depletion driven phenomena, especially phase behavior in model colloids ranging from charged colloids such as polystyrene latex mixed with water soluble polymers[24–27], hard particle colloids mixed with polymer[28, 29] and binary mixtures of spherical colloids[30, 31]. For special geometries microphase separation is observed in mixtures. With binary mixtures of hard spheres this occurs for certain ratios of sphere diameters [32], and for mixtures of rods and spheres microphase separation occurs for certain rod length to sphere diameter ratios[33].

Figure 1.3: A schematic illustration of the origin of the polymer-induced depletion attraction between hard spheres. The centers of mass of the polymer coils with radius of gyration (r_g) are excluded from a thin shell surrounding each particle of radius R. There is no polymer in the lens-shaped region between two nearby particles, leading to a net osmotic force pushing them together.

1.4.2 Solvent mediated attraction or the critical Casimir effect

In 1978, Fisher and de Gennes predicted that the confinement of critical fluctuations of the order parameter in a binary liquid mixture near its critical demixing point T_c gives rise to long-ranged forces between immersed plates or particles. In particular, they pointed out that these long-ranged forces would eventually lead to the flocculation of colloidal particles which are dissolved in a near-critical binary liquid mixture[11, 34]. In 1985, such a solvent-mediated flocculation was observed experimentally for silica spheres suspended in the water and 2,6-lutidine mixture[35]. However, the interpretation of these observations is still under debate. Nevertheless, fluctuation-induced forces as predicted by Fisher and de Gennes
certainly play a essential role to induce this flocculation. From a colloid physics point of view, the solvent-mediated interactions between dissolved colloidal particles are important[36–38]. The fruitful physical properties of attractive system is mainly based on the possibility to tune these effective interactions over wide ranges of strength and form of the interaction potential. Traditionally, this tuning is accomplished by changing the chemical composition of the solvent by adding salt, polymer, or other components[36, 37, 39]. The unique feature of solvent-mediated attraction is that it can be controlled by the temperature. With this attraction, the phase behavior of the colloidal system can be controlled continuously. It opens a new way to study phase transitions in colloidal systems. The sketches of this attraction are presented in Fig.1.4. Recently, microscopic theory of solvent-mediated long-range forces is developed[40–43]. The overlap between the adsorption layers leads to a reduction of the free energy of the three particles, where they join into a close knit group. The solvent-mediated interaction will be discussed in more details in chapter 3.

The three attractive interactions can each lead to a primary minimum as outlined for the standard DLVO theory. In that case the colloidal system flocculates and forms a dense phase, crystal or glass. For instance, when salt is added to a charge stabilized colloidal solution, the Debye length shortens, the system is quenched into the primary minimum. The depletion interaction and the solvent mediated interaction have different origins. The lowering of the free energy is the driving mechanism. They can be represented by an effective interaction. In the paper the first measurements of a system of charge stabilized silica particles in a mixture of 2,6-lutidine/water by Beysens[35], the condensation of silica particles close to the demixing line of the binary fluid mixture was described as aggregation. Fisher and De Gennes also used the term flocculation to describe the process. Flocculation by destabilization implies, however, an irreversible process. For phase diagram B to exist, one expects condensation into the secondary minimum and a blockade of the route of flocculation. This thesis will show the existence of phase diagram B for colloids in binary liquids, it will show that the reversible aggregation can be condensation into a liquid, crystalline or glass phase, and tries to identify the character of the effective potential driving the transitions.

1.5 Scope of this thesis

In this thesis we will investigate colloidal phase behavior in a weakly attractive system. This thesis is organized as follows

• Chapter 2: Experimental techniques used in this work are described and dis-
Figure 1.4: A schematic representation of adsorption-induced attraction. The grey layer represents the adsorption layer, the thickness of layer increases with temperature. The overlap of layers lowers the free energy resulting in attraction. It is the reversible process, if one decreases the temperature, the particles will disperse again. It indicates that the attraction occurs at the secondary minimum.

cussed. These include mainly small-angle x-ray scattering, dynamic light scattering, and confocal microscopy. The standard sample preparation and particle characterization technique are also presented.

• Chapter 3: We propose a mean field model of solvent-mediated interaction to explain the observed condensation behavior. The proposed model is then compared with our experimental results.

• Chapter 4: is dedicated to the experimental studies carried out on colloidal phase behavior. First, the influence of gravity is shown to demonstrate the advantage of a density matched system. Secondly, the evolution of the microstructure is followed by measurements of the structure factor using small-angle x-ray scattering. We observe that the charge stabilized polystyrene par-
particles condense as the temperature approaches the coexistence temperature of the binary mixture. We show the existence of liquid, face centered cubic crystal and glass phases characterized by their structure factors. These phase transitions may be followed directly by tuning the temperature, leading to the change in the interactions between the particles. On the basis of these measurements we can map out the colloidal phase diagram. Combined with the theory the experiments show that there are two important length scales in this system: correlation length and Debye screening length. Measurements on silica particle in lutidine/water show the generality of the behavior, and some of the discrepancies can be attributed to the influence of gravity.

- Chapter 5: The results of experiments using confocal microscopy are presented. Especially, the study of fluorinated particles in a binary mixture. These particles are index-matched with the suspending liquid mixture with Van der Waals interaction absent. We observe comparable condensation phenomena, which now can only originate from the solvent mediated interaction.

- Chapter 6: The dynamics of crystallization is studied. The mechanism of the nucleation and growth are discussed based upon measurements of the structure factor as a function of time. This was only possible because of the density matching. The results compared well with the findings from previous studies undertaken in the microgravity environment of space.

- Chapter 7: The hydrodynamics of two-droplet coalescence are presented in this chapter. The evolution of the bridge between two droplets when they come into contact are studied for different viscosity and constant surface tension and for two colloidal systems with ultra-low surface tension. The results demonstrate the agreement between the experimental results and the proposed analytical theory. From the coalescence measurements we also determine the ultra-low interfacial tensions for the colloid/polymer and colloid in the binary mixture. This is additional proof for the existence of a liquid phase in equilibrium with their colloid poor gas phases.