Effective Interactions and Phase Behavior of Colloidal Monolayers in the Presence of Light-Induced Substrate Potentials

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Matthias Brunner.

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Referent: Prof. Dr. P. Leiderer
Referent: Prof. Dr. R. Klein
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1 Zusammenfassung


Die Erforschung zweidimensionalen Verhaltens beschränkt sich nicht nur auf die direkte Untersuchung atomarer Systeme, auch durch die Betrachtung sorgfältig ausgewählter Modellsysteme kann beachtlicher Fortschritt erzielt werden. Eines der bedeutenden Modellsysteme für die Untersuchung zweidimensionalen Phasenverhaltens sind kolloidale Suspensionen. Verglichen mit atomaren Systemen besitzen Kolloide zwei wichtige Eigenschaften, die sie als hervorragendes Modellsystem auszeichnen. Einerseits sind sie groß genug, um mit optischen Methoden beobachtet zu werden, andererseits immer noch klein genug, um deutliche Brownsche Bewegung auszuführen. Zusätzlich können die Paarwechselwirkung und die Partikel-Substrat Wechselwirkung in kolloidalen Suspensionen kontinuierlich variiert werden, eine Eigenschaft, die in atomaren Systemen nicht anzutreffen ist.


1. Zusammenfassung
direkter Nachweis von Mehrteilchenkräften. Wir präsentieren eine Erklärung dieses Effekts, welche im wesentlichen auf die makroionischen Abschirmung zurückgeht.


Motiviert durch die Arbeiten von Frey u. a. [Frey99], wird die Periodizität des Lichtpotentials verdoppelt während die Partikeldichte konstant bleibt. Dieses System zeigt ein ähnliches Phasenverhalten, jedoch wird bei hohen Potentialstärken eine neue smektische Phase zwischen Flüssigkeit und Kristall beobachtet. Daraufhin präsentieren wir in dieser Arbeit einen detaillierten Vergleich unserer experimentellen Ergebnisse mit den theoretischen
Vorhersagen von Frey et al. Die Bedeutung der thermischen Fluktuationen für die Reichweite des Paarpotentials wird analysiert und eine qualitative Erklärung des lichtinduzierten Gefrieren und Schmelzens wird in Hinsicht auf die freie Energie des Systems gegeben.


Während die experimentellen Ergebnisse im Falle von drei Partikeln pro Potentialtopf gut mit den berechneten energetischen Grundzuständen der numerischen Simulationen von Reichhardt [Reic02] übereinstimmen, wird für zwei und vier Partikel pro Topf ein deutlich unterschiedliches Verhalten beobachtet. Diese Unterschiede könnten dadurch hervorgerufen werden, daß bei der Simulation des Grundzustandes die Entropie und auch die thermischen Fluktuationen nicht berücksichtigt werden.
2 Introduction

Two dimensional (2D) systems are an important field of research. There are fascinating experiments on Abrikosov's vortices in superconducting films, on the 2D-Quantum Hall effect, on adsorbates on atomic substrates and electrons on liquid helium, all of which can be described as two dimensional. Although the reduction of physics to 2D might seem contrived at first glance, the understanding of 2D behavior is of significant physical and technological importance. 2D conductors have become the main object of semiconductor technology. Motivated by recent technological development towards ever smaller semiconductor structures as processing or storage units, it is becoming more important to understand the behavior of mono-atomic layers on structured substrates.

However, progress in understanding 2D behavior has not only been achieved through the study of atomic systems directly, but also via carefully chosen model systems. Some of the most important model systems for 2D phase behavior are colloidal suspensions. Compared to atomic systems, colloidal suspensions have two important characteristics that qualify them as a useful model system: they can be imaged in real space and the inter-particle interaction as well as the particle-substrate interaction in the system may be varied systematically. The size of the particles used in this work is in the micron range, large enough to be conveniently imaged by optical video microscopy, but small enough to exhibit considerable Brownian motion. Consequently the complete trajectories of the particles in the configurational space are experimentally accessible. This is a huge advantage over atomic systems where usually only averaged quantities such as the structure factor are available.

The following example highlights the usefulness of colloidal monolayers as a model system. The basic theories of phase transitions in a mean-field description date back to Landau in 1937, predicting melting to be generally a single first-order transition. In two dimensions, however, this theory dramatically underestimates the importance of thermal fluctuations and leads to qualitative false results. Taking into account the large influence of fluctuations in 2D systems, Kosterlitz Thouless Haperlin Nelson and Young (KTHNY) [Kost72, Nels79, Youn55] developed in 1972 the notion of defect induced melting into an alternative description of 2D phase transitions, expecting a two stage continuous transition with an intermediate hexatic phase. Colloidal suspensions [Kusn95, Murr87, Zahn99] were some of the first systems in which the existence of this hexatic phase was shown on a homogeneous substrate. Proving the existence of a hexatic phase in colloidal systems has enhanced our understanding of 2D structures.

We give a brief introduction to the fundamentals of colloid science in chapter 2. Firstly the basic properties of colloidal suspensions are discussed. Then we outline the peculiarities of phase transitions in 2D system and give a summary of the KTHNY theory, which plays an important role in this work. Next we characterize the pair potential, acting between charged colloidal spheres and also the interaction between the particles and an external light field, responsible for optical tweezers.
The assembly and function of the experimental setup is then described in chapter 3. The setup consists of three distinct parts: the circuit for the colloidal suspension including the sample cell, a computer-controlled galvanostatic mirror unit, creating a scanned optical tweezers and third a flexible interferometer setup to project an interference pattern into the sample cell.

After introducing the experiment, we present the main results accomplished during this work. Before analyzing the phase behavior of a colloidal monolayer in the presence of light-induced substrate potentials in chapters 8 and 9, we first extensively characterized the static properties and the effective interactions of colloidal monolayers on homogeneous substrates in chapters 5 to 7. Using optical tweezers we were able for the first time to vary the particle density of the sample, always using the same set of particles and guaranteeing identical conditions in the sample cell. The trajectories of the particles in configurational space were systematically recorded at regularly timed intervals for different densities. In chapter 5, we calculated from this data the pair correlation function and the pair potential. We observed a density dependence of the pair potential, which is analyzed in detail. In chapter 6 the first direct measurement of many-body interactions in colloidal suspensions is presented. The results are discussed and compared to the findings of non-linear Poisson Boltzmann calculations.

After this analysis of the microscopic features of a colloidal monolayer, we investigate the macroscopic properties. By deriving the 2D pressure of the sample, an averaged macroscopic property, we determined the equation of state in chapter 7. Comparing this equation of state with theoretical predictions for hard-disk systems, we find good agreement for a wide range of densities. This proves that even in a suspension of highly charged particles hard-disk packing effects are the most dominant contribution to the static properties of the sample.

After this exhaustive analysis of a 2D colloidal monolayer on homogeneous substrates, we set out to model the conditions of an atomic monolayer more realistically. To model the influence of the substrate potential, we created a periodic interference pattern inside the sample cell. Following the works of Chowdhury [Chow85b] and Wei [Wei98], we first modeled a periodic one-dimensional potential and reproduced the effect of light induced freezing and melting. For particle densities commensurate with the substrate periodicity it is observed that by increasing the strength of the potential a liquid monolayer changes into a crystalline state. Having now the means to control the particle density of the sample, we conducted systematic measurements as a function of the potential strength and particle density and thus determined the phase diagram for these two parameters. Motivated by the theoretical studies of Frey et al. [Frey99, Radz01] we doubled the periodicity of the laser potential while keeping the particle density constant. This system exhibits mainly similar properties, but in between the crystalline and the liquid phase a new smectic phase was observed and characterized.

In our effort to model 2D atomic systems as realistically as possible, our next step is to replace the one-dimensional potential, which is rarely found in nature, with a 2D triangular lattice, which corresponds to crystallographic (111) surface. Here again we focus mainly on
commensurate densities. For high densities and large surface periodicity one observes that the potential wells of the triangular lattice are occupied by more than one particle and thus *colloidal molecules* are created. For the case of three particles per lattice well at medium potential strength, we observe ordered *colloidal molecular crystals*. As the laser intensity is further increased, this crystal starts to melt into donut-like structures, losing its orientational order. This re-entrance of the disordered phase is again partially due to the large importance of fluctuations in 2D.

Parts of this work have been published elsewhere:


[Loba03] Lobaskin V., Brunner M., Bechinger C., Grünberg H. H. v., On the nature of long-range contributions to pair interactions between charged colloids in two dimensions, 15, 6693 (2003)


2. Introduction
3 Basic properties of colloidal suspensions

In this chapter we will give a short introduction to the basic principles of colloidal physics. This chapter is primarily aimed at readers who are new to the field. After introducing the fundamental properties of colloidal suspensions, we will define some static correlation functions, which will be used frequently in the following chapters to characterize the state of the experimental system. Since the phase behavior in two dimensions is of central interest to this work, we will then focus on the peculiarities of the melting transition in low-dimensional systems and give a brief sketch of the KTHNY-theory in chapter 3.3. The experimental setup used in this work has been kept as simple as possible. As a consequence only two kinds of interactions are important: The pair interaction between the highly charged particles, which is pure electrostatics, and the forces of the laser field on the particles. First an expression for the pair interaction between charged colloids in a solvent is derived and the principles of screening and charge renormalization are discussed in detail. Then the mechanism of the particle-light interaction is described and the effects of the gradient and scattering forces are introduced. Along with the physical explanation references to the development and present state of these concepts are also given. Readers familiar with the principles of colloidal physics may directly proceed to chapter 4, in which the experimental setup is described.

At first sight, colloids are nothing more than microscopic particles, which are usually suspended in a solvent. Most of the properties, which make colloids such an interesting system, are closely related to their size. The particles are significantly larger than molecules, but still small enough to show significant Brownian motion, which is a thermal motion analogous to atomic systems. As a rough definition the colloidal regime describes particles of radius $s$ in the range of $1\text{nm} \leq s \leq 10\mu m$. Residing in a range of particle size that lies between quantum mechanical atomic systems and the macroscopic world, many interesting qualities become apparent.

Examples include many industrial products, such as paints, glues, polishes, lubricants, foods as well as pharmaceuticals and liquid crystals, but also biological materials such as viruses, membranes and DNA. We cannot hope to understand the biological function of a virus if we do not know its atomic structure. However, we can understand a lot about the physical properties of viruses such as the phase behavior without knowledge of its structure. As an example the tendency of the Tobacco Mosaic virus to form colloidal liquid crystals [Fren02] may be explained just by considering statistical mechanics.

Both industrial and biological colloids are generally complex, many-component systems. However, it has been realized that the fundamental physics of model colloids provide a basis on which to build an understanding of more complex systems. The experimental investigation of model colloids of well-defined size, shape and interaction has in recent decades proved to be a rich source of technological advance and physical insight. Such model suspensions also provide a fantastic laboratory for the detailed study of many
fundamental problems in statistical mechanics, such as crystallization in two dimensional systems, which will be analyzed in this work.

The colloid system investigated here consists of polystyrene spheres freely suspended in water. Since we are interested in imaging and manipulating the colloids with optical methods, fairly large particles of a radius between 500\,nm and 1500\,nm are used. We focus our attention on model suspensions of almost single-sized, monodisperse solid spherical particles, with a mean deviation in size of less than 5\%. This allows treatment of all particles as identical and facilitates the comparison between experiment and theory.

### 3.1 Colloids as giant atoms

It may sound too simplified, but the main attraction of colloidal science is the large size of the particles. Instead of complicated x-ray or neutron scattering used for atomic systems, the particles investigated here can be imaged by a standard microscope. This real-space analysis allows tracking the trajectories of the individual particles and makes the time evolution of the system accessible in detail. This information is inaccessible in systems examined by scattering experiments, as the scattering information is available only averaged over the scattering area.

The link between colloidal and atomic systems is achieved by simple scaling arguments. Scaling may be used for example to estimate the time $\tau_s$ it takes a particle to diffuse its own radius $s$, which is a characteristic relaxation time of a system [Poon95].

$$ s^2 = 6D\tau_s \quad (3.1) $$

The diffusion coefficient $D$, see also chapter 3.1.2, may be approximated by the value $D_0$ in the limit of infinite particle dilution, also known as the Stokes-Einstein relation with $\eta$ being the viscosity of the solvent and $k_BT$ the thermal energy of the system at temperature $T$.

$$ D_0 = \frac{k_BT}{6\pi\eta s} \quad (3.2) $$

This equation yields approximately $\tau_s = 1\,ps$ for atomic systems and $\tau_s = 1\,s$ for colloidal systems. This corresponds well with the observed values. Our estimate $\tau_s = 1\,s$ implies that a colloidal crystal will take a macroscopic time to crystallize. Thus colloidal systems open up the possibility of detailed time-resolved studies of crystallization kinetics, impossible in the atomic regime.

It has to be emphasized that the idea of using colloidal particles as a model for atomic systems is only valid in a thermodynamic sense. The equilibrium thermodynamic properties of an assembly of colloids are formally the same as those of an assembly of atoms with a similar inter-particle potential. Thus colloidal particles can frequently be regarded as a system of giant atoms when looking at the many-body properties although the comparison is inappropriate for the individual particles.

Another conceptual advantage of studying colloidal systems is the fact that the interaction potentials may be varied continuously within a wide range. Magnetic colloids interact with a fairly long-ranged dipole-dipole interaction [Zahn99], which decays over distance $r$ as $r^{-3}$, while charged colloids show a exponentially decaying pair potential, as
3.1 Colloids as giant atoms

shown in chapter 6.2. By adding a certain amount of polymers an attractive region in the pair potential may be created, due to the depletion interaction. Therefore for each experimental situation an appropriate pair potential may be achieved. Also the interaction with an external potential may be varied. While the interaction of an atomic surface with an adsorbate depends primarily on the molecules used and cannot easily be manipulated in strength or periodicity, this is easily possible in a colloidal system, as will be described in chapter 3.7.2.

3.1.1 Thermal energy distribution

Colloids can be used as a model for quite a number of atomic systems, such as vortices in super-conducting material, free electrons on films of liquid helium and noble gases adsorbed on substrates. In all these systems the thermal motion makes an important contribution to the total free energy. Therefore all energies involved are usually measured in units of thermal energy \( k_B T \), rather than in [Joule].

Looking at a colloidal suspension through the microscope, one can observe the random movement of the particles. This never ending motion seems to violate the first law of thermodynamics and was first observed by R. Brown in 1827, and is now called Brownian motion. To explain this phenomenon, we should first take a look at the behavior of the molecules of the solvent itself. The evolution of the particle distribution function \( p(x,v,t) \) is described by the Boltzmann master equation. Its equilibrium velocity distribution is simply the Gaussian distribution.

\[
p(v) = \left( \frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} \exp \left[ \frac{-mv^2}{2k_B T} \right] \left( \frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} \exp \left[ -\frac{E_{kin}}{k_B T} \right]
\] (3.3)

The solvent molecules collide statistically with each other and also with the colloidal particles. Hereby momentum and energy is transferred to the particle. This results in a randomly fluctuating force, giving rise to the Brownian motion of the particle. As energy and momentum are conserved in the collisions, the velocity distribution of the colloids is also Gaussian in shape. If the particles are subjected to an external potential, the distribution of the potential energy is described by the Virial theorem. Thus their positional distribution is given by

\[
p(x) = p_0 \exp \left[ -\frac{E_{pot}}{k_B T} \right]
\] (3.4)

By taking gravity as the external potential, this is recognizable as the well-known barometric formula. In 1910 Perrin [Perr10] investigated the density distribution of a dilute colloidal suspension in equilibrium with gravity and found that the distribution can indeed be described by this equation. The fact that colloids and atoms show the same thermal energy distribution is the basis on which the notion is founded of using colloidal suspensions as a model system.
3.1.2 Thermal diffusion

The analogy between colloids and atoms is straightforward when discussing the static properties of colloidal matter, but has to be altered when discussing the dynamics. The reason is that atoms in a dilute gas phase move ballistically, whereas colloids in a dilute suspension move diffusively. The ratio of the mean free path to particle size is in the order of millions in an atomic gas, therefore these systems take a long time to reach the diffusion limit; on the other hand this ratio is only a fraction of a percent in a colloidal suspension. For a particle motion much larger than the mean free path, atomic and colloidal systems exhibit a very similar behavior, which can be described as an over-damped motion. Within this diffusion regime friction dominates over all other forces. As a result the mean square displacement is no longer quadratic in time as for ballistic motion, but is slowed down by the diffusion process. The mean square displacement then increases linearly with time, with a proportionality constant $D_s$, called the self diffusion coefficient. The mean square displacement in 2D for a time difference $\tau$ and $<\ldots>$ denoting the configurational average over all times $t$ and particles $i$, is given by

$$\left< \left[ r_i(t + \tau) - r_i(t) \right]^2 \right> = 4D_s \tau$$

The solvent molecules are not only responsible for the thermal motion and the short mean free path of the particles, but also give rise to other phenomena not existent in atomic systems like the hydrodynamic interaction and the anisotropic diffusion close to a surface. These are very interesting but also quite complicated phenomena. It has been shown [Squi00] that determining static properties in non-equilibrium conditions can lead to qualitatively wrong results, if hydrodynamics are not taken into account correctly. On the other side, the hydrodynamic coupling between particles is still not included in most computer simulations, even though theoretical models are available. This makes the comparison between computer simulations and experimental result difficult. For these reasons, we only performed measurements in equilibrium conditions and focused mainly on characterizing our samples using static properties.

3.1.3 Correlation functions

The knowledge of all particle coordinates, which is experimentally accessible in colloidal video microscopy, is necessary to describe the state of the system in the configurational space. But information is too much to be able to understand the physics of the system. Therefore averaged statistical quantities have to be introduced that extract the important features. From these quantities the thermodynamic properties can then be calculated. In this work, we will make plentiful use of correlation functions. The pair correlation function $g^{(2)}(r_1, r_2)$ is given by the correlation of the particle density $\rho$ [McQu76].

$$g^{(2)}(r_1, r_2) = \left< \rho(r_1) - \left< \rho(r_2) \right> \right> \left< \rho(r_1) - \left< \rho(r_2) \right> \right>$$
The pair correlation function in a canonic ensemble of \( N \) particles can be expressed by the two particle probability distribution \( P^{(2)}(r_1, r_2) \), which can directly be extracted from the time averaged particle coordinates

\[
g^{(2)}_N(r_1, r_2) = \frac{P^{(2)}_N(r_1, r_2)}{P^{(1)}_N(r_1) P^{(1)}_N(r_2)}
\]

\( g^{(2)}_N(r_1, r_2) \) may be interpreted as the probability of finding at the same time two particles a distance \( |r_2 - r_1| \) apart from each other. For a homogeneous isotropic system, the \( g^{(2)}_N(r_1, r_2) \) only depends on the absolute value of the inter-particle distance \( r = (r_1 - r_2) \) and may be written as \( g^{(2)}_N(r) \).

In calculating the pair correlation function \( g^{(2)}(r) \) we chose only a subset of the colloidal particles from the central region of the frame to avoid boundary and finite size effects. In the circle of radius \( r_{\text{max}} \) around a chosen reference particle are \( N \) other particles, which are used to calculate the canonical \( N \)-particle pair correlation function \( g^{(2)}_N(r) \) with the density being \( \rho_N = N/\pi r_{\text{max}}^2 \). Since the local density around a particle may vary between the individual reference particles due to local density fluctuations, \( N, \rho_N \) and \( g^{(2)}_N(r) \) depend implicitly on the individual snapshot frame and reference particle. The grand canonical \( g^{(2)}(r) \) is now obtained by averaging these \( g^{(2)}_N(r) \) over all frames and reference particles, \( \rho = \langle \rho_N \rangle \) being the mean density.

\[
\rho^2 g^{(2)}(r) = \langle \rho^2_N g^{(2)}_N(r) \rangle \quad (3.8)
\]

At medium and high densities, the structure of the colloidal liquid system becomes more and more pronounced. Some of the structural features can not be described by the \( g^{(2)}(r) \) anymore as higher order correlations become influential. The three-body correlation function \( g^{(3)}(r_{12}, r_{13}, r_{23}) \) is useful in expressing this effect; we will use this approach in chapter 5.5. In a canonic ensemble \( g^{(3)}(r) \) is defined as follows, with the second equation being the normalization constraint [Egel94].

\[
g^{(3)}_N(r_{12}, r_{13}, r_{23}) = \frac{P^{(3)}_N(r_{12}, r_{13}, r_{23})}{P^{(1)}_N(r_1) P^{(1)}_N(r_2) P^{(1)}_N(r_3)}
\]

\[
\int d_{r_{12}} g^{(3)}_N(r_{12}, r_{13}, r_{23}) = \langle N - 1 \rangle \langle N - 2 \rangle \quad (3.9)
\]

The correlation functions \( g^{(2)}(r) \) and \( g^{(3)}(r) \) are powerful statistical quantities for characterizing the structure of a sample and from which the thermodynamic properties of the system may be extracted. For example, the isothermal compressibility \( \kappa_T \) is given in a grand-canonical description by the fluctuation of the particle number \( N \) around its mean value \( \langle N \rangle \) [McQu76].

\[
\kappa_T = \frac{1}{k_B T \rho} \frac{\langle \Delta N^2 \rangle}{\langle N \rangle} = \frac{1}{k_B T} \int \left( g^{(2)}(r_1, r_2) - 1 \right) dr_1 dr_2 - \frac{1}{\rho} \quad (3.10)
\]

In chapter 7 we will calculate the equation of state and the compressibility of a two dimensional colloidal monolayer as function of the particle density.
3. Basic properties of colloidal suspensions

But $g^{(2)}(r)$ is not only useful to derive macroscopic information, even microscopic information about the inter-particle potential $v^{(2)}(r)$ may be extracted. This is achieved by inverting the Ornstein-Zernike equation and using an appropriate closure-relation [Orns14]. The Ornstein-Zernike equation relates the total correlation function $h(r) = g(r) - 1$ and the direct correlation function $c(r)$ which is a measure of the correlation between two particles, filtering out the influence of all the other particles. Therefore $c(r)$ depends directly on the inter-particle potential $v^{(2)}(r)$.

In the limit of an infinitely dilute system, the probability of three or more particles interacting at the same time is negligible and both correlation functions $c(r) = h(r)$ are equal. At higher densities $\rho$ the Ornstein-Zernike equation takes into account the possibility that particle 1 influences particle 2 indirectly, by interacting with some arbitrary nearby particle 3, which then influences particle 2 [Orns14]. The summation over all possible third particles is given by the integral

$$h(12) = c(12) + \rho \int d3 c(13) h(32)$$

We inverted this equation to calculate the direct correlation function $c(r)$ from the measured $g^{(2)}(r)$. Once $c(r)$ is known, the inter-particle interaction can be extracted. In the limit of an infinitely dilute system $\beta v^{(2)}(r) = -\ln[c(r)]$, at higher density more elaborate closure relations have to be employed, such as the hyper-netted chain or the Percus-Yevick closure relation [Cruz99]. The OZ equation will be applied in chapter 5.2 to extract the pair interaction potential $v^{(2)}(r)$ charged colloidal particles in a quasi two dimensional system for various densities.

So far, only positional correlations in the system have been considered. The intrinsic geometry of a dense two-dimensional system of purely repulsive particles is hexagonal close packing. In this geometry each particle has six nearest neighbors and the angle between the bonds is $\varphi = 60^\circ$ degrees. Since we will not only analyze colloidal suspensions in the isotropic liquid phase, but also in the crystalline state and under the influence of an external isotropy breaking substrate potential, it is helpful to look at the orientation correlation function $g_6(r_i - r_j)$, which describes quantitatively to which extent the orientational order of the hexatic geometry is preserved in the system [Nels79]. Here $\varphi$ denotes the angle between the bond orientation vector toward the nearest neighbors and an arbitrary but fixed spatial axis.

$$g_6(r_i - r_j) = \left\langle \exp \left\{ i6 \left( \varphi(r_i) - \varphi(r_j) \right) \right\} \right\rangle$$

We will apply $g_6(r_i - r_j)$ in chapter 9.3 to a system of colloidal trimers on a triangular substrate. By the decay of $g_6(r_i - r_j)$ we can determine the range in which the particle orientation is preserved. From this information we can draw conclusions on the coupling strength between particles of adjacent potential wells. This is one of the criterion we use to decide whether a system is in an ordered crystalline or an unordered liquid state.
3.2 Phase transitions in 2D

It is well known that lowering the temperature in a three-dimensional system eventually leads to a phase transition. The structure changes from an unordered liquid state into a crystalline phase via a first order transition initiated by the spontaneous creation of nucleation clusters. In the crystal the particles are periodically arranged on lattice sites, this has the effect that $g^{(2)}(r)$ does not decay to zero.

This behavior is prohibited in two-dimensional systems, as the Mermin Wagner theorem [Merm68, Merm66] implies. It states that order may not persist in those systems at large distanced. More precisely, it states that the expectation value of the order parameter has to be zero. This implies again that $g^{(2)}(r)$ has to vanish in the thermodynamic limit and may not converge to some finite value. Due to the low dimensionality, the number of nearest neighbors of a particle is reduced. As the restoring force, which keeps a particle localized on its lattice site and which depends on the number of neighboring particles, is not sufficient anymore to suppress large thermal fluctuations, the importance of thermal fluctuations increases. These fluctuations eventually lead to the destruction of the long-range order in the system. A local order of the particles may still persist and even extend over a large area, resulting in a slow decay of the pair correlation function [Gold92].

The large role of fluctuations may be simply illustrated by the example of a one-dimensional spin system. In this case the thermal fluctuations are so strong that no ordered state is possible. Considering a system of spins, being only allowed to have an up or down orientation, with only a nearest-neighbor interaction of the energy $-J$, if the spins are parallel and $+J$, if the spins have opposite orientation. The inner energy of the completely oriented state is $E_{\text{order}} = -JN$, and since there is only one possible realization for this case its entropy is zero. The lowest excitation is the case, where thermal fluctuations have created a single boundary at which the orientation flips. This state has the energy $E_{\text{Flip}} = E_{\text{order}} + J$. Its entropy is $S_{\text{Flip}} = k_B \ln(N-1)$, as the boundary may lie between any of the spins. This results into a free energy difference between these two states

$$\Delta F = F_{\text{Flip}} - F_{\text{Order}} = J - T k_B \ln(N-1)$$  (3.13)

In the thermodynamic limit, as $N \to \infty$ this energy difference is always negative for finite temperatures. This means that thermal spin fluctuations always reduce the free energy, making the ordered phase thermodynamically impossible.
3.3 **KTHNY Theory – defect mediated melting**

Taking the large influence of thermal fluctuations into account, Kosterlitz and Thouless proposed in 1972 a theory in which they explained the 2D melting transition as being driven by the creation and dissociation of pairs of thermally excited topological defects [Kost72, Kost73]. Haperlin, Nelson [Nels79] and Young [Youn55] extended this theory to find two kinds of defects to be involved in the melting, dislocations and disclinations, resulting in a two stage phase transition. On the one hand there are dislocations, which are lattice distortions. In 2D even in the crystalline phase, pair-wise bond dislocations may emerge, due to large thermal fluctuations.

Even though the total distortion of the crystal around a dislocation pair vanishes, the offset of the particles destroys the long-range positional order. The envelope of the density-density correlation (see chapter 3.1.3) is expected to show an algebraic decay for large distances, with a decay exponent $\eta$ [Kost72, Kost73]

$$g^{(2)}(r) \propto 1 + r^{-\eta}, \quad 0 < \eta < 1$$

This is called a quasi long-ranged (QLR) order, which is typical for 2D systems. The first melting step consists of the dissociations of these dislocation pairs into individual dislocations. As can be seen in Fig. 3-3 and Fig. 3-4 (c) the free dislocations destroy the QLR positional order, while the orientational order is preserved. Since 2D systems not subjected to a substrate potential always show a hexagonal orientational order, this state of the system is called the hexatic phase.

$$g^{(2)}(r) \propto 1 + e^{-\zeta r}, \quad 0 < \zeta$$

During the second melting step the individual dislocations split up into single disclinations [Nels79, Youn55]. In a perfect hexagonal lattice all particles have a coordination number, the number of nearest neighbors, equal to six. A disclination is a particle that has a different coordination number, usually five or seven. Free disclinations lead to a total distortion of the lattice, breaking the remaining orientational order. The system changes into an isotropic liquid, which is characterized by

$$g^{(2)}(r) \propto 1 + e^{-\zeta \phi}, \quad 0 < \zeta$$

The inverse decay exponent of the envelope of the pair correlation function is also sometimes referred to as the correlation length of the system. It is the length on which the correlations have decayed to $\frac{1}{e}$ of the initial value and therefore defines the length scale on which the ordering in the system is lost.
Fig. 3-3. Two dislocations in a uniaxial crystal with opposite oriented burgers vectors, defined in eq. (3.14). The orientational order of the crystal is preserved. Also the positional order in y-direction remains unchanged. The positional order in x-direction, parallel to the burgers vectors is largely distorted by the two dislocations. Plot taken from [Lyuk92].

To describe the dislocations the Burgers vector $\mathbf{b}(r)$ is defined as the contour integral of the displacement vector $\mathbf{u}$ around a dislocation, with $a$ being the lattice constant. In a perfect lattice the contour closes and the result of the integral is $\mathbf{b}(r) = 0$, around a dislocation the contour cannot be closed and the integral defines the direction of the dislocation, as shown in Fig. 3-4 c).

$$\mathbf{a} \mathbf{b}(r) = \oint d\mathbf{u}$$

(3.14)

Although many experiments have been conducted to determine the order of the melting transition in 2D, no definite conclusion could be drawn so far. Investigation of a large number of 2D systems, such as electrons on liquid helium [Leid82], colloidal suspensions [Tera99, Zahn99], liquid crystals and adsorbed noble gases on graphite surfaces [Pokr86] have shown some evidence for a single phase transition of first order [Chui83] but also for the two stage KTHNY scenario. This leads to the conclusion that 2D melting is not a universal behavior, but strongly depends on the detailed properties of the interactions in the system.

Fig. 3-4. Topological defects in a 2D hexagonal lattice. While disclinations with coordination number 7 (a) and coordination number 5 (b) lead to a total distortion of the lattice, (c) a dislocation, which is a pair of bound disclinations, does not destroy the orientational order of the lattice, Plot taken from [Stra88].
3.4 Effect of the finite system size

The freezing and melting transitions discussed above are well defined only in the thermodynamic limit for infinitely large system size. For small systems considerable deviations are expected and have been observed [Bach00, Bube99]. A system is understood to be small, if its correlation length (see chapter 3.3), the range of the particle interaction, is of the same order as its linear extend.

Inside the liquid phase the correlation length is quite short. Therefore the finite size can be disregarded. As the particle density is increased, the system approaches the phase transition and the correlation length diverges. In this situation the influence of the shape of the boundary conditions can be observed all across the system, see Fig. 3-5. Although we have been careful to disturb the system as little as possible by adjusting the shape of the confinement to the geometry of the system, a certain influence especially close to the transition cannot be ruled out.

![Figure 3-5](image)

**Fig. 3-5.** Grain boundaries induced in a colloidal crystal by the square geometry of the boundary conditions, which are not commensurable with the hexagonal geometry of the crystal.
3.5 **Suspensions of highly charged colloids**

Colloidal suspensions are thermodynamically instable and will eventually coagulate, due to the van der Waals attraction. To slow down the coagulation, the particles used in this work carry a high negative surface charge, resulting in a strong electrostatic repulsion. The electric field of the particles is screened by free ions in the suspension, giving rise to a short ranged repulsive potential between the particles. In the experiments presented below additional external potentials are applied, which are created by laser light exerting pressure and gradient forces on the particles. The mechanisms of these interactions will be discussed in this chapter.

Practically all surfaces in a colloidal system carry electrical charges. This has a considerable influence on the interactions and the behavior of the ensemble. The vast numbers of charges in the system makes it impossible to treat the electrostatics of this many-body system without using some form of approximation. The colloidal particles used in our experiments have anionic surface charges. These consist of up to 20 million sulfate head groups per particle. When the particles are dispersed in water, these sulfate groups dissolve, resulting in a negative charge on the particle and positive counter-ions in the solvent. In addition the glass surface of the sample cell acquires a negative surface charge upon contact with water, due to the dissociation of silanol groups [Iler79]. Additional charges may arise in the system by the self-dissociation of the water molecules and by added salt. Even the water molecules themselves, although they are not charged, carry a strong electric dipole moment that has to be taken into account in the electrostatics of the system. In the volume between two particles, which carry several million charges, we have to take into account the distribution of billions of free ions and several trillions of dipoles to calculate the electrostatic interaction. This huge number simply forbids operating on a molecular level, and enforces a coarse-grained theoretical description in which the degrees of freedom of the solvent and the microscopic particles are integrated out, leaving us with just the coordinates of the large colloidal particles and with effective forces in between them, see also chapter 5.4.

The first approximation is to neglect the atomic structure of the water and treat it as a continuum. The high dipole moment of the water molecules is accounted for by the high dielectric constant. Indeed, water has one of the highest dielectric constants. The electric potential \( \Phi \) of a particle of charge \( Z \) in a dielectric medium of dielectric constant \( \varepsilon_w \) is given by the Coulomb equation

\[
\Phi = \frac{Z}{4\pi \varepsilon_0 \varepsilon_w} \frac{1}{r} \tag{3.15}
\]

On the atomic level of the water molecules the interaction energy of two single electrons of charge, \( Z=1 \), in the solvent can be calculated. This gives an idea of the strength of the electrostatic potential compared to the thermal energy of the system (see chapter 3.1.1).

\[
E(r) = e \Phi(r) = \frac{e^2}{4\pi \varepsilon_0 \varepsilon_w} \frac{1}{r} = \lambda \frac{1}{r} \equiv k_BT \tag{3.16}
\]
Here we have introduced the Bjerrum length $\lambda_B$, which is the distance between two electrons in a solvent at which their electrostatic potential energy equals the thermal energy. At room temperature in a vacuum the Bjerrum length is $\lambda_B = 56\text{nm}$, in water $\lambda_B = 0.71\text{nm}$. The shorter range of the electrostatic energy is due to the polarization of the water molecules. The alignment of the dipole moments leads to an internal counter field that attenuates the electrostatic field of the electrons. The Bjerrum length is used quite frequently in theoretical publications. As a next step it is instructive to determine the self-energy $E_{s}^{C}$ of a colloidal particle of radius $s$ and surface charge density $\sigma_{c} = Z/4\pi a$ in the solvent.

$$E_{s}^{C} = \frac{Z^{2}\lambda_{B}}{2s}$$

This result shows that the self-energy of a colloidal particle depends linearly on the Bjerrum length of the solvent. When going from a medium of low dielectric constant and large $\lambda_{B}$, e.g. from vacuum into water with a small $\lambda_{B}$ the energy of the system is decreased. This is the solution energy in the Born-theory of ionic solution.

### 3.5.1 Screened Yukawa potential

In colloidal suspensions, the large number of free ions poses a far greater problem in calculating the interaction energy between two colloidal particles. Even without adding salt to the suspension, there are always a number of free water ions available, due to the self-dissociation of the water molecules. In the following we will treat the water as a continuum of dielectric constant $\varepsilon_{w}$ and only focus on the electrostatic interaction between the micro ions and the colloidal particles. The standard method for describing the interaction between two charged particles and in general two charged surfaces in a solvent is the non-linear Poisson-Boltzmann equation.

$$\varepsilon_{w} \nabla^{2} \Phi = -e \sum_{i} z_{i} c_{i0}^{*} \exp \left( \frac{-z_{i} e \Phi}{k_{B} T} \right)$$

It describes how the electric potential $\Phi$ of the ions is distributed as a reaction to the electrical field of the colloids, which are usually not treated as part of the system, but included in the boundary conditions of the differential equation.

The electric potential is determined by the distribution of all the charged particles of species $i$ with valency charge $z_{i}$, that have a bulk concentration $c_{i0}^{*}$ in the suspension. The electrostatic interaction favors an ordered and localized ion arrangement, but entropic factors strive to generate a random uniform distribution of ions. The approximation now consists of replacing the individual position coordinates of the ions by their mean value, which is in this case average densities distribution. In the absence of an external potential these densities are spatially uniform. Since the size of the ions does not enter into the calculation, the ions are treated as a structure-less micro-ionic continuum in which size effects as well as correlations between the ions are disregarded. This is a good approximation if the colloidal particles are much larger than the micro-ions. To compare the size of colloids to the size of the micro-ions
the Bjerrum length is a good estimate for the effective size of a micro-ion. It has been shown by [Groo91] that the PB equation is valid as long as $\lambda_b/a z^2 < 0.03$ and as there is no tendency towards the formation of oriented bonds between the ions. The latter is true as long as the kinetic energy exceeds the potential energy of the possible bonds. For the aqueous colloidal suspension considered in this work, with symmetric 1:1 salt ions, which means that the co- and counter-ions have a valency $z = 1$, the PB description leads to very reliable results. Unfortunately this non-linear differential equation generally cannot be solved, except in special geometries such as the Gouy-Chapman result for an infinite wall, which is presented in Fig. 3-6. In the limit of low potential $\Phi$, we can linearize the right hand side of the Poisson-Boltzmann equation.

$$\nabla^2 \Phi = -\frac{e}{\varepsilon_0 \varepsilon_w} \sum_i z_i e_i \left( 1 - \frac{z_i e_i \Phi}{k_B T} + \ldots \right) = -\kappa^2 \Phi$$

(3.19)

Here the Debye screening length $\kappa^{-1}$ is introduced, which is given by

$$\kappa^{-1} = \sqrt{\frac{\varepsilon_0 \varepsilon_w k_B T}{\sum_i (z_i e_i)^2 c_{i0}}} = \left( 8\pi \lambda_B^2 \sum_i (z_i e_i)^2 c_{i0} \right)^{-\frac{1}{2}}$$

(3.20)

This linearized equation in spherical coordinates forms the basis of the Debye-Hückel theory. Assuming a spherical distribution of the micro-ions around the colloids of charge $Z_{Col}$, the equation can be solved to

$$\Phi(r) = \frac{Z_{Col} e}{4\pi \varepsilon_0 \varepsilon_w} \left( \frac{\exp(\kappa s)}{1 + \kappa s} \right) \frac{\exp(-\kappa r)}{r}$$

(3.21)

This is the Debye-Hückel expression for the electric potential of a spherical colloidal particle. As one can see by looking at the first term on the right hand side of eq. (3.21), the potential scales linearly with the charge of the particle. The second term takes into account the finite size of the colloidal particles, as no ion may enter the particle. The third terms shows that the potential decreases exponentially $e^{-\kappa s}$ with distance, rather than following the slow $r^{-1}$ decay of an isolated particle in eq. (3.15). The ion distribution that clusters around the particle screens the potential and effectively makes the electrostatic interaction more short-ranged. One can represent the central particle being surrounded by an ionic cloud, which has a thickness in the order of $\kappa^{-1}$. This picture is the reason why $\kappa^{-1}$ is called the Debye screening length. The charges on the particle surface and the neutralizing diffuse cloud of counter-ions are said to form an electrical double layer. The interaction between two colloidal particles is then determined by the degree to which their ionic clouds overlap.

$$\beta v(r) = Z_{Col}^2 \lambda_B^2 \left( \frac{\exp(\kappa s)}{1 + \kappa s} \right)^2 \frac{\exp(-\kappa r)}{r}$$

(3.22)
3. Basic properties of colloidal suspensions

Fig. 3-6. Schematic plot of an infinite wall with negative (circles) charges on the surface and in the positive (crosses) counter-ions and salt ions in solution. The solid line corresponding to the left scale shows the electrostatic potential $\Phi$ as a function of the distance from the wall. The two scatter plots, corresponding to the left scale, show the distribution of the positive (top curve) and negative (bottom curve) in front of the wall in units of the bulk ion density.

The effective colloid-colloid interaction potential is given by the electrostatic part of the classical Derjaguin-Landau-Vervey-Overbeek (DLVO) theory [Verv48]. In the case of large particles of radius $s$, small charge $Z_{Col}$ and large inter-particle spacing $r$ this theory leads to eq. (3.22). This form is also often called the Yukawa form or the screened Coulomb potential.

3.5.2 Charge renormalization

Considering all the approximations that were necessary to derive this expression, it is important to analyze its validity. The Poisson-Boltzmann equation is excellent for describing charged particles in a 1:1 electrolyte. But the linearization requires the electric potential $\Phi$ to be small. This is true for small particle charges $Z_{Col}$. Also independent of the ion-concentration [Bell98], this long-distance asymptotic law for the ion-averaged potential at infinite dilution of colloids is valid as long as $\kappa(r-2s) \gg 1$.

Indeed, for low colloidal charge the agreement between the full Poisson-Boltzmann calculation and the linearized Yukawa potential is quite good. For higher charge there are obvious deviations. The linear theory overestimates the strength of the highly charged spheres, as can be seen in Fig. 3-7. At short distances non-linear screening effects apparently play an important role. Fortunately the simple Yukawa expression can still be used to describe the interaction between charged colloids at larger distances by replacing the true charge of the particles $Z_{Col}$, which is usually measured by titration, by an effective charge $Z^{\text{eff}}$ that can be orders of magnitude smaller than $Z_{Col}$ [Alex84].
3.5 Suspensions of highly charged colloids

![Graph](image)

**Fig. 3-7** Interaction potential of two charged spheres of diameter $\sigma = 100\text{nm}$ in full PB calculation (symbols) at different screening lengths $\kappa^{-1}$ [Russ99]. (a) While for low charged particles the linearized DLVO result (solid line) shows excellent agreement, (b) for higher charges $Z=400e$ the DLVO result (solid line) over-estimates the strength of the potential. Agreement can be achieved again by charge renormalization (dashed line).

In Fig. 3-7 agreement between the calculation and the DLVO result was achieved by replacing the bare charge of $Z_{\text{col}} = 400e$ electron charges by $Z_{\text{eff}} = 322e$. For the colloids used in our experiments the colloidal charge is in the order of $Z_{\text{col}} \approx 10^7 e$, resulting $Z_{\text{eff}} \approx 10000 e$, depending on the size of the particles. The physical idea behind the effective charge is that most of the counter-ions are captured in the close vicinity of the particle surface, where they effectively screen the charges on the particle, a phenomenon known as counter-ion condensation. For the inter-particle interaction these screened charges are no longer relevant as they are neutralized by their counter-ions. The process of replacing $Z_{\text{col}}$ by $Z_{\text{eff}}$ is equal to replacing the colloid by a similar particle that is insignificantly larger, but carries a much smaller charge, so that the linear theory becomes valid again for large enough distances. As a consequence the number of free counter-ions in the suspension is also decreased. Therefore the Debye screening length $\kappa^{-1}$ is also altered. But this effect is negligible where there are sufficient salt ions in the system.

In general the effective charge depends on the geometry of the particle, the concentration of colloids and the thermodynamics of the electrolyte. Numerical studies have shown [Aubo03] that for low charges $Z_{\text{eff}}$ is proportional to $Z_{\text{col}}$, where for high charges as $Z_{\text{col}} \to \infty$ the effective charge $Z_{\text{eff}}$ saturates to a value $Z_{\text{eff}}^{\text{sat}}$. For spherical particles in a dilute system, an analytical approximation for $Z_{\text{eff}}^{\text{sat}}$ can be found, that seems accurate for $\kappa a \geq 1$ [Aubo03].

$$Z_{\text{eff}}^{\text{sat}} = \frac{4\kappa s^2 + 6s}{\lambda_B}$$

(3.23)

The saturation value $Z_{\text{eff}}^{\text{sat}}$ is independent of the colloidal charge $Z_{\text{col}}$, but it does depend on geometric factors such as the particle radius $s$ and properties of the electrolyte, such as $\kappa$. 
3.5.3 Effective potentials

The simple form of the Yukawa potential may contribute to the impression that the interaction between colloidal particles is quite uncomplicated. But it should not be overlooked, that this potential was derived from a number of approximations, in which all the degrees of freedom of the solvent and electrolyte were neglected and an expression for the pair potential was calculated. It is important to remember that this pair potential has to be regarded as an effective pair potential, whose form may depend on how it was derived [Loui02]. Strictly speaking, the total interaction energy $W$ of $N$ colloidal particles at positions $r$ is a complicated function of all the particle positions. $W(r_1,...,r_N)$ is known as the potential of mean force. It is usual to approximate $W$ as the sum of pair potentials $u(r)$, which for spherical particles are taken to be isotropic. The effects of this coarse-graining procedure are discussed in detail in chapter 5.4.

\[(3.24)\]

\[W(r) = \sum_{i>j} u(r_i - r_j)\]

It has to be emphasized that this is only an approximation. There are many physical systems, which have been proven to be correctly described only if many-body potentials are included.

There are several analogies between a charge-stabilized colloidal suspension and a fluid metal. Essentially a metal consists of highly charged core ions plus the screening charge cloud of the electrons, in which the ions are embedded [Hafn87]. Colloidal suspensions, on the other hand, are composed of large and highly charged particles, i.e. macro-ions which are suspended in a structureless medium and surrounded by a screening atmosphere of micro-ions. Common to both systems are two classes of ingredients (ions/electrons and macro-ions/micro-ions) which move and respond on completely separate length and time scales. Accordingly, similar theoretical concepts can be applied to both the theory of metals and that of colloidal suspensions. One of the major theoretical tasks in the description of metals is to reduce the many-body electron-ion Hamiltonian to an effective ionic Hamiltonian which is expressed as a sum of volume-, pair-, triple-, and multi-ion interactions. This can be achieved by eliminating the electronic degrees of freedom. In a similar manner, one of the fundamental questions in colloidal systems is, how to integrate out the micro-ionic degrees of freedom and to calculate effective macro-ion to macro-ion forces, consisting of the direct Coulomb repulsions and an indirect interaction mediated by the small ions of the electrolyte. In contrast to fluid metal, however, a suspension of charged colloidal particles can be observed directly and studied under an optical microscope. Accordingly, colloidal suspensions provide an ideal testing ground for the various concepts to tackle the interesting many-body problem, as will be shown in chapter 5.4 [Brun02b, Klei02]. Other systems in which many-body interactions arise are adsorbates on surfaces [Bind81] and atomics systems such as liquid krypton [Jaks02], where the three-body Axilrod-Teller interaction [Axil43] is present.
3.6 Van der Waals Interaction

The fluctuation dipole moments on the neighboring atoms separated by an internuclear distance $d$ leads to an attractive dispersion force, known as the van der Waals force, which decays as $d^{-6}$ for atomic particles. For a non-polar atomic particle the time average of its dipole moment is zero, yet at any instant a finite dipole moment exists, given by the instantaneous positions of the electrons around the nuclear protons. This instantaneous dipole generates an electric field that polarizes any nearby neutral particles, inducing a dipole moment. For a thorough analysis of this force a quantum mechanical description is required. The resulting interaction between the two dipoles gives rise to an attractive force between the two atoms. Summing over all pairs of atoms of two spherical particles, each of radius $s$, being separated by a distance $r$, the van der Waals potential between two particles is found to be:

$$\Psi_{vdW} = -\frac{A}{6} \left[ \frac{2s^2}{r^2 - 4s^2} + \frac{2s^2}{r^2} + \ln \left( 1 + \frac{4s^2}{r} \right) \right]$$

(3.25)

The prefactor $A$ is called the Hamaker constant, and depends mainly on the dielectric constants at frequency zero and in the visible range, and on the geometry of the system. For the colloidal particles used in our experiments the Hamaker constant is positive and in the order $0.1 \text{eV}$. Thus the van der Waals interaction is attractive.

For the following experiments, the van der Waals interaction is of minor importance, since it is only of very short range. However, for particle distances below $100 \text{nm}$ (for polystyrene particles in water) the van-der-Waals interaction leads a pronounced aggregation of particles, which may be observed in colloidal suspension with high salt concentration. At even small particle distances, the strength of the interaction becomes very large and is responsible for the irreversible coagulation of the particles and for the adhesion of the particles to the glass surface of the sample cell.

3.7 Theory of optical tweezers

Using light forces to move and control mesoscopic particles has been a very successful technique in colloidal physics. It allows manipulation of particles that are neither charged nor magnetic without much disturbance of the system. The only requirement is that the particles need to have a refractive index that differs from its surrounding at the wavelength of the used laser light. The particles should be mainly transparent, because for highly absorbing particles disturbing thermal effects, i.e. photophoresis, play a dominant role. Since this technique is mostly used to trap particles inside the laser beam, it is called an optical tweezers. Optical tweezers were introduced first introduced by Ashkin [Ashk86]. Due to its general applicability it is not only used in physics, but also frequently in biological and medical research.
3.7.1 Radiation pressure

Two different effects of optical tweezers have to be distinguished. First there is the radiation pressure, which always pushes the particle in the direction of the laser beam. The second one is the gradient force, which draws the particle into the region of the beam of highest intensity. The radiation pressure is due to the momentum that can be assigned to an electromagnetic wave. With \( \vec{S} \) being the Poynting vector, \( \vec{g} \) represents the true momentum density of the laser beam [Jack99].

\[
(3.26) \quad \vec{g} = \frac{\vec{S}}{c^2} = \epsilon_0 \left( \vec{E} \times \vec{B} \right)
\]

The momentum density \( \vec{g} \) of the incident laser beam is in the direction of the Poynting vector \( \vec{S} \) and therefore in the direction of the laser beam. As the light is scattered by the particle, momentum is transferred from the light onto the particle [Gord73]. If the particle is inside a light field that is homogeneous or at least symmetric around the particle, the net momentum transfer is also in the direction of the laser beam. In this geometry the amount of momentum transferred is equal to the amount of scattered light. The radiation pressure now is the transferred momentum per time and area, \( \epsilon_w \) being the dielectric constant of the solvent.

\[
(3.27) \quad p_{\text{scat}} = c \left| \vec{g} \right| = c \epsilon_0 \epsilon_w E_0 B = \frac{\epsilon_w}{c} I_{\text{scat}}
\]

In the case of a small dielectric sphere of radius \( s \) in an oscillating electromagnetic field of wave vector \( k \), the largest amount of scattered light is due to the dipole scattering, which can be described by Rayleigh’s law [Kerk69].

\[
(3.28) \quad I_{\text{scat}} = \frac{8\pi}{3} k^4 s^6 \left( \frac{\epsilon_s - \epsilon_w}{\epsilon_s + 2\epsilon_w} \right) I_0
\]

The radiation pressure of an incident laser beam on a colloidal particle is therefore [Ashk86]

\[
(3.29) \quad p_{\text{scat}} = \frac{8\pi}{3} k^4 s^6 \epsilon_w \left( \frac{\epsilon_s - \epsilon_w}{\epsilon_s + 2\epsilon_w} \right) I_0
\]

In the experiments described here, the particles are confined to the bottom glass plate of the sample cell. Therefore the light pressure will only push them closer to the plate, increasing the two dimensional confinement, but play no role other then that.

3.7.2 Gradient Forces

The second effect is known as the gradient force, because a dipole interacts with the gradient of the electric field. Inside an inhomogeneous intensity distribution the particle is pulled towards the region of highest intensity. The basic mechanism is that the electric field of the incident laser beam polarizes the particle. This induced dipole moment then interacts back with the external electric field. The electric field \( E_s \) inside a spherical particle of dielectric constant \( \epsilon_s \) and radius \( s \) induced by an electric field \( E_w \) in a solvent of dielectric constant \( \epsilon_w \), in our case water, is [Strat41]
3.7 Theory of optical tweezers

\[
E_s = \frac{3\varepsilon_w}{\varepsilon_s + 2\varepsilon_w} E_w
\]  

(3.30)

Due to this internal electric field, the sphere appears to be a dipole \( d \) with a relative strength proportional to the difference in the refractive indices, thus \( d = (\varepsilon_s - \varepsilon_w) V_{sphere} E_s \). The potential \( V_d \) of this polarized sphere inside the external electric field \( E_w \) is then

\[
V_{el} = -\frac{1}{2} d \cdot E_w = -2\pi \varepsilon_w \varepsilon_0 a^3 \left( \frac{\varepsilon_s - \varepsilon_w}{\varepsilon_s + 2\varepsilon_w} \right) E_w^2
\]  

(3.31)

This shows that, if the refractive index of the sphere is larger than that of the solvent, the particle is drawn into the region with the highest electric field, which is the region with the highest laser intensity. Therefore a single laser focus acts as an optical tweezers for the particles. To determine the strength of this laser trap of effective beam width \( \alpha \), we have to calculate the intensity of the laser field by measuring the power \( P_L \) of the laser beam inside the sample cell

\[
I = \frac{P_L}{2\pi \varepsilon_0 \varepsilon_0 a^2}
\]  

(3.32)

In this work we will not only be using tweezers of a single laser focus, but also an extended periodic laser intensity distribution. This periodic intensity distribution creates spatially varying light forces on the particles and thus is used in the following experiments to mimic an external substrate potential.

If the periodicity of the light lattice is in the order of the particle radius, the finite size of the particles has to be taken into account. Obviously the strength of the light forces will decrease dramatically if the particles extend over several periods of the laser intensity, because the contribution of the regions of high and low intensity will be averaged. Let us consider a periodic intensity distribution made by two interfering laser beams, since in the following experiment this is the geometry that was used with the smallest potential periodicity. Such an interference pattern consists of parallel laser lines with a sinusoidal intensity distribution \( \sin(ka) \). All the light contributions that contribute to the force on a particle have to be summed up. The integration of the contribution of all interference lines that a spherical particle overlaps leads to a first order Bessel function. The correction factor yields \( 3 j_1(ks)/(ks) \) [Chow85a]. Finally the total potential, which such an interference pattern exhibits on a colloidal particle, has a sinusoidal form with a potential amplitude \( V_0 \) depending on the laser power \( P_L \) [Loud]:

\[
V_0 = -6\varepsilon_w s^3 \frac{j_1(ks)}{ks} \left( \frac{\varepsilon_s - \varepsilon_w}{\varepsilon_s + 2\varepsilon_w} \right) \frac{P_L}{c\alpha^2}
\]  

(3.33)

As we have seen the particles can be manipulated with an external laser beam, because the scattered light transfers momentum onto the particles. But the scattered light itself can exert a force on the particles. The light scattered by one particle may exert light forces on a neighboring particle, similar to the radiation pressure, but in this case the scattered light contains the same harmonic time dependence as the incident light. Therefore the phase
relation between the scattered wave and the oscillating dipole moment driven by the incident beam is not fixed, but depends on the distance between the two particles. The result will be an alternating attractive and repulsive force as a function of the particles spacing. As the attractive component becomes quite large at small distances and two colloidal particles become tightly bound to each other; an effect called optical binding. It was first measured by Burns et al. [Burn89]. Experimentally they observed significant binding only at short distances as the light forces decay rapidly. Since in our experiments the typical inter-particle distances used are in the order of 20 wave lengths and the applied laser intensities are considerably lower than in [Burn89], no optical binding is expected. This has been confirmed by experiment.
4 Experimental Setup

The setup consists of three independent parts. Firstly, there is the closed circuit of the colloidal suspension that is mainly used to keep the salt concentration inside the sample cell as low as possible. Then a computer controlled laser tweezers is projected into the cell to adjust the particle concentration. Inside the sample cell, an interference pattern of up to four intersecting laser beams was created. Finally the movement of the colloidal particle inside the sample cell is imaged using an inverted long-distance microscope.

4.1 Circuit for Colloidal Suspensions

In our experiments we wish to study the behavior of the repulsively interacting particles on homogeneous and inhomogeneous substrates, since the interplay of the inter-particle and particle-substrate potentials can lead to a variety of interesting phenomena. These become most interesting when these two interactions are of comparable range and amplitude. To achieve this in our experiment, it is important to keep the ion concentration of the system very low.

At high salt concentration the inter-particle potential is very much like that of hard spheres. The particles get very close to each other and therefore also the van-der-Waals interaction has to be taken into account. This leads to experimental difficulties, since the particles may come too close to each other or even touch, so that our data evaluation routine cannot distinguish between two adjacent particles. To obtain a reproducibly low ion concentration in our sample cell, we used a closed circuit for continuous deionization of the solvent. This setup has been successfully applied in our workgroup for over ten years [Palb92]. For deionization the sample cell is connected to a closed circuit that allows the suspension to be continuously pumped through a container filled with ion-exchange resin.

The circuit consists of a preparation reservoir that has a lockable inlet through which the circuit can be easily filled. In our experiments we used polystyrene particles of 1.2µm, 2.4µm and 3µm diameter made by IDC Interfacial Dynamics Corporation and silica spheres of 990nm diameter produced by Duke Scientific. To prevent contamination of the suspension with airborne CO₂ from the air inside the reservoir, the container can be constantly refilled by a second inlet with a protecting argon atmosphere. From the reservoir the suspension is pumped by a peristaltic pump (VQ-360, Ismatec, Switzerland) to a conductivity measuring vessel. We used a pump velocity of about 100mL/min. In the measuring vessel a platinum electrode (LF537, WTW, Germany) was placed to monitor the conductivity of the water. After twenty minutes of continuous deionization a conductivity of 0.07µS/cm is reached. It is known that even in a perfectly deionized aqueous system the conductivity never drops below \( \sigma_{\text{Cond}} = 0.055 \) µS/cm, due to the self dissociation of the water molecules into \( H^+ \) and \( OH^- \) ions. Using the known mobility \( \mu \) of the ions we can calculate the ion concentration \( c_{\text{ions}} \) in the water from its conductivity [Hess00].
(4.1) \[ N_A e c_{\text{water}} (\mu_{\text{OH}^-} + \mu_{H^+}) + n Z_{\text{eff}} c_{\text{part}} (\mu_{\text{col}} + \mu_{\text{ion}}) \]

The screening length is determined by the ion concentration. For a system of only monovalent ions this can be written as [Isra85]

(4.2) \[ \kappa^{-1} = \frac{e_0 c_w k_B T}{\sqrt{\sum_i (z_i e)^2 c_{i0}}} = 0.304 \frac{1}{\sqrt{c_{\text{ion}}}} \]

In our experiments the conductivity of the water allowed us to estimate the value of the screening length to be in the order of \( \kappa = 500 \text{nm} \). Next the suspension is pumped from below through a container that is two thirds filled with mixed bed ion-exchange resin IEX (Serdolit MB, Serva, Germany). The outlets of the container are sealed with a narrow mesh net to keep the ion-exchange particles inside. Next in the circuit comes the sample cell. Each of the Tygon couplings of the sample cell includes a clamp valve to close the cell and decouple it from the circuit. Since very narrow cells, below 200 \( \mu \text{m} \) spacing do not allow high enough pump rates, and in order to be able to clean the rest of the circuit while there is suspension in the sample cell, we installed a by-pass around the cell. Special care was taken during the preparation to assure clean inner surfaces of the sample cell [Vand70]. After the cell the suspension flows back into the reservoir. All vessels and the sample cell are connected by inert Teflon tubes using flexible Tygon couplings.

Since pumping the colloidal suspension continuously through the ion-exchange resin leads to an enormous loss of particles, during the preparation of the experiment only water was contained in the circuit. Then usually around 2 \( \mu \text{L} \) of colloidal suspension was added into the preparation reservoir and only pumped until the particles reached the sample cell. The cell was then sealed. After the particles had sedimented to the bottom glass plate, the cell was horizontally aligned. When using small particles, gravitation was not strong enough to effectively confine the particles to two dimensions. Additional confinement was achieved by using a homogeneous vertical light pressure or a thinner cell.

Fig. 4-1. Setup for continuous deionization of colloidal suspensions. The total volume in the system is 12 \( \text{mL} \). The essential part of the circuit consists of the sample cell, the IEX and the peristaltic pump. Certain critical components, such as the filter can be bypassed by opening the valves V1 and V2.
In order to compare the results of different experiments it is necessary to be able to achieve reproducible ionic conditions inside the sample cell. When working with charged colloidal suspensions, the main problem is keeping the salt concentration constant. In particular the leakage of atmospheric CO\textsubscript{2} through the tubes and the cell into the suspension dramatically changes the pH-value and the ion concentration over time. To keep this effect as small as possible, we used as sample cell a thin silica glass cuvette with a spacing between 200\textmu m and 500\textmu m (QS-136, Hellma, Germany) and (custom made, Rank Brothers, UK). These cuvettes consist of two high quality silica glass plates that are fused together, thus significantly reducing the possible diffusion of ions into the cell. After the suspension had been injected into the cell, the Tygon couplings were tightly sealed with clamps. The Tygon couplings below the clamps were filled with ion-exchange resin to absorb the ions that diffuse through the walls of the tubes. We measured the increase of the inverse Debye screening length as approximately $17\text{nm}^{-1}/\text{hour}$, which corresponds to an ion diffusion rate of $6.5\text{nMol/hour}$. This is an extremely small diffusion rate, verifying the high quality of our cells. Nevertheless it is the change of the ion concentration inside the cell that limited our measuring time to about 24 hours. Having ion-exchange resin inside the cell may lead to various irreproducible results, such as strongly varying particle densities, depleted regions, and a huge collective diffusion of the particles towards the resin. Therefore the use of ion-exchange resin inside the sample cell can only be discouraged. The use of silica glass cells also ensures a homogenous and flat surface inside the cell, and since they are manufactured without glue, any cleaning procedures that do not damage the glass can be applied, such as strong acids, oxidizing agents or commercially available surfactants (Hellmanex2, Hellma, Germany).

### 4.2 Scanned Optical Tweezers

To control and vary the density of our colloidal system, and to create well-defined boundary conditions for our measurements, we used a scanned optical tweezers. A focused laser spot was deflected by a scanner unit to draw a rectangular box in the sample cell, which acted as a boundary box.

The beam of an Argon-Ion laser (Innova 90 $\lambda$=514nm, Coherent, USA), emitting on its TEM\textsubscript{00}-mode is cleaned of spatial noise by a lens-pinhole-lens assembly. Then the beam is deflected by a two axis galvanostatic driven mirror unit (SCANgine, Scanlabs, Germany), that is able to deflect the outgoing beam within a range of 45° in both directions. The mirror unit is controlled by a computer so that the tweezers repeatedly scan a rectangular box with a repetition rate of $300\text{Hz}$. The deflected beam is parallel collimated by a beam expander BX unit and then projected onto the back aperture of a long-distance microscope objective $O1$. Tilting the beam with the scanner unit causes it to pivot around the back aperture, thus moving the trap in the focal plane. The focused beam is deflected by a dichroic mirror (BSP488512, Delta Light and Sound, Denmark) to enter the sample cell from the top and still leave enough room for a second laser for the creation of an interference pattern. The spot size of the laser tweezers inside the sample cell is $1.3\mu m$. 
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Fig. 4-2. A scanned optical laser tweezers cell is created by focusing a laser beam inside the sample. The galvanostatic mirror deflects the beam, changing its incident angle on the rear aperture of the microscope objective, thus moving the focus.

This laser pattern acts as a corral for the colloids, because due to the light forces the particles are ordered in a dense one-dimensional packing along the contour. Depending on the size of the corral, laser intensities between $100mW$ and $500mW$ were required to confine the particles. Since the repetition rate of the pattern is much faster than the relaxation time of the particles, see chapter 3.1.2, the trap can be considered to be static with a measured potential depth of $30k_BT$ and no net drift of the particles was observed. The drawn pattern must be of a continuous shape, since the scanner unit is too slow to allow precise jumps. Possible geometries of the trap that were implemented are rectangular, circular and linear shapes. By slowly and continuously varying the size of the corral, the density of the system inside the box can be conveniently adjusted. This method has the advantage that measurements can be performed at different particle densities, using the same set of particles.

In addition a secondary tweezers was installed, consisting simply of a manually controlled laser spot. This provides a convenient method of moving coagulated particles out of the region of interest during the preparation of the measurement. The strength of this secondary tweezers is estimated to be above $100k_BT$, allowing the fast and easy movement of the tweezed particle.

4.3 Creating the light lattice

The aim of this optical set-up is to create a stable interference pattern inside the sample cell that is nevertheless flexible and easy to adjust. In our experiments we applied interference patterns of linear, hexagonal and quadratic or mixed geometry by using either two, three or four interfering laser beams, see Fig. 4-3. The functionality of the set-up will be outlined in this chapter on the basis of a three beam set-up, producing a triangular interference lattice, which will be used as an external substrate potential in chapter 9. A schematic representation of the set-up is shown in Fig. 4-5.
4.3 Creating the light lattice

Fig. 4-3. Snapshots of different periodic geometries created by (a) two, (b) three and (c) four interfering laser beams. The periodicity of the laser pattern is 10µm for all three pictures.

As a coherent light source we used a frequency-doubled Nd:YVO₄ laser with a maximum power output of 5W (Verdi λ=532nm, Coherent, USA). First the laser beam is broadened by a beam expander (BX). This unit also allows varying the size of the light pattern in the sample cell, by making the beam slightly convergent. Then the beam was divided by a beam splitter with an intensity ratio of 33/66. The height of each beam was then adjusted by passing if through a thick, tilted glass plate (W1, W2). The stronger beam was again split 50/50, so that three beams of equal intensity were produced. These three beams were then aligned parallel to each other by prisms (P1, P2, P3) mounted on translational stages. In this way, the position of the laser beams was easily adjustable to have the same distance from each other. With a convergent lens (L1) the beams were focused so that they intersect in the focus spot of the lens, creating an interference pattern. The focal length of the lens was chosen so that the focus lay inside the sample cell. The period \( d \) of the interference pattern depends only on the vertical angle of intersection of the laser beams. This angle may be varied by controlling their distance \( s \) to each other in front of the lens.

\[
d = \frac{\lambda}{2 \sin \left( \frac{\theta}{2} \right)} = \frac{\lambda f}{s}
\]  

Fig. 4-4 Schematic plot of the dependence of the intersection angle \( \theta \) of the two interfering laser beams on their distance \( s \) in front of the lens \( L1 \) of focal length \( f \), as given by eq. (4.3).

Therefore the period of the interference pattern could be adjusted by changing the distance \( s \) through the translational stages. Special care has to be taken to assure that the incident angles of the laser beam are symmetric so that the components of the wave vectors inside the sample plane balance. A non-vanishing net component of the wave vector leads to a lateral light pressure on the particles, leading to a drift motion of the particles.

A dichroic mirror (M2), which allows the Nd:YVO₄ beam pass unhindered but reflects the argon ion beam, was positioned just in front of the sample cell to allow the laser beam of
the scanned tweezers set-up to access the cell, see chapter 4.2. Behind the cell the laser beams passed through the microscope objective \((O2)\) and were absorbed by a filter, protecting the CCD camera from the intense laser light. To image the colloidal particles the sample cell was additionally illuminated by white light \((Light)\) from above.

An interferometer is very sensitive to changes in the optical path length. Changes in the length of the optical path of one of the beams of only a fraction of the wavelength, caused by thermal expansion or vibrations, can lead to a movement of the interference pattern. Therefore an active stabilization (OptiSeek 150-2, Piezomechanik GmbH, Germany) was added. Two of the mirrors were mounted on piezoelectric actuators \((Piezo1, Piezo2)\), which were controlled by a feedback loop. One interference maximum was selected by a pin hole and imaged on a photo diode. If the position of this maximum shifts, the intensity on the photo diode decreases, triggering the feedback loop to vary the actuators and thus moving the interference pattern back to its initial position.

**Fig. 4-5.** The setup to create the optical substrate potential basically consists of an extended Mach interferometer. The laser beams interfere inside the sample cell, creating a well-defined periodic intensity distribution. The prisms \(P1, P2\) and \(P3\) are mounted on translational stages for easy adjustment of the period of the interference pattern.

In the following experiments, this laser pattern is regarded as an external light potential for the colloidal particles. Therefore the properties of the laser potential must be fully characterized. These properties are the geometry, the period and the strength of the laser potential. The geometry is controlled by the construction of the interference pattern, and its period can be directly measured with digital video microscopy. The strength of the laser potential can be calculated using eq. (3.33), if the laser intensity inside the sample cell is known. Using the laser’s maximum power, potential strengths of up to \(V_0 = 200k_BT\) can be achieved. \(V_0\) can not only the calculated but also measured directly. Therefore we could make use of the fact that mesoscopic colloidal systems have a thermal energy distribution.
4.4 Two dimensional confinement

The probability distribution of the particles inside an external potential is governed by the Boltzmann distribution, see eq. (3.4). This way, we can determine the strength of the external laser potential by measuring the colloidal averaged density distribution, which is proportional to the probability as our system is in equilibrium. To exclude effects from the inter-particle potential, we recorded the particle distribution only at very low densities.

\[ p(x) = p_0 \exp \left( \frac{-E_{\text{pot}}}{k_B T} \right) \]  (3.4)

The resulting potential was fitted, using a squared cosine function, which is the expected functional behavior of an interference pattern. The additive constant \( \ln[p_0] \) was chosen to assign the minima of the laser potential, which are points without laser light, the value zero. As can be seen in Fig. 4-6, the calculated and measured potential strengths show excellent agreement.

**Fig. 4-6.** The measured potential strengths \( V_0 \) (symbols) and calculated one, using eq. (3.33), (dashed line) show excellent agreement. (Inset) The strength of the laser potential \( V_0 \) can be determined from the density distribution of a dilute suspension by fitting a squared cosine function to the measured potential.

4.4 Two dimensional confinement

A colloidal system is regarded as being two dimensional, if the thermal out-of-plane fluctuations of the particles are orders of magnitude smaller than their in-plane movement. For large colloidal particles, gravity is strong enough to effectively press the particles onto the bottom glass plate of the sample cell. At small distances of the particle from the glass plate the electrostatic potential becomes quite steep, dramatically limiting the range of the fluctuations. Smaller particles have less weight, but have the same thermal energy. Therefore the out-of-plane fluctuations are much larger, causing the particles to create second layer on top of the first monolayer. Under these circumstances additional confinement is needed. The
4. Experimental setup

The simplest way to achieve this is using thin cells, which are on the other hand difficult to make and also to clean. We used the vertical light pressure of the incident Nd:YVO$_4$ beam to confine the particles into two dimensions. Whereas the gravitational force is in the order of ten femtonewton, the light pressure can be well over one hundred piconewton. The vertical potential of a colloidal particle without the influence of a laser beam was checked using the technique of total internal reflection microscopy [Grünl01] and generalized to include the pressure of the laser light according to eq. (3.29). Even at medium light pressure the out-of-plane fluctuations are smaller than 100nm, which is less than 3% of the particle radius. Consequently the system can be regarded as two dimensional.

4.5 Data Acquisition

To image the colloidal particles we used long-distance microscope objectives (Achroplan, Zeiss, Germany). Depending on the particle size an objective of magnification factor $20\times$ or $63\times$ was utilized with a numerical aperture of 0.4 and 0.6 respectively. The microscope was used in the transmitted light bright field mode, with the sample cell illuminated with light from above. The image of the particles was projected onto a CCD camera (Teli, CS8310, Japan). To analyze the particle data, the camera signal was directly digitalized using a frame grabber and the center of mass coordinates of the particles were calculated in real time and saved on hard disk for further analysis (IPS, Visiometrics, Germany). Depending on the number of particles in the system, the setup was capable of taking up to 8 pictures per second. Since taking pictures too frequently, so that they are not statistically independent, does not improve the statistics, usually only one picture per second was recorded.

The optical resolution of the microscope set-up depends largely on the numerical aperture of the objectives. The diffraction limit of the microscope is around 600nm, which means that two particles 600nm apart can be resolved as separate objects. On the other hand the precision of determining the relative position coordinates of the center-of-mass of a spherical particle depends mainly on the number $n_{pix}$ of pixels over which the particle image extends and the magnification ration $f_{pix}$ in [nm/pixel] and can be estimated to be [Croc96]

$$
\Delta d = \frac{1}{\sqrt{n_{pix}}} f_{pix} \approx 50nm
$$

(4.4)

This was confirmed by imaging fixed particles, which that were adhered to the sample cell. For those measurements, in which we used the high magnification microscope objective, a resolution of $\Delta d = 25nm$ was achieved.
5 Structure and pair potential of a colloidal liquid monolayer

In this chapter systematic measurements of the pair correlation function $g^{(2)}(r)$, eq. (3.7) of a two-dimensional colloidal system at different particle densities $\rho$ will be presented. The density variation is achieved by means of a scanned optical laser tweezers which serves to create a boundary box for the system. By changing the size of this boundary box, the density can by varied without having to prepare a new system. The structure of the colloidal system will be analyzed in terms of pair and three-body correlation functions. In section 5.5 these correlation functions will be compared to each other, showing the importance of three-body correlations in the system. From the pair correlation functions we obtained the effective pair potentials of the particles through an inversion of the Ornstein Zernike equation. While for low particle densities perfect agreement with the Yukawa-like potentials is observed, considerable deviations from this form are found at higher densities. This result will be interpreted at the end of this chapter as the effect of many-body interactions and the concept of macro-ion screening will be introduced. In the following all lengths will be given in unitless values of $[n/\sigma]$, rescaled to the particle diameter $\sigma$.

5.1 Liquid structure

As a colloidal system we used aqueous suspensions of highly charged sulphate-terminated polystyrene particles of $\sigma = 3\mu m$ diameter with an average polydispersity below 4% (Interfacial Dynamics, USA). The sample cell had a spacing of 500$\mu m$, and was disconnected from the de-ionization circuit during the measurements (chapter 4.1). Due to the high quality of the silica cell, the increase of the concentration of salt ions in the cell was slow, creating stable conditions for over 24 hours. The colloidal system was confined to 2D by a widened beam of a power of 0.4$W$ of a Nd:YVO$_4$ laser, which was directed vertically into the sample cell (chapter 4.3). The particles were thus exposed to vertical light forces which pushing them towards the negatively charged bottom plate of the sample cell, effectively confining the system to two dimensions. Using higher laser intensities did not lead to any significant changes in behavior of the particles; thus ruling out light-induced effects such as optical binding (chapter 3.7.2). The Gaussian profile of the laser, full width at half maximum of 600$\mu m$, is expected to produce some gradient forces towards the center of the beam. Therefore the light intensity was chosen as low as possible. It was constantly monitored that the density distribution was homogeneous over the whole field of measurement.

The variation of the particle density was achieved by a scanned optical laser tweezers, which acted as a corral for the investigated area of the colloidal suspension inside the cell (chapter 4.2). The snapshot, Fig. 5-1, demonstrated the confinement achieved by the scanned laser tweezers. By changing the size of the rectangular box, the density of the enclosed particles could be changed in a controlled manner. This method has the advantage that
measurements of the structure of colloidal system at different densities can be conducted at constant screening length $\kappa^{-1}$ and using an identical set of particles.

**Fig. 5-1.** Snapshot of a colloidal liquid monolayer at medium density. The length of the black bar equals 50$\mu$m. The density of the system is distributed homogeneously. The effect of the scanned laser tweezers can be seen, as the particles on the laser trap align like a pearl-necklace, creating an impenetrable barrier for the particles inside.

From the recorded particle positions we determined directly the structure of the system. For the details about $g^{(2)}(r)$, please see chapter 3.1.3. In the case of the complete loss of correlations for large distances, $g^{(2)}(r)$ is expected to converge to unity. The following statistical mechanical identity was used to check the correct normalization [McQu76].

\[
\rho^2 2\pi^2 r_{\text{max}}^2 \int_0^{r_{\text{max}}} r g^{(2)}(r) dr = \langle N^2 \rangle - \langle N \rangle
\]

Hereby the radius $r_{\text{max}}$ denotes the largest distance, up to which $g^{(2)}(r)$ is calculated. The mean number of particles $\langle N \rangle$ inside this circle of radius $r_{\text{max}}$ also depends on $r_{\text{max}}$. The measured pair correlation functions are shown in Fig. 5-2 for six different values of the reduced density $\rho\sigma^2$ between $\rho\sigma^2 = 0.04$ and $\rho\sigma^2 = 0.19$, above this value the suspension starts to crystallize. By increasing the density, several systematic changes in $g^{(2)}(r)$ are observed. The dominant feature is the increasing range of the oscillating behavior. This is caused by the packing of the particles due to their finite size; an effect also to be seen in hard-sphere systems. In addition it can be observed that the position of the first peak of the pair correlation function shifts slightly towards smaller particle distances and the slope preceding the first peak becomes steeper. This is caused by the increase of the internal pressure towards higher densities, which has the effect of pushing the particles closer together. As the particles get closer, the electrostatic potential becomes steeper, due to its roughly exponential shape. This is reflected by the increasing initial slope of the pair correlation function.
5.2 Inverting the OZ equation

Starting from the measured \( g^{(2)}(r) \), we determined the effective pair potential in the colloidal suspension by an inversion of the Ornstein Zernike (OZ) equation as described in [Cruz99], see also chapter 3.1.3. By calculating the Fourier transformation of the total correlation function \( h(r) = g(r) - 1 \), we obtain \( \hat{h}(k) \). \( \hat{h}(k) \) is related to the Fourier transform of the direct correlation function \( \hat{c}(k) \) via the OZ equation, eq. (3.11), which in Fourier space can be written as

\[
\hat{c}(k) = \frac{\hat{h}(k)}{1 + \rho \hat{h}(k)} \quad (5.2)
\]

With another Fourier transformation back into real space, the direct correlation function \( c(r) \) can be calculated. \( c(r) \) is connected to the effective pair potential via the closure relations. The general form of all closure relations is [McQu76]

\[
h(r) = \exp\left[-\beta u^{\text{eff}}(r) + h(r) - c(r) + b(r)\right] - 1 \quad (5.3)
\]

Neglecting the so-called bridge function \( b(r) \), this expression is called the hypernetted-chain (HNC) closure relation. It is known to work well with charged systems but usually overestimates the true pair potential. We also used the Percus-Yevick (PY) closure relation, which is the result of the linearization of the exponential function of the HNC.
Fig. 5-3 Pair potentials (symbols) extracted from the pair correlation function of a simulated colloidal system, using the Ornstein Zernike equation and the hypernetted chain and Percus-Yevick closure relation. The solid line represents the true Yukawa potential used in the Monte Carlo simulation. The inversion procedure is seen to produce reliable potentials at low density (a), but slightly inaccurate potentials at higher densities in (b). Figure (c) shows the same data as (b) but multiplied by $r$ and plotted logarithmically (Klein, 2002 #3).

The PY is especially suitable for hard sphere systems [Hans90]. Applied to charged systems, PY usually underestimates the effective pair potential. The third closure relation applied is the mean spherical approximation (MSA), which take the simple form of $\beta u(r) = -c(r)$. All closure relations produce correct pair potentials for low densities, but they fail at higher colloid densities, as the assumptions on which the closure relations are based break down. Before using this inversion procedure, we therefore have to test the range of densities for which the closure relations produce reliable results.

This can be done with the help of Monte Carlo simulations. For this purpose, we first simulated a 2D colloidal system using a Yukawa pair potential with parameters that roughly correspond to the experimental situation. The resulting pair correlation function was inverted via the OZ equation to extract the pair potential again. These extracted potentials could then be compared to the initial potential actually used in the simulation. Ideally both potential should be identical. Fig. 5-3 (a) proves that for low densities this is indeed the case. We compare the true potential with the potentials calculated using the HNC (open square symbols), PY (solid dots) and the mean spherical (open dots) closure relation and find almost perfect agreement at a reduced density of $\rho \sigma^2 = 0.036$. At $\rho \sigma^2 = 0.14$ the agreement is still reasonable, see Fig. 5-3 (b). The solutions obtained by the HNC and PY closure relation show slightly different results, which indicate that the error of the potential produced by the inversion method itself increases with density. Just as in the case of three dimensional suspensions, however, it is found that the true pair potential is bracketed by the HNC and PY-based potentials for all densities. This offers a convenient method to keep track of the error range produced by the inversion procedure, by considering the HNC-based potential as upper bound and the PY-based potential as lower bound of the true potential. A more detailed analysis of the validity and precision of this method will be presented in chapter 5.2.1.
5.2 Inverting the OZ equation

Fig. 5-4. Measured effective pair potentials at 5 different densities, obtained from the pair correlation functions of Fig. 5-2. The solid line shows the result of the HNC closure relation, the dotted line the PY closure relation. The thick dashed line corresponds to the reference Yukawa potential {Klein, 2002 #3}.

In the following we will often plot the effective pair potential on a logarithmic scale in units of $(ru(r))$, see Fig. 5-3 (c). Multiplying the pair potential by the distance $r$ and taking the logarithm makes the Yukawa potential appear as a straight line with the slope of the screening constant $\kappa^{-1}$. When using a logarithmic scale special care has to be taken to assure that the calculated pair potential really decays to zero at large distances, otherwise the Yukawa potential would not be a straight line. The pair potentials calculated by the OZ equation are only reliable where the measured data have sufficiently good statistics. The potential values especially at very small particle distances are prone to have a large statistical error, since these high potential values are sampled only with a very low probability.

The potentials obtained from the inversion procedure of the measured pair correlation function of Fig. 5-2 using the HNC and the PY closure relation are shown in Fig. 5-4. Let us first consider the plots for the three lowest densities (a), (b) and (c) in Fig. 5-4. Here we indeed obtained potentials of almost perfect Yukawa form, just as the standard DLVO theory predicts. We chose the potential derived via HNC at density $\rho \sigma^2 = 0.0924$ as the reference curve and fitted to it a Yukawa function $\beta u(r) = A \sigma \exp(-kr)/r$. We thus obtained $A = 2.510^5$ and $\kappa \sigma = 5.5$, corresponding to a Debye screening length $\kappa^{-1} = 545 nm$. This Yukawa potential is plotted as reference potential in all five plots of Fig. 5-4 (thick dashed lines).

At higher densities $\rho \sigma^2 = 0.142$ and $\rho \sigma^2 = 0.169$ some deviations were observed in the potential obtained by inverting the simulated pair correlation function in Fig. 5-3 (c). As
can be seen, the true potential (solid line) of the simulation was still located between the HNC-based (open square symbols) and the PY-based (solid dots) potential. For the measured pair potential at high densities this is not the case. The HNC and PY-based result both lie below the reference line, see Fig. 5-4 (d) and (e). The measured pair potential decreases much more rapidly than the Yukawa form predicts. Looking at the whole sequence (a) to (e) of Fig. 5-4, the influence of the particle density on the pair potential can easily be identified.

These deviations increase towards larger particle distances. It can also be observed that at short distances the measured potentials match the straight lines in Fig. 5-4. This means that the short range behavior of the potentials agrees well with the Yukawa form. Since the slope of the straight lines stays the same in Fig. 5-4 (a) – (e), it follows that the value of the screening length $\kappa^{-1}$ is independent of the colloid densities. As shown in chapter 3.5.1 $\kappa^{-1}$ depends only on the concentration of colloids and salt. Therefore one must conclude that for our system the screening is dominated by the salt ions such that the increase of ions due to the increased colloid density is irrelevant. This is important because otherwise a trivial density dependence of the pair potential would have occurred, due to a change in $\kappa^{-1}$. We also performed experiments using suspension that were even more highly de-ionized, in which this trivial density dependence was observed. The density dependence of the pair potentials presented here is not due to a change in $\kappa^{-1}$, but is rather caused by many-body contributions in the particle interaction, as will be shown in chapter 5.3.

### 5.2.1 Validity of the Inversion procedure

Before interpreting the density dependent pair potential, the validity of the inversion procedure and its resolution limit has to be determined. The inversion of $g^{(2)}(r)$ is a challenging task. For low particle densities the inversion routine works quite well. The error produced by the different closure relations is small. As can be seen in Fig. 5-3 (a) for the analysis of $g^{(2)}(r)$ calculated using Monte Carlo (MC) simulations, the differences between the pair potential resulting from the Percus-Yevick and hypernetted-chain closure relation to the pair potential used in the simulations are minimal. Towards higher densities the precision of the inversion decreases, Fig. 5-3 (b), and the solutions of the two closure relations deviate. As mentioned above, it is found that the true potential used in the simulations is always bracketed by the HNC and PY-base results. However, since we want to determine the pair potential from the measured $g^{(2)}(r)$, this still leaves a wide range of possible potentials. At very high densities, close to the critical density for spontaneous crystallization, both closure relations fail to give reasonable results.

To determine the experimental pair potentials more precisely, we also employed a different inversion procedure, the inverse Monte Carlo method (IMC) [Hend74, Lobaskin, 2001 #87], which already has been successfully applied to charged colloidal systems [Lyub95]. This method uses a Monte Carlo simulation to calculate the structure of the system for an assumed initial pair potential and compares the calculated $g^{(2)}(r)$ with the experimental ones. The differences between these $g^{(2)}(r)$ are analyzed to obtain an improved pair potential that better describes the true structure of the measured $g^{(2)}(r)$. Using the improved pair potential as a new initial potential, this procedure is then repeated until convergence of the
5.2 Inverting the OZ equation

calculated and measured $g^{(2)}(r)$ is achieved. This data evaluation has been performed by V. Lobaskin for several sets of our measurements [Loba03].

The pair potential $u^{(2)}(r)$ which results from this procedure depends on a free parameter, the maximum potential range $r_{\text{max}}$, also called cut-off limit. For particle distances larger than $r_{\text{max}}$ the pair potential is forced to zero in the MC calculations. Evaluating the same $g^{(2)}(r)$ but with different $r_{\text{max}}$ may lead to slightly different results. The influence $r_{\text{max}}$ exerts on $u^{(2)}(r)$ is analyzed by systematically varying the parameter $r_{\text{max}}$. The results of the IMC method are presented in Fig. 5-5. (b) for three different values of $r_{\text{max}}$. All three derived curves show good agreement for short particle distances, smaller than $2\sigma$. The distance region in which good agreement between the curves is found is only partially plotted. For particle distances larger than $2\sigma$ and corresponding potential values smaller than $0.3k_BT$, the curves deviate considerably. Some of the potentials, derived using a large $r_{\text{max}}$, show an attractive minimum of up to $0.3k_BT$ depth. The reader is referred to [Loba03], where in a more detailed discussion it is shown that the pair potential decomposes into two parts: a short-ranged and $r_{\text{max}}$ independent repulsive part, which is highly reliable, and a long-ranged part, which has a higher uncertainty of about $0.3k_BT$. The cross-over point dividing the potential into an $r_{\text{max}}$ independent and an $r_{\text{max}}$-dependent part is called the branching point. Beyond this critical length noticeable branching of the different IMC curves sets in. We have observed that the position of the branching point coincides with the position of the first maximum of the $g^{(2)}(r)$ [Loba03]. We stress that even at distances smaller than the branching point, the effective potentials are clearly seen to be less repulsive than the Yukawa interaction, Fig. 5-5 (b). This effect increases with particle density and is not affected by the uncertainty of the inversion procedure.

In principle it has been proven that a bijective one-to-one mapping between $g^{(2)}(r)$ and a unique $u^{(2)}(r)$ exists [Chay84, Hend74]. But towards high densities, packing effects dominate and in this case different pair potentials may lead to approximately the same structure $g^{(2)}(r)$. Therefore, even though our data is highly accurate, it is impossible to determine a unique pair potential. While all of the derived potentials coincide at short distances up to $r = 2\sigma$, pronounced deviation towards larger distances are observed. Even considering this range of uncertainty, it can be concluded that the Yukawa form is inappropriate to correctly reproduce the functional behavior of the pair potential. This can also be seen by looking at the pair potentials in Fig. 5-5 (b), but also by comparing the experimentally determined $g^{(2)}(r)$ with the results of the IMC method and with the best fitting $g^{(2)}(r)$, calculated by a MC simulation using a Yukawa potential in Fig. 5-5 (a). The agreement between the experimental $g^{(2)}(r)$ and the results of the IMC method, which are all based on three different $u^{(2)}(r)$ is excellent. On the other hand, the $g^{(2)}(r)$ based on the Yukawa potential deviates by more than 10% in the vicinity of the first peak and increases with density. In the following section the deviation of the pair potential from the expected Yukawa form will be explained in terms of many-body contributions to the pair potential.
5. Structure and pair potential

Fig. 5-5. (a) The pair correlation function of a system of charged colloids at density $\rho \sigma^2 = 0.187$, determined by experiment (dotted line) does not agree too well with Monte Carlo simulation assuming a Yukawa potential (solid line). The pair correlation function determined by using two potentials derived through the inverse Monte Carlo method, leads to much better agreement with experiment. (b) Pair potentials derived from the adjacent experimental pair correlation function, using the inverse Monte Carlo method at three different cut-off radii $r_{\text{max}}$.

5.3 Macro-ion screening

A density dependence of the pair potential means that the mutual interaction of two colloidal particles depends on their local environment. Two colloids isolated in an unbound electrolyte interact differently than two colloids with the same distance and the same salinity but in a more highly concentrated suspension. The interaction thus depends on the other colloidal particles in the suspension. This density dependence of the pair potential recognizable in Fig. 5-4 is a direct experimental observation of many-body interactions.

A qualitative understanding of the results follows from the observation that deviations of the measured potential take place at distances comparable to the mean inter-particle distance $a = (\rho \sigma^2)^{-0.5}$. Two colloidal particles in a suspension which are separated by $r > a$ are likely to have a third particle nearby or even in between. The Yukawa potential on the other hand is based on the assumption of only two interacting particles, each surrounded by an unperturbed spherical double-layer. This obviously cannot lead to the correct interaction potentials in cases where a third macro-ion in between the two particles effectively blocks the mutual interaction. We call this effect macro-ion screening. The presence of a third macro-ion reduces the repulsion between two colloidal particles and therefore actively contributes to the electrostatic screening. This effect might be caused by the excluded volume of the third particle, which is impenetrable for the micro-ionic fluid and has a different dielectric constant as the electrolyte. It is also possible that the charge of the third particle should be included into the Debye screening constant $\kappa^{-1}$. Since the huge effective charge of the macro-ion enters squared into the calculation of $\kappa^{-1}$, this would lead to a dramatic screening effect.
5.3 Macro-ion screening

Fig. 5-6. To the measured pair potential at high particle density, as shown in Fig. 5-4 (e), a cut-off (vertical thick line) is introduced as the pair potential decreases to $e^{-1}$ of the value expected by the Yukawa form.

Looking at the pair potentials in Fig. 5-4 (d) and (e), measured at high densities, it can be seen that the macro-ion screening reduces the electrostatic repulsion and almost completely blocks the interaction between the particles. We approximate the experimentally determined pair potential by Yukawa potential for short distances plus a density dependent cut-off at the distance $r_{\text{cut}}$. We define the position of $r_{\text{cut}}$ to be at that distance at which the deviations between the potential derived using the HNC closure relation and the expected Yukawa potential become larger than 50% of the expected value. This definition is purely pragmatic, but leads to an appropriate description of the measured pair potential, as can be seen in Fig. 5-6. This cut-off parameter can be used to include the effect of macro-ion screening in computer simulations. In chapter 6.5 the calculated phase diagram of a three dimensional Yukawa system including a density dependent cut-off will be presented.

Next we determine the position $r_{\text{cut}}$ of the cut-off as a function of the particle density, shown as symbols in Fig. 5-7. Hereby we can analyze for which particle distance the macro-ion screening becomes relevant. Following qualitative arguments for macro-ion screening presented above, it is expected that $r_{\text{cut}}$ scales with the mean particle distance $a = (\rho \sigma^2)^{-0.5}$, which is plotted as a dotted curve in Fig. 5-7. As can be seen, this dotted curve lies within the correct range, but underestimates the screening effect. This discrepancy is not convincing, due to the arbitrariness in the definition of $r_{\text{cut}}$. The solid line in Fig. 5-7 is a numerical fit to $r_{\text{cut}}$ and has the functionality $y = 1.15 \sigma (\rho - 0.01)^{-0.5}$. This dependence of $r_{\text{cut}}$ on the particle density clearly demonstrates that the macro-ion screening is a systematic effect where the interaction between two colloidal particles is reduced through the presence of surrounding particles.
5.4 Effective potentials

It is self-evident to expect the pair potential to depend only on the properties of the two particles and their interaction. If a third particle nearby alters the strength of the potential, it is inconsistent to continue to talk about a pair potential. The reason for this behavior is that the Yukawa pair potential we generally use, is an effective potential, derived from integrating out the micro-ionic degrees of freedom, see also chapter 3.5.3 and [Klei02]. In this section we will show how many-body interactions contribute to the effective pair potential.

In the primitive model, where all micro-ions are described individually, the configurational part of the Hamiltonian \( H(r_1,...,r_{N_1};R_1,...,R_{N_2}) \) depends on the positions of the \( N_1 \) macro-ions and on the positions of the \( N_2 \) micro-ions. The averaging over all configurations of the micro-ions \((R_1,...,R_{N_2})\) leads to an expression for the \( N_1 \)-body potential \( H_{\text{eff}} \), known as the one component model. In the process of averaging it has to be ensured that the thermodynamic properties remain unchanged. The resulting interaction potential \( W \) depends only on the configuration of the macro-ions. To correctly describe the energy of the system only in terms of the configuration of the macro-ions a purely pair-wise description is insufficient. The averaging of the micro-ions has led to the emergence of many-body state-dependent potentials. The resulting interaction potential can be written as

\[
W(r_1,...,r_{N_1}) = \sum_{i<j} v^{(2)}(r_i,r_j) + \sum_{i<j<k} w^{(3)}(r_i,r_j,r_k) + \ldots
\]

According to the McMillan-Mayer theory of mixtures, [Rowl69] the pair correlation function between two macro-ions at \( r_1 \) and \( r_2 \) is given by the integral of the Boltzmann factor of the many-body potential \( W \), taken over all macro-ion positions except at \( r_1 \) and \( r_2 \). The approach that we used to extract the pair potential \( u^{(2)}(r_1,r_2) \), using the Ornstein-Zernike (OZ) equation followed a different route. The OZ equation is based on the assumption that all particle interactions are pair-wise additive, which allows only true pair potentials to be present.
in the system. In a case where many-body interactions are present, the inversion of the pair correlation function will result in an interpretation of the microstructure of the system in terms of effective pair potentials. An inversion method based on higher order correlation functions would be needed to extract existing many-body potentials. Only in the case where higher than two-body potentials of the McMillan-Mayer theory are absent, will the effective pair potential $u^{(2)}(r_1, r_2)$ of the OZ procedure coincide with the two-body potential $v^{(2)}(r_1, r_2)$ of the McMillan-Mayer theory. This is expected to be the case in highly diluted suspensions and has also been observed in our experimental data, see chapter 5.2. Otherwise, the two potentials must differ and the difference between $u^{(2)}(r_1, r_2)$ and $v^{(2)}(r_1, r_2)$ simply expresses the fact that there are contributions of the many-body potentials to the effective pair potential.

Considering for a moment only an additional three-body term, its influence on the effective pair potential may be written as

$$u(r_1, r_2) = v(r_1, r_2) + \rho \int d \mathbf{r}_3 \frac{g^{(3)}(r_1, r_2, r_3)}{g^{(3)}(r_1, r_2)} \left( \exp \left[ -\beta w^{(3)}(r_1, r_2, r_3) \right] - 1 \right)$$  \hspace{1cm} (5.5)

This equation is exact to the third order of many-body contributions. The only term in this equation that shows explicit density dependence is the one also containing the three-body potential. If the effective potential $u^{(2)}(r_1, r_2)$ changes with density, as observed in the experiments, this directly proves that $u^{(2)}(r_1, r_2)$ does not only depend $v^{(2)}(r_1, r_2)$ alone but higher order contributions. Hence this is direct evidence that many-body interactions are present in the system. To describe the effective potential in a dense colloidal system correctly, it is not enough to consider three-body terms only. It seems logical that many-body terms at least up to the order of coordination number, which is the average number of nearest neighbors, must be taken into account. This makes it very difficult to extract the three-body potential from our measured data via the three-body correlation function.

### 5.5 Three-body correlations

The pair correlation function $g^{(2)}(r_{12})$ can be interpreted as the normalized probability distribution of finding a second particle at a distance $r_{12}$ from a fixed reference particle, normalized to the value one in the uncorrelated case. As shown in chapter 3.1.3 for an isotropic system the pair correlation function depends only on the magnitude, not on the direction of the distance vector $\mathbf{r}$. The next order density-density correlation function is the three-body correlation function $g^{(3)}(r) = g^{(3)}(r_{12}, r_{13}, r_{23})$ which by analogy may be interpreted as the normalized probability of finding a second particle at a distance $r_{12}$ from a fixed reference particle times the probability of finding a third particle at a distance $r_{13}$ from the reference particle and at the same time at $r_{23}$ from the second particle. The Kirkwood approximation expresses the $g^{(3)}(r)$ in terms of a superposition of $g^{(2)}(r)$, thus neglecting any explicit three-body correlations [Krik52].

$$g^{(3)}(r_{12}, r_{23}, r_{13}) \approx g^{(2)}(r_{12}) g^{(2)}(r_{23}) g^{(2)}(r_{13})$$  \hspace{1cm} (5.6)
Comparing the $g^{(3)}(r)$ determined by the measurement, with the $g^{(3)}(r)$ of the Kirkwood approximation gives an idea how pronounced triple correlations are for describing the system structure correctly.

Since the complete $g^{(3)}(r)$ is a complicated three dimensional array, it is convenient to plot its projection on certain geometries. Fig. 5-8 shows the $g^{(3)}(r)$ for an equilateral triangular configuration, with the constraint $r_{12} = r_{13} = r_{23} = r$. The experimentally determined $g^{(3)}(r)$ for three different densities $\rho \sigma^2 = 0.07$, $\rho \sigma^2 = 0.142$ and $\rho \sigma^2 = 0.18$ are shown as triangular, circular and square symbols, respectively. The corresponding results of the Kirkwood approximation are plotted as solid lines. While in the dilute case the superposition of $g^{(2)}(r)$ correctly describes the structure of $g^{(3)}(r)$ (triangles), the approximation fails towards higher densities, as pronounced deviations emerge. The Kirkwood approximation neglects the three-body correlations. Neglecting correlations makes the system appear more homogeneous and therefore systematically underestimates the total structure.

Next, we will compare the $g^{(3)}(r)$ and $g^{(2)}(r)$ result for a specific geometry, most likely to be found in a colloidal system close to the freezing transition, where three-particle correlations might play an important role. The position of the second particle is fixed as the distance $r_{12} = r_{\text{peak}}$, which is the distance, where the $g^{(2)}(r)$ first peaks. $g^{(3)}(r)$ and $g^{(2)}(r)$ are plotted in (Fig. 5-9) as a function of the position of the third particle. In both plots the probability of finding the third particle in the vicinity of the first two particles is zero. It should be noted that for large distances the correlation functions do not decay to one, but to the value of about 1.5, which is the height of the first peak of $g^{(2)}(r)$. This is to be expected, since particle two is held fixed to this value. While the superposition of pair correlation functions, Fig. 5-9 (a) demonstrates a smooth functional behavior to the left and right of the two particles, $g^{(3)}(r)$ shows a pronounced hexagonal structure. By fixing the second particle isotropy is broken and the $g^{(3)}(r)$ reflects the local hexagonal ordering of the particles. This effect can not be described by a superposition of $g^{(2)}(r)$.
5.5 Three-body correlations

Fig. 5-9. Three-body correlation function of a two dimensional colloidal system. The distance between two particles is fixed to the distance corresponding to the first maximum of the pair correlation function. The color code represents the value of $g^{(3)}(r)$ as the position of the third particle is varied in the $xy$-plane. The size of the black bar is 2 particle diameters. (a) The superposition of three pair correlation functions appears structureless compared to (b) the complete three-body correlation function. This illustrates the failure of the Kirkwood approximation [Russ03b].

To highlight the differences between the $g^{(3)}(r)$ and $g^{(2)}(r)$, Fig. 5-10 illustrates the quotient of the $g^{(3)}(r)$ of Fig. 5-9 (top) and the Kirkwood result of three superposed $g^{(2)}(r)$, Fig. 5-9 (bottom). The most likely position of the third particle is at a distance $r_{\text{peak}}$ from particle one and two. This position is marked as Pos1 in Fig. 5-10. The value of the quotient in this region is about one. This proves that the superposition of $g^{(2)}(r)$ correctly describes the high probability of finding a third particle at this position. At Pos2, on the other hand the Kirkwood approximation dramatically fails. Since Pos1 is occupied by a particle with high probability, it is unlikely to find another particle next to it at Pos2, as this would dramatically disturb the generic local hexagonal order of a two dimensional liquid [Russ03b].

The quotient of the $g^{(3)}(r)$ and $g^{(2)}(r)$ can also be interpreted as the three-body contribution to the potential of mean force, having the form

$$
\beta W(r_{12}, r_{23}, r_{13}) = -\ln \left[ \frac{g^{(3)}(r_{12}, r_{23}, r_{13})}{g^{(2)}(r_{12}) g^{(2)}(r_{23}) g^{(2)}(r_{13})} \right]
$$

(5.7)

In the infinite dilution limit the potential of mean force $w(r_{12}) = -\ln \left( g(r_{12}) \right)$ approaches the pair potential $v^{(2)}(r)$. In the same way, it is in principle possible to derive the three-body potential $v^{(3)}(r_{12}, r_{13}, r_{23})$ from the extrapolation of $g^{(3)}(r)$ to the limit of infinite particle density. This approach has not yet yielded conclusive results, due to large uncertainties in the calculation of the density derivative of $g^{(2)}(r)$. This interesting problem is currently under investigation by C. Russ and H. H. von Grünberg [Russ03a].
5.6 Conclusion

In this chapter we presented structural measurements of a two dimensional system of charged colloids at low to high densities. The measurements were conducted using an identical set of particles and by adjusting the density of the sample, using a particle corral made of a rectangular scanned laser tweezers. Special care was taken to assure reproducible and identical ion concentrations in all measurements, by using scanned optical tweezers to vary the density of the sample. We inverted the pair correlation function, using the OZ equation to arrive at the effective pair potential $u^{(2)}(r_1, r_2)$ for all colloid densities and also discuss the limitations of this inversion procedure. This set of potential curves contains information about the importance of many-body contributions in our system. We observed that the derived effective pair potential depends on the particle density. Indeed, we found that $u^{(2)}(r_1, r_2)$ agrees well with the Yukawa potential at low densities but shows systematic deviations towards higher densities. This is a direct experimental observation of many-body effects in colloidal suspensions. The model of macro-ion screening was presented to provide a qualitative explanation of this effect, as we identified that the interaction between two particles is reduced by the presence of a third particle close to or in between the pair. It was shown that the shape of the pair potential including the many-body effects may be approximated by introducing a density dependent cut-off. At last we calculated the three-body correlation function, and pointed out the particle configurations for which the explicit three-body correlations become most important.
6 Direct measurement of three-body potentials

It has been shown in the previous chapter that the total energy of a system cannot be described by the sum of all pair-potentials alone. Because the electrostatic repulsion in a suspension of charged colloids is mediated by the distribution of the micro-ions between the particles, the pair interaction between two colloidal particles is directly related to the overlap of the electric double layers, see also chapter 3.5.1. If more than two colloids are close enough to be within the range of their double-layers, then more than two ion clouds overlap and many-body contributions to the total potential are the inevitable consequence. The leading term of the additional many-body contributions is the three-body potential. Here, we present the first direct measurement of three-body interactions, which has been performed using a colloidal system comprised of three negatively charged silica spheres [Brun03c]. Two of the particles are confined by means of a scanned laser tweezers to a line-shaped optical trap where they diffuse due to thermal fluctuations. When a third particle is approached, the total interaction energy of the system became considerably smaller than the sum of all pair-interactions. This difference is interpreted in the framework of the McMillan-Mayer theory as an attractive three-body potential. The results are supported by additionally performed non-linear Poisson-Boltzmann (PB) calculations. It will be shown that this attractive three-body term is primarily caused by local density variations of the micro-ionic fluid, an effect correctly described by the PB equation, but not by the linear DLVO theory.

6.1 Measurement

As colloidal particles we used charge-stabilized silica spheres with 990nm diameter suspended in water. These particles are considerably smaller than the ones used in other experiments presented in this work. Although smaller particles are more difficult to handle and approach the limits of the optical setup, there are two major considerations that suggest the use of these particles. For three-body contributions to be large enough to be measured, it is necessary that the electric double layers of three particles overlap considerably. Since the screening length is already as large as possible in aqueous suspensions, this effect can only be increased by making the ratio of particle size to screening length as small as possible. The second advantage is that smaller particles diffuse much faster, resulting in faster sampling of the potential and therefore better statistics.
A highly diluted suspension was confined in a silica glass cuvette with 200\(\mu m\) spacing. The cuvette was connected to a closed circuit, to de-ionize the suspension and thus increase the interaction range between the spheres as explained in chapter 4.1. Before each measurement the water was pumped through the ion exchanger and typical ionic conductivities below 0.07\(\mu S/cm\) were obtained. Afterwards a highly diluted colloidal suspension was injected into the cell, which was then disconnected from the circuit during the measurements. This procedure yielded stable and reproducible ionic conditions during the experiments. The change in the screening length \(\kappa^{-1}\) due to ion diffusion into the sample cell was determined to be constant around \(\Delta\kappa^{-1} = 0.05\mu m/hour\). This change has been considered in the PB calculations.

Inside the sample cell a scanned optical tweezers in the form of a straight line was created by the beam of an argon ion laser, deflected by a galvanostatic mirror unit, for details see chapter 4.2. The time averaged intensity distribution along the scanned line was chosen as being Gaussian distributed. The laser intensity distribution perpendicular to the trap, due to the shape of the laser focus can also be regarded as Gaussian with \(\sigma_y \approx 0.5 \mu m\). This yields an external laser potential acting as a stable trap for the particles. Due to the negatively charged silica substrate, the particles also experience a repulsive vertical force, which is balanced by the particle weight and the vertical component of the light force. The potential in the vertical direction is much steeper than the in-plane laser potential, therefore vertical particle fluctuations can be disregarded. The particles were imaged with a long-distance, high numerical aperture microscope objective of 63x magnification onto a CCD camera and stored every 120ms.
6.2 The pair potential

First only one particle was inserted into the trap to determine the external laser potential due to the optical line trap acting on a single particle. From the recorded positions the distribution \( P^{(1)}(x, y) \) was evaluated. \( P^{(1)}(x, y) \) depends only on the temperature and the external potential created by the laser tweezers \( u_L(x, y) \) according to the Boltzmann probability distribution, introduced in chapter 3.1.1. \( P_L(x, y) = P_L \exp(-\beta u_L(x, y)) \), with \( P_L \) being a normalization constant. Taking the logarithm yields the external potential \( u_L(x, y) \) with an offset given by \( \ln(P_L) \). The measured external potential is plotted in Fig. 6-2 for three different laser intensities. It can be seen that the shape of the laser potential is independent of the laser intensity and the potential strength is directly proportional to the intensity. Any possible thermal influence caused by the laser can therefore be ruled out. The Gaussian fit (solid line) in Fig. 6-2 determines the half-width to be \( \sigma_x \approx 4.5 \mu m \).

Next we inserted a second particle in the trap. The four-dimensional probability distribution is now

\[
P(x_1, y_1, x_2, y_2) = P_{12} \exp\left(-\beta(u_L(x_1, y_1) + u_L(x_2, y_2) + \nu^{(2)}(r))\right)
\]

with \( x_i, y_i \) being the position of the i-th particle relative to the laser potential minimum and \( \nu^{(2)}(r) \) the distance dependent pair-interaction potential between the particles. This can be projected to

\[
P(r) = \iiint P(x_1, y_1, x_2, y_2) \delta\left(\sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2} - r\right) dx_1 dx_2 dy_1 dy_2
= P_0 e^{-\nu(r)} \iiint e^{-\beta(u_L(x_1, y_1) + u_L(x_2, y_2))} \delta\left(\sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2} - r\right) dx_1 dx_2 dy_1 dy_2
\]
In principle the integral is constituted of all possible configurations of two particles with distance \( r \). Performing the full four-dimensional integration, however, is difficult because of the limited experimental statistics. This problem can be overcome with the following two considerations. First, due to the Gaussian shape of the external potential, the most likely particle configurations are symmetric with respect to the potential minimum of \( u_L \), because any asymmetric configuration at constant distance \( r \) has a higher energy. Secondly, particle displacements in \( y \)-direction are energetically unfavorable because \( \sigma_x \gg \sigma_y \). Accordingly, for constant distance \( r \) the minimum energy configuration is the symmetric configuration \( \{ (x_1 = r/2, y_1 = 0), (x_2 = -r/2, y_2 = 0) \} \). It has been confirmed by a calculation with the experimental parameters that all other configurations account only for less than 1\% of the value of the integral in eq. (6.2). Accordingly, eq. (6.2) can be expressed as

\[
P(r) = P_0 \exp \left[ -\beta \left( v^{(2)}(r) + 2u_L \left( \frac{r}{2}, 0 \right) \right) \right]
\]

From the measured \( P(r) \) we can thus obtain the interaction potential \( v^{(2)}(r) \). The normalization constant \( P_0 \) was chosen in a way that \( v^{(2)}(r) \to 0 \) for large particle separations. As expected, the negatively charged colloids experience a strong electrostatic repulsion which increases as the particles approach each other. The pair-interaction potential of two charge-stabilized particles in bulk is well known to be described by a Yukawa potential [Verv48], introduced in chapter 3.5.1, where \( Z^* \) denotes the renormalized charge of the particles, \( \lambda_B \) the Bjerrum-length characterizing the solvent, \( \kappa^{-1} \) the Debye screening length (given by the salt concentration in the solution), \( s \) the particle radius and \( r \) the centre-centre distance of the particles.

\[
\beta v^{(2)}(r) = (Z^*)^2 \lambda_B \left( \frac{\exp(\kappa s)}{1 + \kappa s} \right)^2 \frac{\exp(-\kappa r)}{r}
\]

Fig. 6-3 shows the experimentally determined pair-potential (symbols) together with a fit to eq. (3.22) (solid line). As can be seen, our data are well described by the Yukawa form of eq. (3.22). As fitting parameters we obtained \( Z^* \approx 6500 \) electron charges and \( \kappa^{-1} \approx 470 \text{nm} \) respectively. \( Z^* \) is in good agreement with the value \( Z^* = 6900 \) of the saturated effective charge of our particles, predicted by [Aubo03]. As we have already seen in the case of the effective pair potential derived by an inversion of the Ornstein Zernike equation for low densities in chapter 5.2, the pair potential can be successfully described by the Yukawa potential, even in the presence of a charged substrate. This is consistent with the experimental works of [Behr01] and theoretical calculations of [Netz00, Stil61]. The Yukawa potential captures the leading order interaction also for colloids close to a charged wall. A confining wall introduces only a very weak interaction due to additional dipole repulsion in the order of \( 0.1k_B T \), which is below our experimental resolution.
6.3 The three-body potential

We used an additional point shaped laser tweezers of focus size 1.3µm to control a third particle, and to hold it at a distance \( d \) on the perpendicular bisector of the scanned laser line away from the two particles, see Fig. 6-1. Doing so, we carefully checked that this additional optical trap has no influence of the two particles on the line tweezers. As the third particle approaches the line tweezers, we expect the occurrence of three-body interactions. Accordingly, the total interaction energy \( W(r, d) \) in this situation should not simply be given by the sum of the pair-interaction potentials alone but should also contain an additional term. Since we are considering a system of exactly three particles, higher order terms are absent, and the total potential of mean force \( W(r, d) \) of the McMillan Mayer theory from equation (5.4) in chapter 5.4 can be written as

\[
W(r, d) = v^{(2)}(r_1, r_2) + v^{(2)}(r_1, r_3) + v^{(2)}(r_2, r_3) + w^{(3)}(r_1, r_2, r_3)
\]  

(6.4)

Here \( v^{(2)}(r_i, r_j) \) denotes the pair potential between particles \( i \) and \( j \), defined in eq. (3.22) and \( w^{(3)}(r_1, r_2, r_3) \) the three-body interaction potential. Since the third particle is positioned symmetrically with respect to the line tweezers, an average configuration can be characterized by \( r = r_2 - r_1 \), the positions of the two particles in the line tweezers and the distance \( d \). Following the same procedure as described above, from the measured probability distribution \( P(r, d) \) of the two particles inside the laser trap we can again extract \( W(r, d) \) using eq. (6.3).
Fig. 6-4 Experimentally determined interaction energy $W(r,d)$ (symbols) for a system of two particles on a line tweezers in the presence of a third particle fixed at four different distances $d$ on the perpendicular bisector of the line trap. The calculated result of the superposition of three pair potentials is plotted as lines.

When approaching the third particle, the two particles in the trap are slightly displaced in the $y$-direction at small distances. Accordingly, the minimum energy configurations of the two particles are not on a straight line as before. The most likely configuration at given distance $r$ is $\{(x_1 = r/2, y_1 = y(r)), (x_2 = -r/2, y_2 = y(r))\}$ with $y(r)$ given by the measured particle positions. Since we have full knowledge of the two-dimensional external laser potential, we could compute $u_L(r/2, y(r))$ for every given configuration and use it in eq. (6.3) instead of $u_L(r/2, 0)$. This was not necessary, since no significant difference between the two results was observed.

The results are plotted as symbols in Fig. 6-4 for the distance of the third particle $d = 4.1, 3.1, 2.5$ and $1.6$ µm, respectively. As expected, $W(r,d)$ becomes larger as $d$ decreases due to the additional repulsion between the two particles in the trap and the third particle. In order to test whether the interaction potential can be understood in terms of a pure superposition of pair-interactions, we first calculated $W(r,d)$ according to eq. (6.4) with $w^{(3)}(\ell_1, \ell_2, \ell_3) = 0$. This was easily achieved because the positions of all three particles were determined during the experiment and the distance-dependent pair-potential is known from the two-particle measurement described above. The results are plotted as dashed lines in Fig. 6-4. Considerable deviations from the experimental data can be observed, in particular at smaller $d$. These deviations can only be explained, if we take three-body interactions into account. Obviously, at the largest distance, i.e. $d = 4.1$ µm our data is well described by a sum of pair-potentials. This is not surprising, since the third particle cannot influence the interaction between the other two, as it is far enough away from both. In agreement with the theoretical predictions of [Russ02], the three-body interactions therefore decrease with increasing distance $d$. 
Fig. 6-5. The measured three-body potential $w^{(3)}$ (symbols) is attractive for all distances $d$. The potentials obtained from the solutions of the non-linear Poisson Boltzmann equation are plotted as lines. The parameters of the calculations were chosen so that the pair potentials were correctly reproduced.

It might seem surprising that it is possible to sample the potential up to energies of $15k_BT$, as configurations of such a high energy statistically happen only with very low probability. In this experiment we can chose the energetic range of the potential we want to sample by adjusting the strength of the line tweezers. The laser potential pushes the particles together, which therefore sample different ranges of the electrostatic potential. Thus, to achieve a better resolution for smaller particle distance and higher potential values, respectively, the strength of the line tweezers has to be increased.

According to the McMillan Mayer theory, eq. (6.4), the three-body interaction potential is given by the difference between the measured $W(r,d)$ and the sum of the pair-potentials, i.e. by the difference between the measured data and their corresponding lines in Fig. 6-4. The results are plotted as symbols in Fig. 6-5, using the same symbols as in Fig. 6-4. It can be clearly seen that in the case of charged colloids the measured three-body potential $w^{(3)}$ is entirely attractive and becomes stronger as the third particle is approached. It is also interesting to see that the range of $w^{(3)}$ is of the same order as the pair-interaction potentials.

This demonstrates that in the case of three colloidal particles, three-body interactions present a considerable contribution to the total interaction energy and must therefore be taken into account. Whenever dealing with systems comprised of more than three particles, in principle also higher-order terms have to be considered. The relative weight of such higher-order terms depends on the particle number density $\rho$. While at low enough $\rho$ a pure pairwise description should be sufficient, with increasing density first three-body interactions and then higher-order terms come into play. We expect an intermediate density regime, where the macroscopic properties of systems can be successfully described by taking into account only two- and three-body interactions. In colloidal systems we have shown the three-body interactions to be comparable in magnitude to the corresponding pair-interactions, therefore
we can expect large macroscopic three-body effects in this intermediate density range. At even larger particle densities $n$-body terms with $n > 3$ have to be considered in addition, which may partially compensate.

### 6.4 Comparison to numerical calculation

In order to obtain more information about three-body potentials in colloidal systems, we additionally performed Poisson-Boltzmann (PB) calculations, in a similar way as in [Russ02]. The PB theory provides a mean-field description in which the micro-ions in the solvent are treated within a continuum approach, neglecting correlation effects between the micro-ions. As discussed in chapter 3.5.1, it has been demonstrated by [Groo91] that in the case of monovalent micro-ions the PB theory provides a reliable description of colloidal interactions. We used the multi-centered technique, described and tested in other studies [Dobn03b] to solve the non-linear PB equation for the electrostatic mean-field potential $\Phi(x,y,z)$, which is related to the micro ionic charge density $\rho_e = -(\kappa^2 / 4\pi\lambda_B) \sinh \Phi$. Integrating the stress tensor, depending on $\Phi(x,y,z)$, over a surface enclosing one particle, results in the force acting on this particle. Calculating the force $f_{12}$ and from this the pair potential between only two particles, we first numerically reproduced the measured pair interaction of Fig. 6-3 in order to determine the correct colloidal bare charge and screening length. The superposition of three such electrostatic pair potentials leads to a total interaction potential, calculated in a purely pair-wise additive picture. The resulting potentials are presented in Fig. 6-4 as dashed lines. The calculation of full PB three-body potentials was then carried out by calculating the total force acting on one particle in the line trap and subtracting the corresponding pair-forces $f_{12}$ and $f_{13}$ obtained previously in the two-particle calculation. The difference is integrated to obtain the three-body potential. The results are plotted as lines in Fig. 6-5 and show reasonable agreement with the experimental data, in particular with respect to the range and size of $\omega^{(3)}$. This strongly supports our interpretation of the experimental results in terms of three-body interactions. The remaining deviations between theory and experiment are probably due to small variations in salt concentration but may also be due to small differences in the size and surface charge of the colloidal particles used in the experiment, which have been assumed to be identical in the PB calculations.

The interaction potential is an integrated quantity obtained from the electrostatic potential $\Phi$. Therefore, the observed three-body effect should also show up at the level of electrostatic potentials. Of course, to a large extent $\Phi$ is just the superposition of potentials around individual particles, but since the solutions of nonlinear equations cannot in principle be superposed, we expect to find small differences. It is indeed these small differences that are ultimately responsible for the three-body interaction. In order to demonstrate this, we performed additional PB calculations and examined the deviations of the electrostatic potential from the linear superposition predictions.
We started by reconsidering the two-particle problem. First, we solved the PB equation around a single isolated colloid to obtain the one-body electrostatic potential. Next we calculated the electrostatic potential for two colloidal particles at distance \( r \) and compared this potential to the superposition of two one-body potentials. This rather complicated approach of analyzing the difference to one-particle solution has proven to be very useful. Because the results of the PB calculations increase rapidly and reach large values for small particle distances \( r \), the deviations we are interested in cannot be seen by looking directly at the potential. The difference of the electrostatic potential is shown as a contour-plot in Fig. 6-6. It can be seen that micro-ions are rearranged in a complex way between the colloids and that there is a weak polarization of the counter-ion cloud very close to the particle surfaces. However, all these effects are rather small and therefore, except for very small particle separations \( r \), the superposed solution should still describe the two-body interaction quite accurately. For a system of three colloids this is not the case. We compared a superposition of three two-body electrostatic potentials with the correct non-linear three-body electrostatic potential. The difference is shown in Fig. 6-7. Obviously, differences are now much larger than in Fig. 6-6. The counter-ion cloud polarization close to the colloid surface is apparently correctly taken into account by two-body terms, while the ion distribution among the colloids is poorly described by adding up two-body electrostatic potentials. Since this is the only major difference, this change in the ion distribution can be identified as the main physical reason which gives rise to the three-body interaction in this system. By integrating the potential difference from Fig. 6-7, one recovers the attractive three-body potential, already discussed above, which is thus demonstrated to be a consequence of the nonlinearity of the physical equations governing the interactions in our system.
6. Direct measurement of three-body potentials

Fig. 6-7. Difference between the electrostatic potential $\Phi$ calculated for three identical particles with the nonlinear PB theory and the result of the superposition of three two-particle potentials. The distance between the two particles on the left is $r = 2.5\,\mu m$ and the position of the right particle is given by $d = 1.6\,\mu m$, being the closest distance $d$ realized in the experiment. The black bar represents a length of $1\,\mu m$.

So far we have only considered mid-plane configurations, i.e. two particles are confined in linear dimension and the third particle is kept a distance $d$ on the perpendicular bisector away. The question then arises of how does the strength of the three-body interaction depends on the specific geometry and which configuration leads to the strongest interaction. This question has been studied in detail by Russ et al. [Russ02] in numerical Poisson-Boltzmann calculations. Fig. 6-8 shows their results for the three-body potential $W^3(r)$ in scaled units $\bar{\Omega} = W^3(r) \lambda_b / \sigma k_B T$ as a function of the circumference $L = r_{12} + r_{23} + r_{13}$, the summed up distances between the three particles. Other than the mid-plane configuration, plotted as square symbols in Fig. 6-8, they also studied the co-linear configuration (diamonds), in which all three particles are kept on a line and the equilateral triangular geometry (circles), where all three particles have the same distance from each other. The three-particle potential is found to be attractive for any geometry. Surprisingly the data of all three geometries collapses onto one master curve if plotted as a function of the circumference $L$. This master curve may be fitted remarkably well to a Yukawa potential

$$\beta \bar{\Omega}(r) = A e^{-\gamma r}$$

The smallest value of $L = 3\sigma$ can only be achieved in the equilateral triangular configuration. For any other geometry the minimal value of $L$ is larger. Therefore the data for small $L$ in Fig. 6-8 is available only for the triangular geometry. It has to be emphasized that the calculations of Russ et al. were performed for small particles of diameter $\sigma = 32\,nm$, low surface charge $Z = 300$ and small inverse screening length $\kappa \sigma = 0.16$. It cannot be ruled out at the moment that not only quantitative but also qualitative differences in the behavior of the three-body interaction arise between this parameter regime and the experimental one.
6.5 Consequences for the phase behavior

Before closing this chapter we would like to present the results of two numerical studies by Russ et al. [Russ02] and Dobnikar et al. [Dobn03a, Dobn03b] that demonstrate the influence of many-body interaction on the phase behavior of colloidal suspensions.

Russ et al. [Russ02] were able to show that the attractive three-body potential may supply the needed cohesive energy to induce a fluid-fluid phase separation in a two dimensional system of charged colloids. Using perturbation theory, they extended the van-der-Waals theory for repulsive pair interaction to include an attractive three-body potential. In this way they obtained a criterion for the ratio between the strengths of the pair and three-body potential, necessary to induce a critical point in the system. On this basis, they predict the existence of such a fluid-fluid phase separation, which they expect to be located in the parameter region of medium to high particle charges and, most important, large screening lengths \( \kappa \sigma < 1 \), as can be seen in Fig. 6-9 (a). Dobnikar et al. extended the idea of incorporating the many-body interactions into an effective pair potential by a density dependent cut-off into three dimensions, see also chapter 5.3. They confirmed via full Poisson Boltzmann calculation that also in three dimensions this model potential is capable of including the effects of many-body interactions to a certain extent Using this model potential, they carried out molecular dynamics simulations and determined the solid-liquid phase boundary using the Lindemann melting criterion. Their results for fcc and bcc crystals are shown in Fig. 6-9 (b).
6. Direct measurement of three-body potentials

Fig. 6-9 (a) Phase diagram of a two dimensional system of charged colloids in the parameter space of particle charge $Z$ and inverse screening length $\kappa \sigma$. The circles represent parameter configurations at which a fluid-fluid coexistence is expected, the crosses and diamonds represent the parameter region where the cohesive energy is expected to be too weak to allow a fluid-fluid phase separation. The solid curve is an estimate for the phase boundary [Russ02].

(b) The melting line as reduced temperature $T$ of a pure Yukawa system, obtained by Robbins et al. is plotted as a solid line, as a function of $\kappa a$ the inverse screening length times the mean particle distance. The dashed lines represent the melting line of Dobnikar et al, assuming a truncated Yukawa potential. The symbols represent the phase boundary determined by full Poisson-Boltzmann calculations. Graph taken from [Dobn03a]

The solid line in

Fig. 6-9 (b) represents the results by Robbins, Kremer and Grest [Robb88] for a system of point-like particles interacting via a Yukawa potential. For high salt concentration, large inverse screening length $\kappa a > 8$, good agreement between both models is found. However reducing the amount of salt, i.e. decreasing $\kappa a$, increases the importance of many-body contributions and leads to pronounced deviations of the simulation results from the Robbins, Kremer and Grest melting line.

The works of Russ and Dobnikar thus prove that many-body interaction may considerably change the phase boundary of colloidal suspensions and therefore have to be considered in an accurate description of colloidal phase behavior.

6.6 Remark on four body potentials

Whenever dealing with systems comprised of many (much more than three) particles, in principle also higher-order terms have to be considered. The relative weight of such higher-order terms depends on the particle number density $\rho$. While at low enough $\rho$ a pure pairwise description should be sufficient, with increasing density first three-body interactions and then higher-order terms come into play. We expect that there is an intermediate density regime, where the macroscopic properties of systems can be successfully described by taking into account only two- and three-body interactions. There are some physical examples such as liquid rare gases [Jaks02] and the island distribution of adsorbates on crystalline surfaces.
[Öste99], where the thermodynamic properties are correctly captured by a description limited to pair- and three-body interactions. For colloidal suspensions, on the other hand, there is no physical reason to assume that all higher order contributions vanish.

There are numerical Poisson-Boltzmann calculations by [Russ02] that have investigated the four-body potential in a four particle system. They found the four-body potential to be attractive for any of the particle configuration discussed above: the triangular, mid-plane and co-linear configuration. The typical magnitude of the four-body attractions is found to be much weaker than any of the corresponding three-body attractions.

The logical extension of the previous experiment would be to add a forth particle to the system. This can be achieved by an additional point-like laser tweezers. We expect to observe the strongest four-body effect in a systematic arrangement of the particles. Two particles should be placed on the scanned laser line, as done before, and two particles are held by two tweezers on both sides of the perpendicular bisector with the same distance $d$ to the laser line. Some preliminary experiments have already been performed. As the four-body potential is derived by determining the total interaction and subtracting from it all two- and three-body contribution, quite large errors arise. But the work is still in progress, and decisive results are expected soon.

6.7 Conclusion

We have demonstrated that in the case of three colloidal particles, three-body interactions represent a considerable contribution to the total interaction energy and must therefore be taken into account. We presented an simple experiment of only three colloidal particles, and measured the three-body potential directly. The three-body interactions are shown to be comparable in magnitude to the corresponding pair-interactions, therefore we there expect large macroscopic three-body effects in this intermediate density range. At even larger particle densities $n$-body terms with $n >3$ have to be additionally considered, which may partially compensate. Even in this regime, however, many-body effects are not cancelled out, but lead to notable effects, e.g. to a shift of the melting line in colloidal suspensions [Dobn03a].
The equation of state

In the previous sections we paid a lot of attention to the specific features of the inter-particle potential. In this section we focus on the thermodynamic properties of the system. Details of the pair interaction are neglected and we try to describe the equation of state (EOS) of the particle using the hard-disk (HD) model. This might seem to be a little farfetched, but it is definitely worthwhile, since HD fluids play a prominent role in liquid state theories. This is due to the fact that, firstly, they often serve as reference systems in perturbation theories of two-dimensional liquids (just as hard-sphere fluids do for liquids in three dimensions), and that, secondly, at high densities the behavior of every 2D fluid is dominated by volume effects, which in turn depends on the short-ranged hard-core part of the inter-particle potential. Mainly for these two reasons, the HD EOS appears also in many theories on monolayer adsorption on solid surfaces [Stee74], an aspect illustrated for example in [Heim95] where the HD EOS is used in statistical mechanical theories modeling the binding of peripheral globular proteins on lipid membranes. The important role of the HD system explains the overwhelming number of theoretical studies on the EOS of a HD fluid, dating from as early as 1959. Most approaches to the EOS are based on specific re-summations of the virial series and the construction of sophisticated Padé approximants [Baus87, Hend75]

7.1 The two dimensional colloidal pressure

In this chapter, we exploit the fact that we are now in the fortunate position of knowing the pair potential as well as the static structure of the system. Utilizing the concepts of statistical mechanics we can now calculate the EOS and derived quantities. The macroscopic properties of the system can be described by state variables like temperature T, pressure P or total Volume V. These variables are not independent but related by the EOS, which usually is taken in the form

\[ p = p(V, T) \]

The following pressure equation is derived from the canonical partition function based on the assumption of pairwise-additive interactions. The effect of many-body interaction has been highlighted in the previous sections, but since the many-body contributions are below \( 1k_BT \), pair-wise additivity is still a good approximation in colloidal systems, especially towards higher salt concentrations, as in this case the double layer overlap considerably less. Towards higher particle densities minor deviations may occur, as many-body contributions become more pronounced. In two dimensions the pressure equation for an isotropic 2D system reads in dimensionless form [Hans90]

\[ \frac{\rho \sigma^2}{k_B T} = \rho \sigma^2 - \frac{\rho^2 \sigma^2}{4k_B T} \int_0^\infty r^2 \frac{dy(r)}{dr} g(r) 2\pi r dr \]
As in our situation, for known pair potential and pair correlation function $g(r)$ the pressure of the 2D liquid can be directly calculated as a function of the 2D particle density $\rho$. The particle density may be varied conveniently in our experiment by means of optical tweezers, described in chapter 4.2. We have thus realized a 2D colloidal model fluid for which the EOS, i.e. the $p(\rho)$-diagram, can be directly determined. Comparing the experimental to the theoretical EOS of HD's, we find the colloidal liquid behaves like a 2D fluid of HD's over a wide density range from the fluid to the solid phase.

In order to experimentally realize a hard disc system with colloidal particles, it is important to ensure that the inter-particle potential is extremely short ranged and that no attractive parts in the potential exist. We have decided not to work with sterically stabilized colloidal particles as this stabilization usually leads to a structured pair potential in the distance region were the polymer brushes start to overlap [Marc97]. Instead we chose to use charge-stabilized colloids at moderate salt concentrations. A screening length $\kappa^{-1}$ between 50nm and 200nm yielded optimal results. Higher salt concentrations lead to such small particle distances that a pronounced aggregation of particles due to the van-der-Waals interaction was observed. For the same reason it proved unpractical to use very thin sample cells, as this is known to induce attraction [Behr01]. The colloidal system employed consisted of charged sulphate-terminated polystyrene spheres of $\sigma = 3\mu m$ diameter (IDC Cooperation) and of charged sulphate-terminated silica particles of $\sigma = 2.4\mu m$ diameter. The suspension was injected into a sample cell made of fused silica plates with 200\mu m spacing. We performed measurements at high and at low salt concentration, i.e. at $\kappa\sigma = 21.1$ and $\kappa\sigma = 6.9$. The experiments were conducted in the same way as described in chapter 5.1. The measured $g^{(2)}(r)$ were inverted using the Percus-Yevick and HNC closure relations, analogously to chapter 5.2. Applying eq. (7.2) to the resulting effective pair potentials $u(r)$ and the measured $g^{(2)}(r)$ were obtained the desired EOS $p(\rho)$.
7.2 Hard disk equation of state

To compare the experimental and simulation results with the predictions of the HD calculation of [Hend75, Vela97], it is necessary to assign the colloidal system an effective hard disk diameter. This diameter should be larger than the true particle diameter $\sigma$ and in sensitively dependent on the strength of the inter-particle interaction, which is on the double layer thickness around the particles. For an ideal gas of $N$ particles at density $\rho$ the EOS obeys

\begin{equation}
\rho = \frac{Nk_B T}{V} = \rho k_B T
\end{equation}

In real systems, such as hard disks or colloidal suspensions, the effect of the inter-particle interaction and the finite size of the particles change the relation between the state variables. The virial equation of state expresses the deviations from ideal behavior as an infinite power series in $\rho$.

\begin{equation}
\frac{P}{k_B T} = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \cdots
\end{equation}

In two dimensions the second virial coefficients are given by the following equation. The term in brackets in the integrand may be abbreviated by the Mayer’s $f$-function.

\begin{equation}
B_2(T) = -\pi \int_0^\infty \left( \exp\left[\frac{-f(r)}{\rho \sigma^2}\right] - 1 \right) r \, dr = -\pi \int_0^\infty f(r) r \, dr
\end{equation}

In order to compare the pressure of the experiment with the HD calculations, the second virial coefficient of experimental system must be equated with the coefficient of a pure HD system $B_2^{(HD)} = \frac{1}{4} \pi \sigma^2$ [Bark67]. We obtain $\sigma_{\text{eff}} = 1.084\sigma$ for the $\kappa\sigma = 21.1$ measurement, $\sigma_{\text{eff}} = 2.16\sigma$ for and $\kappa\sigma = 6.9$. For better comparison the pressures in Fig. 7-2 (a, b) are shown as a function of $\rho \sigma_{\text{eff}}$. The precision of our procedure is primarily limited by errors made in the determination of the pair potential. They lead to small variations in the computed pressure and also in the effective hard core diameter $\sigma_{\text{eff}}$. As both, the $x$- and $y$-axis of Fig. 7-2 (a, b) depend on $\sigma_{\text{eff}}$ the error bars appear tilted.

Fig. 7-2 (a) shows as solid symbols the experimentally determined pressure of a 2D colloidal system in the high salt regime with $\kappa\sigma = 21.1$ and $\sigma_{\text{eff}} = 1.084\sigma$. For low densities the measured EOS is compared with theoretical predictions by Henderson [Hend75] (dotted line) for the fluid, based on the virial expansion. Up to a density of $\rho \sigma_{\text{eff}}^2 = 0.85$ excellent agreement is found. For intermediate densities, across the region of the fluid–solid phase transition, the measured EOS is compared to Monte Carlo data from Velasco and Mederos [Vela97] (blank circles) and also to the results of density functional theory within the solid phase (dashed line). For all densities excellent agreement between theoretical predictions and experimental results is found.

To obtain more information on the character of the different phases in Fig. 7-2 (a), we also examined the orientational correlation function $g_6(r)$ (chapter 3.1.3). Up to a density of $\rho \sigma_{\text{eff}}^2 = 0.85$ the system exhibits a pure liquid phase, confirmed by the isotropic pair-correlation function $g(r)$ and the exponentially decaying $g_6(r)$. 
7. The equation of state

Fig. 7-2. (a) The experimentally determined equation of state (squares) of a high salt colloidal system in the fluid and solid density range is compared to theoretical predictions based on the hard disk model. (b) The equation of state (squares) of a low salt colloidal system deviates from the hard disk behavior (lines) towards high densities. For details, see text.

On the other hand, at densities above $\rho\sigma_{\text{eff}}^2 = 0.95$ the system is in stable crystalline state, with a slow algebraically decaying pair correlation function and a constant orientational correlation function. However, in between, i.e. for $0.85 < \rho\sigma_{\text{eff}}^2 < 0.95$, there is a transition region, in which $g_{\alpha}(r)$ decays slower than exponentially and a local hexagonal order can be observed. It has not yet been determined whether this is the hexatic phase or a very polycrystalline state. In contrast to the measurement of Marcus and Rice [Marc97] no pronounced liquid-hexatic and hexatic-solid coexistence region has been observed, which is most likely due to the fact that their pair-potentials had weak attractive parts, while ours are purely repulsive.

Surprisingly, even for low salt concentration, $\kappa\sigma = 6.9$ and $\sigma_{\text{eff}} = 2.16\sigma$, the colloidal system can still be successfully mapped to a hard disk fluid, at least for medium densities, see Fig. 7-2 (b). For $\rho\sigma_{\text{eff}}^2 > 0.7$, there are marked deviations from the HD EOS. We performed MC simulations to compute pair-correlation functions $g^{(2)}(r)$ of a quasi-2D fluid system, using the lower (dashed line) and upper bond (dotted line) of Yukawa part of $u(r)$ of the $\kappa\sigma = 6.9$ measurement. These two pressure curves, computed from the MC-generated pair-correlation functions, are plotted as in Fig. 7-2 (b). The deviations of the MC results from the predictions of Henderson (solid line) and Baus and Colot [Baus87] (dashed dotted line) demonstrate that mapping a soft Yukawa potential onto a hard disk system leads to an overestimation of the pressure. The fact that the experimental pressures of the $\kappa\sigma = 6.9$ measurement are below even the results of the MC simulation using the lower bond of the pair potential leads to the conclusion that these differences must be due deviation of the experimental pair potential from the assumed Yukawa form. The experimental pair potential shows a density-dependent truncation in $u(r)$, which has been ignored in the MC simulation. We ascribe these deviations to the effect of macro-ion screening discussed in chapter 5.3.
7.3 Compressibility of 2D suspensions

Fig. 7-3. Comparison between the pair correlation functions of experimental (symbols) high salt ($\kappa \sigma = 21.1$) and low salt ($\kappa \sigma = 6.9$) colloidal suspensions and the theoretical predictions [Baus87] (solid line) for the hard-disk fluid at two different densities.

Baus and Colot [Baus87] have suggested a semi empirical expression for the direct correlation function of a HD fluid which can be related to $g^{(2)}(r)$ via the Orstein-Zernike equation. Fig. 7-3 shows the resulting pair-correlation functions (solid lines) for various densities and compares them with our measured $g^{(2)}(r)$. We emphasize that after matching the second virial coefficient no free parameter was used. While in the case of high salt concentration excellent agreement was found, for the low salt measurement differences were observed mainly for small particle separations, where the first peak seems to be rounded off and is less pronounced compared to that of the HD fluid, due to the softer pair potential. For larger distances, packing effects dominate, and in both cases the agreement is again good.

7.3 Compressibility of 2D suspensions

The elastic properties of two dimensional colloidal systems were investigated by [Will01] using paramagnetic particles in the crystalline phase by the means of volume fluctuations and by measuring the relaxation response from a well defined lattice perturbation. Here we will determine the compressibility $\kappa_T$ of a system of charged particles in the liquid state. From the recorded particle positions we can directly compute the particle number fluctuations $\left< \Delta N^2 \right>/\left< N \right>$. As described in chapter 3.1.3, this quantity which is related to the isothermal compressibility $\kappa_T$ via eq. (3.10)

$$\kappa_T = \frac{1}{k_B T \rho} \left< \frac{\Delta N^2}{N} \right> = \frac{1}{k_B T} \int \left( g^{(2)}(r) - 1 \right) dV - \frac{1}{\rho}$$ (3.10)
Fig. 7-4. Compressibility of a colloidal monolayer of charged spheres is plotted as a function of the particle density is plotted for suspensions with high salt concentration (circles) and low salt concentration (squares). The compressibility values obtained from analyzing the particle number fluctuations are shown as blank symbols, while the results of taking the density derivatives of the $p(\rho)$ of Fig. 7-2 are shown as filled symbols. The compressibility is compared to the theoretical prediction for an infinite system eq. (7.6) (solid line) and a finite system [Roma99] (dotted line).

The results of this calculation are shown in Fig. 7-4 as open symbols. Alternatively, we can calculate $\kappa_T$ from the density derivative of the pressure, $\kappa_T k_B T \rho = (\beta \partial p / \partial \rho)^{-1}$, computing the differences between neighboring experimental values of Fig. 7-2. The results are plotted in Fig. 7-4 as filled symbols. The compressibility, calculated in both ways, is compared with the derivative of Henderson's EOS [Hend75]

$$\rho k_B T \kappa_T = \left[ \frac{1 + \eta^2/8}{(1-\eta)^3} + \eta \frac{\eta + 8}{4(1-\eta)^3} \right]^{-1}$$  \hspace{1cm} (7.6)

This curve is plotted in Fig. 7-4 as a solid line. While the density derivatives of the experimental pressure values agree nicely with the theoretical prediction of eq. (7.6), the results using eq. (3.10) show deviations, especially for the low-salt measurement. One reason for this discrepancy may be a finite size effect. To estimate this effect, we used the pair-correlation functions, suggested by Baus and Colot for the infinite system, to calculate the particle number fluctuation in a finite sub-volume of a hard-disc fluid composed of a fixed number of particles (1000 particles), using a method described in detail by Roman et al. [Roma99]. The result is plotted in Fig. 7-4 as a dotted line and the small correction illustrates that, at least for the high salt measurement, the observed differences can be explained with a finite size effect. For the low salt measurement, the remaining differences are probably due to insufficient sampling.
7.4 Conclusion

In this chapter we computed the pressure of a two-dimensional system of charged colloidal particles from the measured particle configurations. Direct experimental control over the particle density by means of scanned optical tweezers allowed the precise measurement of the pressure as a function of the particle density. The EOS subsequently obtained was compared to the predictions for hard-disk systems without any free parameter. The effective HD radius of the colloidal particles is correctly defined by simply imposing an equal second virial coefficient in both descriptions. We also compared predictions for the pair-correlation function and the compressibility of a hard-disk fluid with the corresponding quantities obtained from our colloidal model fluid. Here also we find good agreement, especially for suspensions with higher salt concentration. Therefore 2D colloidal suspensions are an excellent model for a hard-disc system. This applies both to the structure as well as to the thermodynamics.

On the atomic level, the EOS of 2D fluids can be derived from adsorption isotherms [Stee74]. As opposed to these experiments, we have the full structural information, controllable substrate-particle interactions and tunable inter-particle potentials. This highlights once again the usefulness of colloids as a model system in statistical mechanics.
Colloidal monolayers on one-dimensional periodic substrate potentials

The phase behavior of two dimensional systems is an active field of research. While there are a number of studies, both theoretical and experimental, on the melting transition of two dimensional colloidal systems on homogenous substrates, only a few experiments have been performed on patterned substrates. This proportion is in contradiction to practical relevance. The properties of the monolayer are deeply connected to those of the underlying surface. It has been shown by studies of atomic adsorbates on crystalline surfaces [Pokr86] that monolayers on patterned substrates exhibit a richer and more complicated phase behavior than on nearly flat substrates. Systematic analyses are rarely possible in atomic systems as the inter-particle interaction, as well as the strength and shape of the substrate potential, may only be varied within a small range.

In contrast to atomic systems this is easily achieved in colloidal suspension. Instead of creating a topological substrate, it has proven to be more successful to insert the colloidal particles into a sample cell with a flat glass surface, as in the previous chapters, and create an external laser field, which acts via light forces as an external potential. Chowdhury et al. [Chow85b] were the first to demonstrate that a 2D colloidal system may crystallize due to the presence of an external laser potential. This provides a convenient and flexible way to produce optical substrate potentials. The strength of the substrate potential may be varied by changing the laser intensity.

By overlapping two laser beams Chowdhury et al. created a periodic one-dimensional interference pattern, which acted as a one-dimensional periodic potential on the particles. When the periodicity of the light pattern was chosen to be commensurate to the mean particle distance, the colloidal liquid was observed to crystallize if the light intensity was strong enough. Later Wei et al. [Wei98] showed that the induced crystal may melt if the potential strength is increased above a critical value; becoming a modulated liquid again.

In the following experiments, we investigate the phase behavior of a dense colloidal monolayer with a mean particle distance $a$ in the presence of a one-dimensional substrate potential of periodicity $d$. As in the experiments of Chowdhury and Wei, we focus on the commensurate case, with commensurability ratio $p$. The commensurability ratio is the value of the projection of the mean particle distance vector of the colloidal lattice on the vector of the substrate lattice divided by the periodicity $d$. The colloidal density $\rho$, the mean particle distance $a$ and commensurability ratio $p$ are coupled by these relations.

$$\rho = \frac{2}{\sqrt{3}a^2}; \quad pd = \frac{\sqrt{3}}{2}a$$ (8.1)

After characterizing the different phases for the commensurability ration $p = 1$, similar to those published by Wei, we present for the first time the phases in the case of a commensurability ratio $p = 2$, where the emergence of a new smectic phase will be shown and
characterized. Then we return to the case of $p = 1$ and explore the full regions of the different phases to extract the complete phase diagram of the system, through systematically varying the potential strength $V_0$ and the particle density $\rho$. The phase diagram is compared to the predictions of the theoretical renormalization group analysis of Frey et al. [Frey99] and the importance of positional fluctuations on the stability of the crystalline phase is highlighted.

### 8.1 Characterizing the phases for $p = 1$

The following experiments have all been performed using the experimental setup described in chapter 4. As sample cells we used quartz glass cuvettes of 500 mm spacing. As colloids we used sulfate-terminated polystyrene particles of diameter $\sigma = 3 \mu m$ with a polydispersity of 4% (Interfacial Dynamics Corporation, USA). The Debye screening length was $\kappa^{-1} = 400 \text{nm}$, and the effective charge was determined to be around $Z_{\text{eff}} = 20000$ electron charges. The total charge of the particles, measured by titration, is specified by the manufactures as $Z = 1.6 \times 10^7$ electron charges. For details of the colloidal inter-particle potential see chapter 3.5.2.

The laser potential was created by the interference of two linearly polarized laser beams. The proportionality factor of the potential strength $V_0$ and the laser power $P$ has been determined experimentally, as explained in chapter 4.3. At maximum laser power $P_{\text{max}} = 2W$ a potential strength of $V_0 = 18k_BT$ was achieved. To distinguish the different thermodynamic phases we calculated the time averaged density distribution $\rho(x,y)$ of the system and also the two-dimensional pair correlation function $g(x,y)$. Here $x$ and $y$ denote the direction perpendicular and along the potential lines respectively. For a definition of $g(x,y)$ please see chapter 3.1.3.

The particle density of the colloidal monolayer was kept constant at around 5% below the critical density required for spontaneous crystallization. In the absence of the laser potential, the system is therefore in the state of an isotropic liquid, as can be seen in $g(x,y)$ in Fig. 8-1 (b). The local order decays within a few mean particles distances. The first peak of the pair correlation function corresponds approximately to the mean particle distances, which in this experiment was $a = 8.6 \mu m$.

In contrast to the isotropic liquid, considerable changes in the structure of the monolayer were observed when the laser potential was applied. Even a weak external potential $V_0 = 0.6k_BT$ is sufficient to break the isotropy of the system and leads to a pronounced density modulation Fig. 8-1 (c). The density modulations are small in the $y$-direction. The correlation function, Fig. 8-1 (d), shows only a local order but is smeared out for larger distances. Since the positional order of the particles along the laser lines is still of short range, as in the case of the isotropic liquid, this colloidal phase is called a modulated liquid.
8.1 Characterizing the phases for $p = 1$

Fig. 8-1 Contour plots of the density distribution $\rho(x,y)$ (left) and the pair correlation function $g(x,y)$ (right) for four different potential strengths (a, b) $V_0 = 0k_BT$, (c, d) $V_0 = 0.6k_BT$, (e, f) $V_0 = 2.1k_BT$ and (g, h) $V_0 = 10k_BT$. All length scales are in $\mu m$, the potential period is $d = 7.5\mu m$. 
By increasing the potential to $V_0 = 2.1kB_T$, light induced freezing is observed. Now $\rho(x,y)$ and $g(x,y)$ are both modulated in $x$ and also in the $y$-direction, Fig. 8-1 (e, f). The particles are trapped on lattice sites and fluctuate only around the equilibrium position. Since the crystal may still move as a whole along the potential lines, but not perpendicular to them, this phase is called a locked floating solid. Similar to any phase transition, this light induced crystal occurs if the free energy of the crystalline state is lower than the one of the liquid state. This is not expected as the density of the sample is below the density of spontaneous crystallization. The light induced freezing takes place because the external laser potential selectively reduces the entropy of the modulated liquid phase, while the entropy of the crystal remains almost the same. In the modulated liquid the laser potential largely reduces the possibilities in which the particle can arrange, as the regions of high potential energy are accessible only with low probability. Hereby the number of possible representations of the ensemble decreased, and accordingly entropy as well.

In the case of the light induced crystal, the possible particle configurations are already reduced by the inter-particle interaction. As the particles confine each other to certain lattice sites, the accessible volume in configurational space is much smaller. The effect of the laser potential only adds to the confinement caused by the particles themselves and therefore only lead to a minor change in entropy. As a consequence the entropy of the modulated liquid decreases much faster than the one of the crystalline phase for increasing potential strength and the entropy difference between the two phases diminishes. Therefore the entropic contribution to the total free energy loses its importance and the inner energy becomes dominant. As the inner energy is lower in the crystalline phase than in the liquid, the system crystallizes even at low particle densities.

If the light intensity is increased even further to $V_0 = 10kB_T$ the particles become more strongly confined to the potential minima. This does not lead to a more stable crystalline phase, as one might expect, but a complete loss of the crystalline order along the laser lines is observed. The densities in Fig. 8-1 (g, h) are again smeared out along the $y$-direction and resemble the results of the modulated liquid presented above. Obviously enhancing the potential modulation caused the system to melt again.

More evidence for the assignment of the different phases mentioned above is derived from the analysis of the pair correlation function along the $y$-direction $g(y)$, shown in Fig. 8-2. For the modulated liquid at $V_0 = 0.6kB_T$, the modulation of $g(y)$ is short ranged and rapidly decays to one, which represents the total loss of correlation. The envelope of this curve can be fitted to an exponential decay; Fig. 8-2 (a) dashed line. According to the results of the KTHNY theory presented in chapter 3.3, this identifies the structure of the particles along the $y$-directions liquid. At the intermediate potential strength, Fig. 8-2 (b), the pair correlation function decays much slower and its envelope cannot be accurately described by an exponential function. In contrast, we find that the data can be fitted well to an algebraic decay, with an exponent $\eta = 0.6 < 1$. This characterizes the phase as crystalline and agrees well with the fact that in two dimensions only a quasi long-range order exists.
8.2 Characterizing the phases for $p = 2$

Reducing the period $d$ of the substrate potential by 50%, while keeping the particle density and the Debye screening length constant, leads to a new commensurate scenario with a commensurability ration $p = 2$. For this situation Frey et al. have predicted the existence of an additional intermediate locked smectic phase, which we were able to observe in our experiments for the first time.
8. Colloidal monolayers on a one-dimensional

Fig. 8-3. (a, b) are color scale plots, the white representing a zero value and more intense color levels higher values of \( \rho(x,y) \) and \( g(x,y) \), respectively. (a) Two dimensional profile \( \rho(x,y) \) of the time-averaged density distribution for a 1000s measurement of a modulated liquid phase. (b) Two dimensional pair correlation function \( g(x,y) \), the periodicity of the laser potential can easily be identified. (c) The pair correlation function along the laser lines exhibits only a local short range order. The length units perpendicular and along the potential lines are given in \( \mu m \).

Using the same experimental setup as in the first part of this chapter and doubling modulation of the laser potential, we detected more complex phase behavior with three different thermodynamic phases: the modulated liquid, the locked smectic and the locked floating solid [Bruno03d]. The experiments were all carried out at the same laser power and gradually changing the inter-particle interaction energy via the Debye screening length. The following results are presented in the order of increasing inter-particle energy.

8.2.1 Modulated liquid

For low interaction energies the system exhibits a liquid state in which the density is periodically modulated by the external laser potential. Fig. 8-3 (a) shows a plot of the system density distribution for a measurement of 1000 pictures, taking one picture each second. It can be seen that the particles are mainly located inside the potential troughs, but the distribution of the particles appears random [Baum03]. The two dimensional pair correlation function \( g(x,y) \) clearly demonstrates this lack of order. \( g(x,y) \) also shows a fairly large excluded area around the reference particle. In \( x \)-direction, i.e. perpendicular to the potential lines, the low interaction energy is still strong enough to prevent two particles from occupying two adjacent potential grooves. In the vicinity of the reference particle the density of the particles does not seem to be modulated by the laser potential only, but also shows a circular structure of rings of nearest and next-nearest neighbors. The \( g(x,y) \) of the modulated liquid appears as the convolution of radial symmetric structure of \( g(x,y) \) of an isotropic liquid, as shown in Fig. 8-1, with the periodic one-dimensional structure of the laser potential. The pair correlation function \( g(y) \) in the direction of the laser potential proves that only a short-ranged local order around the reference particle is present which decays on the length scale of a few mean particle distances. Analogous to the case of \( p = 1 \), we generally tried to fit an algebraic as well as an exponential function to the envelope of \( g(y) \) to determine which functional form is better suited. Since this decay only describes the long-range behavior of the correlation function, we the first two peaks were not considered in the fitting route. In the modulated liquid we found a clear exponential decay with a decay constant of around six mean particle distances.
8.2 Characterizing the phases for \( p = 2 \)

** Locked smectic phase **

The novel smectic phase distinguishes itself from the modulated liquid by different translational symmetry. Whereas the modulated liquid exhibits a discrete translational symmetry perpendicular to the laser potential of minimal displacement vector \( d \), this symmetry is reduced in the smectic phase to a value of \( 2d \). In Fig. 8-4 (a, b) this symmetry can be observed as the particles are confined to a subset of the laser lines, leaving every second trough empty. This alternating filling of the laser troughs is the result of a complex interplay of the inter-particle and particle substrate interaction. The system may be described as a self-assembled periodic stack of one dimensional liquids. This is the reason, why this phase has been named smectic; it displays a finite shear modulus only perpendicular to the laser lines [Radz01]. As in the case of the modulated liquid, the locked smectic phase exhibits only short-range density correlations, identifiable by the fast decay of \( g(y) \), Fig. 8-4 (c). The decay constant of the exponential fit to the envelope is approximately eleven mean particle distances. This means that the smectic phase possesses only liquid-like correlations between the particles along the troughs. This lack of correlation is presumed to cause the shear modulus to vanish along the laser lines [Radz01].

This smectic phase should not be confounded with the generic smectic phases found in liquid crystals. While smectic phases in liquid crystal may exist without an external potential, the smectic phase discussed here depends on the explicit symmetry breaking caused by the laser potential.

** 8.2.2 Locked floating solid **

In contrast to the modulated liquid and the locked smectic phase, the locked floating solid displays a well defined triangular arrangement of the particles, see Fig. 8-5 (a). As in the case of the locked smectic phase, every second potential trough is filled by particles. But now, due to the interaction between the particles, the periodic confinement of the particles perpendicular to the lines leads to an induced ordering also along the laser lines, assigning each particle to a lattice site, Fig. 8-5 (b). This order is quasi long-range, typical for two-
Fig. 8-5. (a) The density profile $\rho(x,y)$ of a two dimensional colloidal system in the solid phase displays a regular triangular structure. (b) The pair correlation $g(x,y)$ displays a long range order in the direction perpendicular to the laser lines and along the laser lines. The pair correlation $g(y)$ along the laser lines exhibits an algebraic decay. Units in $\mu m$, see also Fig. 3-1.

dimensional solids. The envelope of $g(y)$ is best described by an algebraic function. The fitting of an exponential decay to $g(y)$ yields an unreasonable decay length of over a hundred mean particle distances, Fig. 8-5 (c). The unusual name of this phase is due to the locking of the crystal in the direction perpendicular to its troughs on one side, which is the reason why it is called a locked solid. On the other side the one-dimensional symmetry of the potential allows the system to move freely along the potential lines, giving rise to the name floating solid.

8.3 Comparison with theory

Stimulated by the measurements of the light-induced freezing and melting of Wei et al. [Wei98], analytical calculations were performed by Frey [Frey99] and Radzihovsky [Radz01]. On the basis of the KTHNY theory of defect mediated melting and the renormalization approach they were able to predict the qualitative shape of the phase diagram of a 2D system subjected to a one-dimensional periodic substrate potential. Since this is also the same experimental scenario as in our measurements presented above, it is appropriate to compare our results with their findings. Before we do so, we should look at some of their results. The analytical calculations are based on the assumption that only nearest neighbor interactions play a dominant role. This is certainly a good approximation in the case of charged colloidal suspensions, especially if one considers the effect of the macro-ion screening discussed in chapter 5.3. For long reaching pair potentials or very large screening lengths, $\kappa a < 5.6$, the shapes of the following phase diagrams are expected to change considerably.

The phase that the colloidal system exhibits depends primarily on three parameters, the strength and periodicity of the external substrate potential and the commensurability ratio $p$. The relative orientation of the 2D crystal and the periodic substrate troughs are also important, as the orientation selects a set of Bragg planes of the colloidal system running parallel to the troughs, effectively influencing the commensurability ratio. At present we will only consider commensurate systems with $p = 1$ and $p = 2$. The predicted qualitative phase diagrams are shown in Fig. 8-6.
To compare these qualitative predictions with the experimental findings, it is necessary to establish a relationship between the melting temperature $T_m$ used in the theoretical works and the mean interaction strength $\kappa a$ used in the experiments. It turns out that the melting temperature $T_m$ is proportional to the elastic moduli, which in turn are proportional to the potential strength. For $\kappa a \gg 1$ Frey et al expected $T_m$ to display a dependence on the screening length as

$$T_m \propto (\kappa a)^2 e^{-\kappa a} \quad (8.2)$$

This means that $T_m$ is a monotonous function for large $\kappa a$, as is the case in these experiments. Transforming the theoretically predicted phase diagrams into the experimental parameters therefore leads only to a stretching of the diagram.

Before discussing the phase diagram, it is helpful to identify the different thermodynamic phases, as done in the previous experimental section. Even at low potential strengths the external laser potential leads to a spontaneous symmetry breaking. This symmetry breaking destroys the isotropy of the liquid phase and leads to a periodic density modulation. As a consequence the static structure function $S(q)$ displays Bragg peaks at integer multiples of the reciprocal lattice vector of the imposed one-dimensional periodic potential. The structure function $S(q)$ of a density modulated liquid, as predicted by [Radz01], is shown as an inset in Fig. 8-6 (a) for commensurability ratio $p = 1$ and in Fig. 8-6 (b) for $p = 2$. The corresponding $S(q)$ of the experiment are shown in Fig. 8-7 (a, c) and Fig. 8-8 (a), respectively. For the case $p = 2$ only half the peaks of the $p = 1$ scenario are present, as the reciprocal lattice vector $q_{\text{rec}} = 2\pi / d$ has twice the length.

![Fig. 8-6](image-url)

**Fig. 8-6.** (a) Schematic phase diagram with commensurability ratio $p = 1$. $T_h$ indicates the transition temperature from the hexatic to the isotropic liquid phase for vanishing external potential (b) Phase diagram for $p = 2$, thin lines suggest a continuous transition, the thick line between solid and liquid is expected to be of first order. (Insets) Schematic structure functions of the different phases, crosses indicate Bragg peaks, while shaded circles indicate algebraic peaks. Plots taken from [Radz01].
Fig. 8-7. Static structure function \( S(q) \) of the experimental data presented in chapter 8.1. The axis are in units of \( q = 2\pi/r \); The central intense color represents values larger than 50%, the surrounding dark color values larger than 10% and white area values smaller than 10% of the maximum value. (a) For the modulated liquid at low potential strengths, (b) the crystalline phase at an intermediate potential and (c) the recurring modulated liquid at high potential strengths. The peaks on the central axis correspond to the expected Bragg peak of Fig. 8-6, while the off-axis spots may be identified as spontaneously induced algebraic peaks.

For \( p = 2 \) an intermediate smectic phase arises between the modulated liquid and the solid, see Fig. 8-6 (b) and Fig. 8-8 (b). The symmetry of the smectic phase is reduced to a value of \( 2d \), as mentioned above. Therefore structure factor of the smectic shows spontaneously induced Bragg peaks at \( q = 2\pi/2d \) in addition to the Bragg peaks at \( q = 2\pi/d \) induced by the laser potential. Thus the symmetry of the smectic phase for \( p = 2 \) resembles the symmetry of the modulated liquid for \( p = 1 \). This leads an almost identical appearance of \( S(q) \). The small off-axis peaks represent the correlations between adjacent particles of different laser lines.

The structure function of the crystalline state, the locked floating solid is quite unusual and Fig. 8-6 (inset), Fig. 8-7 (b) and Fig. 8-8 (c). According to [Radz01] the locked floating solid displays a set of delta-function Bragg peaks at multiples of the reciprocal lattice vector of the laser potential. Besides these explicitly induced Bragg peaks there are other spontaneously induced Bragg and quasi-Bragg peaks.

Fig. 8-8, Static structure function of the experimental data presented in chapter 8.2 (a) for the modulated liquid at low pair interaction energy, (b) the locked smectic phase at intermediate interaction and (c) the locked floating solid at high pair interaction energies. The theoretically expected \( S(q) \) of Fig. 8-6 (b) agree well with the experimental findings. See also Fig. 8-7.
8.4 Light-induced freezing and melting

Until now we have only considered the phase behavior of the $p = 1$ system as a function of the strength $V_0$ of the substrate potential at constant density and constant inter-particle potential, which is basically equivalent to a constant screening length. In the next step we also varied the particle density and were thus able to measure step-by-step the phase diagram. Particular attention was paid to the fact that the periodicity $d$ of the laser potential was properly adjusted to obtain a commensurable hexagonal crystal, following the density dependence of $d$ of eq. (8.1). A distorted lattice would otherwise be the result. On the horizontal axis of the phase diagram in Fig. 8-9 the strength $V_0$ of the laser potential is plotted in units of the thermal energy $k_B T$. The vertical axis is in units of $\kappa a$ with $a$ being the mean distance between neighboring particles. $\kappa a$ can be regarded to be proportional to the strength of the inter-particle potential at distance $a$. As can be seen, the value of $\kappa a$, where the transition to the crystalline phase occurs, decreases as a function of $V_0$ at small laser intensities. For larger values of $V_0$, however, the separation line between the crystal and the liquid region is shifted back to higher $\kappa a$ values and starts to saturate. It is this up bending that gives rise to the re-entrant melting phenomenon. If $\kappa a$ is in the range between 20 and 22 one observes with increasing $V_0$, the following sequence of phases: isotropic liquid – modulated liquid – crystal – modulated liquid. This way of crossing the phase diagram, used for the measurements for the commensurability ratio $p = 1$ in chapter 8.1, is illustrated in Fig. 8-9 by the horizontal arrow.

The qualitative shape of the phase diagram agrees well with the predictions of Frey, shown in Fig. 8-6 (a). Towards stronger potential strengths $V_0$, the phase boundary increases monotonically towards larger values of $\kappa a$. After reaching a maximum the phase boundary decreases and approaches a constant limit $\kappa a(V_0 = \infty)$ for high laser strengths. In both diagrams, this limiting value for high potential strengths is considerably higher than the phase boundary for $\kappa a(V_0 = 0)$. The relationship between these two values is predicted to have the ratio

$$\kappa a(0) - \kappa a(\infty) \approx 2 \ln \left( \frac{1.3 \kappa a(\infty)}{\kappa a(0)} \right) > 0$$

In agreement with theory, the experimental phase diagram obeys the relation $\kappa a(0) - \kappa a(\infty) > 0$. The numerical value is deviates by a factor of 4. This discrepancy may be caused by the finite size of the experimental system and because the theory neglects any finite renormalization of the elastic constants.

The re-entrant phase transition has also been studied in computer simulations. While earlier Monte Carlo studies from the same laboratory arrived at contrary results [Chak95, Das98]. Recent simulations conclusively verified the re-entrant phase behavior and the phase diagram for hard disk [Stre01] and Yukawa systems [Stre02]. This suggests that light-induced freezing and melting is a generic effect present in many systems, applicable to a broad set of inter-particle interactions.
8. Colloidal monolayers on a one-dimensional

Fig. 8-9. Experimentally determined phase diagram. The open symbols denote the modulated liquid and the closed symbols denote the crystalline phase. For clarity, error bars are plotted only for a few data points.

8.5 Effect of fluctuations

Colloidal monolayers on one-dimensional periodic substrate potentials are a powerful system for studying the importance of thermal fluctuations on the phase behavior. Although one-dimensional substrates are quite rare in nature, from a theoretical point of view they have two major advantages. First of all, the expectation values of the particle positions on the potential lines are independent of the size of the positional fluctuations. Increasing the strength $V_0$ of the substrate potential will only lead to a stronger confinement of the particles, reducing the positional fluctuations, but for all non-vanishing strengths $V_0$ and commensurate densities the average position of the particles will always be in the minima of the substrate potential. This is not the case for the trimer system on a triangular substrate which will be presented in chapter 9.2. Secondly, on a one-dimensional periodic substrate the strengths of the fluctuations in $x$ and $y$-direction are not coupled as in the case of triangular or quadratic substrates. The strength of the fluctuations in the $x$-direction, perpendicular to the laser lines may be controlled by the potential strength, without directly influencing the behavior of the particles in the $y$-direction.

To explain the mechanism of the light induced freezing and melting, it is important to note that the fluctuation of a particle around its average position may enhance the range of its inter-particle interaction. This will now be explained in detail. Even at low potential strengths the particles sense the presence of the laser potential, resulting in a density modulation of the otherwise isotropic liquid. This behavior is easy to understand if one takes into account the free energy of the system, usually consisting of the inter-particle interaction energy $U$ and the entropy $S$ times the temperature $T$, is now additionally dependent on a term $V$, which considers the energetic contribution of the laser potential.

\[
F = U_{\text{pair}} + V - TS
\]
For low laser strengths large particle fluctuations away from the laser line make only a minor contribution to $F$, while leading to a large increase in $S$. Therefore at low laser strengths the free energy favors large particle fluctuation, resulting in an unordered state of the system. For intermediate laser strengths, $V$ becomes relevant. The energetic costs of large particle fluctuation increases and finally balances with $TS$. This leads to a broad confinement of the particles to the laser lines. Now the pair interaction $U$ energy comes into play. Because the particles are trapped inside the laser troughs, the possible arrangement of the particles is limited by two extremes: the triangular and the quadratic crystal and of course all the possible configurations between these extremes. The triangular ordering is energetically highly favored, although there are also other particle arrangements present to satisfy entropy. For a certain strength of $U$ this will be the dominant contribution to the free energy. Therefore the confinement of the particles to the laser lines induces via $U$ an ordering along the lines. This induced order leads to freezing; the system enters the solid phase. One may say that the external laser potential $V$ shifts the break-even point between the entropy dominated liquid phase and the energetically favorite solid towards lower values of $U$. This therefore allows for a freezing transition at lower particle densities than the critical density of spontaneous crystallization.

Another way of looking at this laser induced freezing is to consider the Lindemann phase criterion [Lind10]; the criterion has been adapted for two dimensional systems by Bedanov and Dadgyak [Beda85]. The Lindemann criterion in its original form for three dimensional system states that a crystal is expected to melt if the mean thermal fluctuations, e.g. the root mean square displacements are larger than 19% of the mean particle distance. Analogously reducing the particle fluctuations in the liquid phase, i.e. by an external laser potential, may then lead to crystallization. Such a behavior can generally be anticipated.

The surprising fact is that the laser induced crystal melts again upon further increase of the potential strength. This re-entrant melting seems to violate the Lindemann criterion. As described in chapter 8.1 and shown in Fig. 8-1, increasing the potential strength leads to an even better localization of the particles in the laser troughs and also to a decoupling of particles of adjacent laser lines. At first glance it seems that amplifying the laser potential leads to a reduced interaction between particles of adjacent laser lines. This interpretation is indeed correct. Calculating the expectation value of the inter-particle energy $W$ of the system, with $W_{nt} = V(d,V_0,x) + W(d,V_0,x)$ being the total energy of the system, one observes, that this mean inter-particle interaction decreases as the laser potential $V$ is increased.

$$
\langle W(d,V_0) \rangle = \int d\tilde{x} \ W(d,V_0,x) \ \exp \left[ -\frac{W_{nt}(d,V_0,x)}{k_BT} \right]
$$

We tried to numerically model the experimental situation with a one dimensional system of particles at constant density with mean inter-particle distance $a$ inside a sine-like external potential with commensurate periodicity $d = a$. The particle fluctuations were modeled as Gaussian distributed around their equilibrium position [Brun00]. Only nearest neighbor interaction energies were taken into account. This approximation is well justified, as
the Yukawa potential decays rapidly. The result of $\langle W \rangle$ as a function of the potential strength $V_0$ is plotted in Fig. 8-10. Allowing particle fluctuations in the system may lead up to a 30% increase in the interaction between particles of adjacent laser troughs from its static value $V_0 \to \infty$ of $\langle W \rangle = 0.823 \, k_B T$. Thus fluctuations amplify the strength of the inter-particle interaction. This result is highly dependent on the nature of the pair potential and is only valid for potentials of short range, such as the Yukawa potential.

The process of re-entrant melting may now be explained in the following way. At high laser potential strengths, the positional fluctuation perpendicular to the laser lines decreases considerably, resulting in a weaker coupling between particles of adjacent laser lines. As the strength of the thermal fluctuations along the laser line stays constant, the reduced inter-particle interaction causes the crystal to melt again.

**8.6 Conclusion and Outlook**

We investigated the phase behavior of a two-dimensional suspension of charge stabilized polystyrene spheres in the presence of a one-dimensional periodic light field. We focused on measurements, in which the particle density was commensurate with the periodicity of the laser potential. First the commensurability ratio was chosen to be $p = 1$. In compliance with earlier experiments, a liquid-solid followed by a solid-liquid transition was observed when the light intensity of the laser potential was increased. These transitions are known as laser-induced freezing and melting. We then switched to the case of a higher periodicity of the laser potential, $p = 2$, in which particles of the crystalline state only occupy every second laser line. In addition to the known crystalline and modulated liquid phase a new smectic was observed.

The different phases were characterized using the pair correlation function $g(r)$ and the structure function $S(q)$ and compared to theoretical results and the theoretically predicted phase diagram was presented. By varying both the mean particle distance in addition to the strength of the laser potential, we obtained the phase diagram for $p = 1$. This phase diagram
agrees well with the qualitative predictions of Frey as well as with recent numerical studies by Strepp, which both exhibit the re-entrant melting. To explain this re-entrant effect, we show by a simple calculation that thermal fluctuations may enhance the strength of the pair interaction between particles of adjacent laser lines.

So far, we have only investigated the influence of periodic, one dimensional potentials on the phase behavior of colloidal particles. By interfering more than two laser beams, however, we can also produce two dimensional potentials of hexagonal, quadratic or rhombic geometry which would then mimic a more realistic surface potential.
9 Colloidal monolayers on triangular substrate potentials

In this chapter we investigate colloidal monolayers interacting with a light potential of triangular symmetry. We adjusted the particle density by means of a computer-controlled scanned laser tweezers to certain values of the commensurability ratio $p$. For two dimensional substrates $p$ is defined as the ratio of the number density of the colloidal particles to the density of potential troughs. Equivalently $p$ can also be interpreted as the average number of colloidal particles found per substrate minimum. We concentrate on the case of trimers, i.e. $p = 3$. Trimers may exhibit an additional internal degree of rotational freedom. This leads to a distinct phase behavior, different from homogeneous systems or those on one-dimensional substrate potentials. Upon increasing the strength $V_0$ of the laser potential a crystalline assembly of trimers with high positional and orientational order arises. Surprisingly, further enhancement of $V_0$ leads to a loss of orientational order, similar to the re-entrant melting, presented in the previous chapter. The angular correlation function and the dynamic properties of this phase sequence are analyzed in detail. The cases of commensurability ratio $p = 2$ and $p = 4$ are also briefly discussed and compared to the ground-states determined by numerical simulations.

9.1 Commensurate two dimensional crystals

The experimental setup used in chapter 8 for the measurement of the light induced freezing and melting was also used in this experiment. We again used a suspension of highly charged polystyrene particles of diameter $\sigma = 3 \mu m$. For experimental details on the sample cell and the suspension used, see chapter 8.1. By adding a third laser beam to the interference pattern, it was possible to create a laser potential with triangular symmetry. A snapshot of the laser potential is shown in Fig. 9-1. This corresponds to a (111) surface in an atomic system. The triangular symmetry of the substrate potential matches the inherent geometry of the 2D crystal, which is also triangular. It is thus expected that the laser potential can lead to laser induced freezing of the colloidal monolayer over a wide range of densities.

Having realized for the first time a colloidal system on a realistic two-dimensional surface geometry, we may investigate a huge variety of interesting effects, most of which have also been observed in atomic systems. Therefore it is now certainly justified to regard colloidal monolayers as a powerful model for atomic systems. For a systematic study of the phase behavior, two distinct methods come into consideration. The first one is to vary the particle density independently of the periodicity of the laser potential. In this scenario incommensurability transitions may be studied. These transitions are quite common in atomic systems, as either the density or the spacing of the atoms is incommensurate with the substrate potential. In two-dimensional colloidal suspensions, some initial observations of characteristic solitons structures have already been made in our workgroup at particle densities incommensurate with the substrate geometry.
9. Colloidal monolayers on triangular substrate

Fig. 9-1 (a) Image of the triangular laser lattice, created by three interfering laser beams (b) Snapshot of the colloidal system at high laser intensity. The position of the laser minima is sketched as circles. The trimers, loosely bond by the surface potential can be identified.

In the following section we exploit the advantages of colloidal suspension, as we are able to precisely adjust the particle density. We chose to work with accurate commensurate particle densities, where the commensurability ratio \( p \) takes integer values. Under these conditions the direct influence of the substrate potential can be easily identified, and sharp transitions are expected. For a dense colloidal fluid with commensurability ratio \( p = 1 \), we indeed observed that the presence of the substrate at potential strengths as low as \( V_0 = 0.1k_BT \) was sufficient to force the system to crystallize. As the case \( p = 1 \) does not promise any intriguing phase behavior, we focus on higher particle densities with \( p > 1 \).

In the following experiment, we adjusted the particle density by means of the scanned laser tweezers to be \( p = 3 \) times the density of the substrate minima. Fig. 9-1 (b) presents a snapshot of the colloidal monolayer for \( p = 3 \) subjected to the laser lattice shown in Fig. 9-1 (a) at high laser intensity. It can be observed that three colloidal particles, a trimer, are “bond” together inside a potential minimum. These loosely bond aggregates are also called colloidal molecules [Reic02]. This commensurability ratio promises an interesting phase behavior, as each trimer possesses an additional internal degree of freedom.

9.2 Trimers

In order to study the effect of the substrate potential depth on the structure of the colloidal system, we varied the laser intensity and determined the spatially resolved average particle density \( \rho(x,y) \) in a central region of the interference pattern. In addition, we also calculated the averaged local particle density in a substrate potential well \( \rho_{LS} \). Both quantities are plotted for five different potential strengths, as in the left and right column of Fig. 9-2, respectively. During the experiments the particle density was adjusted to about 5% below the critical density required for spontaneous crystallization. Accordingly, the system is in a liquid state when no 2D light lattice is applied, as shown in Fig. 9-2 (a), (b).
Fig. 9-2. The horizontal axis is the $x$-direction, the vertical axis the $y$-direction, all units shown are in $\mu m$. Brighter colors represent higher values of the (Left column) lateral density distribution $\rho(x,y)$ and the (Right column) averaged local density $\rho_{LS}$ within a potential well.
When the laser field is turned on, however, considerable changes in the structure of the 2D colloidal system are observed. Figs.2c-h show contour plots of $\rho(x,y)$ and $\rho_{LS}$ for three different laser intensities, corresponding to substrate potentials $V_0$ of 40 $k_BT$, 60 $k_BT$ and 110 $k_BT$, respectively. The values of the potential strength might seem quite large on first sight, but one has to remember that the particles inside the potential well repel each other, leading to an internal pressure in the trimer. To obtain sufficient statistical data, we analyzed more than 1000 pictures with 1s time interval each, see also [Brun02a, Brun03a].

At $V_0 = 20k_BT$, Fig. 9-2 (c), (d), the particles begin to interact with the substrate potential. At this low substrate strength, however, most of the particles are able to surmount the barriers between the substrate potential wells and only a few particles become trapped in confined regions. Accordingly, the corresponding plot of $\rho_{local}$ shows a relatively broad particle distribution with a slight maximum between 5$\mu m$ and 10$\mu m$, but the distribution is almost isotropic.

At a moderate strength of $V_0 = 40k_BT$ the density distribution is no longer homogeneous Fig. 9-2 (e). The development of small ordered regions can be observed, but the inter-well diffusion seems to be still too large to allow for a long-ranged positional order. The $\rho_{LS}$ Fig. 9-2 (f) shows the emergence of three distinct lattice sites on a broad background. Upon increasing the substrate strength the localization of particles increases and at $V_0 = 60k_BT$ essentially all of the potential wells are occupied with trimers Fig. 9-2 (g). Due to the interplay of the repulsive inter-particle forces and the triangular geometry of the laser potential in principle only one orientation of the trimers is energetically favorable. As is seen in Fig. 9-2 (h), these trimers indeed possess a very high degree of orientational order. It has been confirmed by numerical simulations [Reic02] that a crystalline phase with both positional and orientational order is indeed the energetic ground state. The results of their simulations are presented in chapter 9.4. In addition to the three most pronounced spots which indicate the main orientation of the trimers, Fig. 9-2 (h) shows another three weak spots which correspond to defects, which can also be identified in $\rho(x,y)$, Fig. 9-2 (g), where the orientation of trimers is rotated by 60 degrees. These two orientations correspond to the twofold degenerate ground state of the system. When crystallization starts, we initially observe small regions, Fig. 9-2 (e), with both trimer orientations until finally a region of one orientation grows at the expense of the others Fig. 9-2 (g). In some experiments we also found stable grain boundaries between crystallites having different trimer orientation. This suggests that the orientational freezing is of first order.

When the substrate strength is further increased to 110$k_BT$, the centers of the trimers become more localized at the lattice sites of the interference pattern. In contrast to the enhanced positional order, however, the orientational order of the trimers becomes much weaker as is seen from the ring-shaped density distribution in Fig. 9-2 (i). This is supported by Fig. 9-2 (k) which shows that the orientation of the trimers is more diffuse in angular directions. These results clearly demonstrate that increasing the depth of the potential wells leads to a loss of orientational order between the trimers.
9.3 Melting of the colloidal molecular crystal

The orientational melting can be analyzed in a quantitative way by calculating the order parameter for orientational order of the trimers

$$\psi_k = \exp[i 3 \Theta_k]$$  \hspace{1cm} (9.1)

$\Theta_k$ is the orientation of the vector between a particle and the center of the corresponding substrate potential well with respect to some fixed reference axis. Similar to the bond orientational correlation function in isotropic 2D systems [Nels83], here we define the orientational correlation function of the trimers

$$g_3(r_{kl}) = \text{Re} \left\{ \langle \psi^*_k \psi^*_l \rangle \right\}$$  \hspace{1cm} (9.2)

with the brackets representing the summation over all particles forming the trimers. With this definition a perfect orientational order of the trimers corresponds to $g_3(r) = 1$ while perfect anti-correlation yields $g_3(r) = -1$, [Brun02a]. For $V_0 = 40k_B T$ the orientational correlation between the trimers is short ranged and decays almost to zero after 25$\mu$m, corresponding to about two lattice periods, reflecting total loss of orientational order. At $V_0 = 60k_B T$ the decay of $g_3(r)$ occurs on much longer length scales and even after 10 lattice periods $g_3(r)$ corresponds to about 25% of its initial value Fig. 9-3 (b). At the highest substrate strength, $V_0=110k_B T$, the decay is faster again, Fig. 9-3 (c). This is in agreement with the orientational re-melting of the trimers as observed in Fig. 9-2 (i, k).

![Fig. 9-3](image-url)

**Fig. 9-3** The orientation correlation function $g_3(r_{kl})$ of the two dimensional colloidal system as defined by (9.2) is plotted as symbols. As mentioned in the text, only for intermediate potential strengths a long-ranged orientational ordering is found. The solid line is an algebraic fit to the data. For the values of the algebraic exponent $\eta$, see also Fig. 9-4.
Fig. 9-4. The exponent $\eta$ of an algebraic fit to the orientation correlation function shown in Fig. 9-3 plotted as a function of the potential strength $V_0$. The ordered phase is found in the region between $V_0 = 40k_BT$ and $V_0 = 100k_BT$, where $\eta$ is found to be around one or smaller.

To understand why the coupling between the trimers is lost at high potential strengths, one has to consider two mechanisms of similar importance: On the one hand, a stronger substrate potential increases the radial pressure on the trimers and therefore reduces their mean extent. This results in larger distances between particles of different trimers. Due to the exponential distance dependence of the DLVO potential, see chapter 3.5.2, this leads to a reduction of the trimer interaction when $V_0$ is increased. On the other hand, the colloidal particles are subjected to thermal fluctuations which amount in the crystalline phase to about 50% of the inter-particle distance. The radial fluctuations of the particles inside the trimers contribute to their interaction strength. This becomes most important in the crystalline phase where these fluctuations lead to an angular registration between trimers, i.e. to long range orientational order. When $V_0$ is increased, both the lateral fluctuations and the mean lateral extent of the trimers decrease, which reduces the coupling between adjacent trimers and thus leads to orientational melting. The second mechanism is in principle the same as the fluctuation stabilized crystalline phase, presented in chapter 8.5, in the case of a one-dimensional periodic substrate. In contrast to those experiments, the behavior of the trimers is more complex as the mean radial extent of the trimers and strength of their radial fluctuations are coupled and cannot be changed independently from each other.

The relationship between radial and angular fluctuations can be estimated from the orientational correlation function at distance zero, i.e. $g_3(0)$ which corresponds to the self-correlation of the trimers. The deviation of $g_3(0)$ from 1 characterizes to what extent thermal fluctuations cause an angular deviation of the trimers from an ideal equilateral triangle. As is seen in Fig. 9-3 (b, c), $g_3(0)$ at $60k_BT$ exceeds the corresponding value at $110k_BT$ by about 20%.
This means that although the localization of trimers inside the potential wells increases at higher substrate strength, a stronger deviation in the angular shape of the trimers occurs. This strongly supports the hypothesis mentioned above that the reduction of the radial fluctuation leads to an increase in the angular fluctuation in trimers.

To be able to compare the decay of the orientation correlation function of the different phases quantitatively, we tried to analyze the decay by fitting a simple algebraic function \( g_3(r) \propto (r - b)^{-\alpha} \). Whether the true functional behavior is indeed algebraic or rather exponential has to be clarified by a thorough theoretical analysis of the melting scenario. This phenomenon is currently being investigated by E. Frey et al [Frey03]. But for now the algebraic fit seems to be an adequate description, as can be seen in Fig. 9-3. As a straightforward generalization of the KTHNY theory, presented in 3.3, it is expected that the ordered crystalline phase is characterized by an exponent \( \alpha < 1 \). Fig. 9-4 shows the exponent of the algebraic fit to the correlation function \( g_3(r) \) for a wide range of potential strengths \( V_0 \).

At low densities, we find \( \alpha > 1 \). With the onset of the ordered phase at around \( V_0 = 40k_BT \) \( \eta \) drops below one and stays at a value of \( \eta = 0.5 \) well within the crystalline phase. At even higher laser intensities \( \eta \) rises monotonically. Close to the orientational melting at around \( V_0 = 100k_BT \) the exponent becomes larger \( \alpha > 1 \) again.

As the last step in data evaluation of the trimer system, we calculated the mean square displacement (MSD) of the particles, to analyze the influence of the fluctuations. The specific geometry of the system suggests calculating the MSD in radial and angular coordinates respective to the center of each potential minimum, in order to successfully describe the orientational diffusion of the melting towards higher \( V_0 \). The results are shown in Fig. 9-5. The freezing transition towards the colloidal molecular crystal results in a dramatic decrease of the angular MSD. Throughout the crystalline phase the angular diffusion vanishes, but increases again monotonically towards higher \( V_0 \). The radial MSD decreases rapidly at low \( V_0 \) also. This indicates that in the crystalline phase the radial confinement of the particles is only
partially due to the surface potential, and that pair interaction with the particles of the adjacent potential well might play an important role in limiting the radial diffusion. As the orientational order decreases at around $V_0 = 80k_BT$, this additional confinement breaks down, see also the decay of the orientational correlation function in Fig. 9-4. This consequently leads to a small increase of the radial MSD, shown in Fig. 9-5 at $V_0 = 80k_BT$. We have to admit that this effect lies almost within the error range of the experimental resolution. Further statements about the importance of the radial and angular fluctuations seem to be inappropriate at the present state of research due to the large experimental error bars.

### 9.4 Comparison to Simulation

At the time we finished the measurements on the trimer system on a triangular lattice, C. Reichhardt et al. published [Reic02] their results on Langevin dynamics simulation of two dimensional systems, subjected to triangular and also quadratic substrate potentials. They determined the ground state configuration at $T = 0k_BT$ for four different commensurability ratios, $p = 1, 2, 3$ and $4$, by starting in the unordered high temperature phase and gradually cooling down the system. The particles were assumed to be point-like and to repel each other by a Yukawa interaction potential. C. Reichhardt et al set the screening constant $\kappa^{-1}$ to be half the period of the substrate potential. Transferring this value onto our experimental scale, this would correspond to $\kappa^{-1} = 5\mu m$, which is ten times larger than the largest screening length we achieved in our experiment.

The results for the ground state are shown in Fig. 9-6. The monomer case, in which every potential well is occupied by a single particle, is shown in Fig. 9-6 (a), the oriented dimer state in (b). The trimer scenario, which we also investigated in our experiments in the previous chapter, is presented in Fig. 9-6 (c). Although our experiments have all been performed at finite temperature, comparing our experimental findings with these numerical results reassured us that the colloidal trimer crystal we found is indeed the energetic ground state. The commensurability ratio $p = 4$ leads to the diamond shaped quadrumer with four particles occupying a single potential well, Fig. 9-6 (d).

### 9.5 Dimers & Quadrumeres

Inspired by these numerical simulations, we set out to confirm the predicted dimer and quadrumer ground state experimentally. Therefore we changed the density of the colloidal system by means of the scanned laser tweezers up to a commensurability ratio of $p = 2$ and $p = 4$. Although the preparation of these ordered states do not seem to be much different than for $p = 3$, they are much harder to realize experimentally in a system of charge-stabilized colloids [blei03]. The monomer case matches the inherent triangular structure of a spontaneously formed crystal.
In this case, minimizing the inter-particle energy and the particle-substrate interaction leads to the same configuration of particles. The timer case represents only a minor distortion of the hexagonal particle arrangement and therefore crystallization may readily be achieved. On the other hand, for the dimer and quadrumer case the hexagonal order is heavily distorted. The particles inside each potential well are pushed closely together, increasing the distances between particles of adjacent wells are increased.

This leads to very inhomogeneous distribution of inter-particle distances. As the pair potential of charged stabilized particles decays faster than exponentially, this has two consequences. On one side a very high potential energy is necessary to confine the particles inside the laser wells and therefore minor inhomogeneities of the laser potential may lead to a local arbitrary orientation of the particles. On the other side the interaction between particles of different wells almost vanishes, due to the large inter-particle distance. This has the consequence that the contribution of the coupling between particles of adjacent wells makes only a minimal contribution to the free energy and is thus easily overruled by the gain of entropy of an arbitrary particle orientation. It is thus almost impossible to create samples with a long-range order. In the following we will present some selected examples, where collective behavior of the system has been observed.
Fig. 9-7 shows snapshots of (a) a colloidal monolayer on a triangular surface potential with two individual particles occupying each potential well, (b) with a tightly bond dimer on each lattice site and (c) tightly bond dimers on a rectangular substrate. The black bars correspond to a length of 10µm.

The dimers scenario has proven to be the most difficult. Therefore we will only present some snapshots at this stage to give an overview over the experimentally realizable arrangements. Fig. 9-7 (a) shows a colloidal monolayer on a triangular surface potential, with two particles occupying each potential well. This configuration is stable over a long time, yet the orientation of the dimers generally does not agree with the orientation of the ground-state calculated by [Reic02]. The same experiment has been repeated, Fig. 9-7 (b), using coherent dimers instead of two individual particles. This allowed us to reduce the periodicity of the laser potential. No pronounced changes in the behavior were observed. The lack of orientational order for these two cases can be explained by low coupling interaction between the dimers. As pointed out above, in such a case entropy is always the dominant contribution to of the free energy. We believe that the ordered dimers state is observed in the computer simulations by [Reic02], because an unphysical large screening length was chosen.

Finally Fig. 9-7 (c) shows coherent dimers on a rectangular laser lattice. As the potential is quite strong the dimers are pinned to the laser spots. A translational motion of the dimers is suppressed. The spacing of the particles within the rows is much closer than along the columns. Therefore the different rows do not interact significantly and are thus decoupled. The system can be regarded as a stacking of quasi one-dimensional rows, only interacting with dimers of the same row. As the interaction energy between adjacent dimers is chosen to be large enough, an aligned system may be observed.

To fit four particles inside one potential well, the periodicity \( d \) of the laser potential had to be slightly increased. Increasing the periodicity \( d \) of the substrate potential is not a good option, as this also increases distance between the particles of adjacent potential well, hereby de-coupling the quadrumers. On the other hand forcing four particles into one potential well dramatically increases the pressure between the colloids inside each potential well. This has two severe experimental consequences. As explained for the trimer case, the effective confining strength of the substrate potential on one particle is given be the potential strength \( V_0 \) minus the repulsive potential created by the other three particles inside the well. To achieve even medium effective potential strengths, a very high laser power is necessary, approaching the experimental limits of our setup.
Fig. 9-8. shows the density distribution of a colloidal molecular crystal of quadrumers on a triangular laser potential at high potential strength $V_0 = 180k_BT$, averaged over a measurement of 1000s. The white area represents regions of vanishing particle density, a darker shade of gray represents an increasing density.

The second effect of the internal pressure of the quadrumers is that even at high laser powers it has been repeatedly observed that particles jump out of the sample plane of the monolayer and from a partial second colloidal layer on top. To be able to keep the particles inside the plane even at low potential strengths additional confinement such as a very fine sample cell is needed. Nevertheless we managed to make some first measurements; one of which is presented in Fig. 9-8. The formation of quadrumers can easily be identified. But unlike the results of the numerical simulation the orientation of the quadrumers is not centered around the $y$-direction, (up-direction on this page), but tilted sideways. We carefully checked that the potential wells have an almost circular shape, but a small generic hexagonal contribution in the interference pattern cannot be ruled out. We do not believe though, that the tilted particle arrangement can be completely explained by this minor anisotropy in the laser potential.

While the experimental results at densities, where three particles are inside a potential well, agree nicely with the numerical simulations presented by Reichhardt [Reic02] for zero temperature, pronounced deviations may be observed at those densities, at which two or four particles occupy one potential well. This raises the question of whether a numerically determined ground state of the colloidal system for zero temperature, neglecting entropy and thermal fluctuations, is appropriate to describe the experimentally observed structures. Thus numerical simulations and colloidal experiments together lead to a complementing association. The trajectory in configurational space acquired in colloidal experiments is otherwise only accessible through computer simulations. In this sense measurements of colloidal suspensions may also be perceived as real-time simulations at finite temperature.
9.6 Conclusion

We have studied the phase behavior of a charged-stabilized two dimensional suspension subjected to a triangular substrate potential. The particle density was adjusted by computer controlled scanned optical tweezers. We focused on a commensurate density with three times as many particles as potential wells. Upon gradually increasing the substrate potential the colloidal particles first become localized as trimers inside the potential well. At intermediate potential values the system exhibits a long-range orientational and positional order. Towards higher potential strengths the orientational order is lost, leaving the trimers to rotate in the potential well. While for the trimer case good agreement is found between the experimental observations and the results of numerical simulations, in the case of two or four particle per potential well, large discrepancies in the arrangement of the particles can be seen. This is most likely due to the fact that in the simulation a different parameter for the screening lengths than in the experiment was used.
Outlook

In this work we presented a new way of controlling the particle density of a colloidal monolayer. With the help of scanned laser tweezers we constructed a boundary box for the particles inside the sample area, which is impenetrable for particles yet easy to adjust in size. This allowed us to make new measurements at systematically varied densities, while always keeping the same set of particles and the same bulk ionic concentration. This setup opens up many new possibilities in colloidal science. So far we have focused our attention mainly on the static properties of a liquid monolayer at particle densities below the threshold of spontaneous crystallization. It seems worthwhile to extend these studies to higher densities well within the crystalline range and also to include dynamical quantities.

Apart from these general considerations on further experiments of colloidal monolayers on homogeneous substrates, there are also questions which arise as a direct consequence of the experiments presented in the first part of this work. We have shown that the effective pair potential in a many particle system shows a cut-off at higher particle densities. For this effect we gave a qualitative explanation in terms of macro-ion screening. The next step is to pursue a quantitative analysis of this effect in terms of many-body potentials. So far, the three-body potential is known for certain configurations. It is experimentally not feasible to measure complete three-body potential matrix, apart from focusing on certain prominent geometries and determining the potential value of the intermediate configurations by numerical PB calculations. The next step is to determine the four-body term, which is expected to be much smaller. It is not clear yet, if these many-body terms are always attractive or whether they change sign, forming an alternating row in which some contributions might cancel out. If at least the three- and four-body terms are known, it might be possible to calculate the effective pair potential by integrating over the positions of all but two particles. Finding now agreement between the effective pair interactions determined via the many-body terms and directly via the many particle experiment would be a proof of the consistency of our measurements. This project might seem currently impractical, but first measurements on the four-body potential have already been performed.

In the second part of this work we presented for the first time measurements of colloidal monolayers subjected to a realistic two-dimensional substrate potential. Since the surface potential depth can be continuously varied by the laser intensity, investigations on colloidal model systems might help in understanding the details of the phase behavior of atomic adsorbates on crystalline substrates.

In the case of two-dimensional substrate geometries an interesting scenario is expected for colloids on a square potential for a commensurate density with commensurability ratio $p = 1$. The particle density chosen should be high enough so that the monolayer behaves like a dense liquid or even crystallizes in the absence of the external potential. Then for weak potentials, the substrate can be regarded as a perturbation, which causes only a small density modulation. As the inter-particle interaction dominates, the particles are expected to exhibit a
local triangular order, inherent in two-dimensional systems. On the other hand, for strong 
substrate potentials the quadratic geometry will be enforced on the particle arrangement. 
Therefore at intermediate potential strengths, with the inter-particle and particle substrate 
interaction being of the same magnitude, we expect to see interesting geometric transitions 
between triangular and quadratic order.

Also time-dependent substrate potentials can be investigated. By rapidly turning on the 
laser potential the situation of quenching condensation of an atomic gas on a very cold 
substrate can be modeled. In this process the topological defects are frozen.

The realization of triangular and quadratic substrate geometries opens the possibility 
to address in principle all issues of surface science. It should be possible to go through any 
standard text book on atomic monolayers on crystalline surfaces and apply our experimental 
strategy to any appealing topic, such as commensurate-incommensurate transitions, defect 
diffusion, solitons structures and thermodynamics of incommensurate crystals. It is certain 
that through the real-space data available in colloidal experiments, which can then be 
compared with theoretical predictions and atomic measurements, new insights can be won.
In this work the thermal equilibrium properties of a two-dimensional colloidal system are characterized. The colloidal particles in an aqueous suspension are confined inside an optically flat sample cell, where they form a monolayer structure on the bottom glass plate of the sample cell. Since the out-of-plane fluctuations of the particles are by several orders of magnitude smaller than their in-plane motion, the system may be described as two-dimensional.

We observed the movement of the particles using digital video microscopy. This approach has the advantage that it enables us to determine the trajectories of a many-body system in configurational space. This information allows us to use the methods of statistical mechanics in an inverted way. In most experiments, especially in systems, only averaged quantities such as pressure and structure factor, integrated over the configurational space trajectory are available. On the other hand, in colloidal systems, the particle configurations are directly observable, giving access to information about the microscopic state of the system. Usually statistical mechanics builds a connection between the inaccessible microscopic states and the averaged observables. Knowing the trajectory of the system in configurational space, however, allows us to derive any averaged physical quantity from this knowledge.

In the first part of this work we characterized the static properties of a colloidal monolayer on a homogeneous and isotropic substrate. Using optical tweezers we were able to vary the particle density of the sample always using the same set of particles and guarantying identical conditions in the sample cell. The trajectories of the particles in configurational space were systematically recorded in equally timed steps for different densities. From an experiment of a colloidal monolayer on a homogeneous substrate, we calculated the pair correlation function and the pair potential. This is a standard procedure, but due to the scanned laser tweezers we are now able to isolate the dependence of the pair potential on the particle density while ruling out artifacts caused by a change in salt concentration and particle charge. We observed indeed a dependence of the form pair potential on the particle density. This is direct evidence for the presence of many-body effects. We present an explanation of this effect in terms of macro-ion screening and also a method to qualitatively include this effect in future numerical simulation.

To isolate the three-particle potential, we then conducted a high resolution experiment of confining three particles with the help of laser tweezers. From the particle configurations we extracted the three-body potential, which was found to be of the same strength and range as the pair potential. The results agree well with Poisson Boltzmann calculations. It is found that the three-body potential is caused for the most part by a redistribution of the micro-ions between the colloids, rather than by excluded volume effects or by micro-ion condensation.

In the process of thoroughly characterizing the colloidal system, we did not limit our analysis to microscopic properties only, but also investigated the macroscopic thermodynamic behavior. We determined the equation of state of a colloidal monolayer at different salt
concentrations in the suspension, thereby changing the strength and reach of the pair interaction potential. The results are compared with the theoretical prediction for hard-disk systems. In the case of high-salt suspensions we find excellent agreement. Even for de-ionized suspensions good conformance for a wide range of densities was observed. This proves that even in a suspension of highly charged particles packing effects are the most dominant contribution to the static properties of the sample.

After this analysis of the static properties of colloidal monolayers on homogeneous substrates, we applied a substrate potential created a periodic laser field. Equivalent to optical tweezers, the laser field exerts light forces on the particles, thus creating a highly flexible external potential, as the potential strength may be varied simply by changing the laser intensity. First we modeled a periodic one-dimensional potential. For particle densities commensurate with the substrate periodicity it is observed that by increasing the strength of the potential, a liquid monolayer changes into a crystalline state. Increasing the laser power even further does not lead to a better crystalline order, as one might expect, but to a complete loss of the crystalline order along the potential lines. Therefore at high laser strengths the system melts again. This effect is called light-induced freezing and melting. Having now the means to control the particle density of the sample by the scanned laser tweezers, we conduct systematic measurement as a function of the potential strength and particle density and thus determined the phase diagram of this interesting system. With this phase diagram we can now determine the parameter regions of density and potential strength, in which the re-melting scenario occurs.

Next we doubled the periodicity of the laser potential while keeping the particle density constant. This system exhibits similar properties but between the crystalline and the liquid phase a new smectic phase was observed and characterized. We present a detailed comparison of the structure factors of these two experiments with the theoretical predictions of Frey and also with some numeric simulations. The influence of positional fluctuations on the inter-particle interaction in a light-induced crystal is then discussed. Fluctuations are in fact responsible for melting and also stabilizing the crystal. A qualitative explanation of the intriguing re-melting phenomenon is presented.

In our effort to model 2D atomic systems as realistic as possible, our next step is to replace the one-dimensional potential, which is rarely found in nature, by the common 2D triangular lattice, which corresponds to crystallographic (111) surface. Here again we focus on commensurate densities. For high densities and large surface periodicity one observes that the potential wells of the triangular lattice are occupied by more than one particle and thus colloidal molecules are created. For the case of three particles per lattice well at medium potential strength, we observe ordered colloidal molecular crystals. As the laser intensity is further increased, this crystal starts to melt into donut-like structure, loosing its orientational order. This re-entrance of the disordered phase is partially due to the large importance of fluctuations in 2D.
Bibliography


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## List of symbols and abbreviations

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\[ h(12) = c(12) + \rho \int d^3 c(113) h(32) \]

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<td>( d )</td>
<td>8</td>
<td>periodicity of the laser lattice</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>5</td>
<td>particle diameter</td>
</tr>
<tr>
<td>( s )</td>
<td>3</td>
<td>particle radius</td>
</tr>
<tr>
<td>( \varepsilon_W )</td>
<td>3.5</td>
<td>dielectric constant of water</td>
</tr>
<tr>
<td>( \lambda_B )</td>
<td>3.5.1</td>
<td>Bjerrum length, in water ( \lambda_B = 0.71 nm )</td>
</tr>
<tr>
<td>( Z_{\text{bare}} )</td>
<td>3.5.1</td>
<td>Bare charge of particles ( Z_{\text{bare}} \approx 10^7 e )</td>
</tr>
<tr>
<td>Symbol</td>
<td>Physical Meaning</td>
<td>Page</td>
</tr>
<tr>
<td>-----------------</td>
<td>----------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>$Z$, $Z_{\text{eff}}$</td>
<td>Renormalized particle charge, $Z \approx 20000e$</td>
<td>3.5.2</td>
</tr>
<tr>
<td>$\kappa^{-1}$</td>
<td>Debye screening length, in this work</td>
<td>3.5.1</td>
</tr>
<tr>
<td>$z$</td>
<td>Valency of salt ions; in this work $z = 1$</td>
<td>3.5.1</td>
</tr>
<tr>
<td>$c_i$</td>
<td>Concentration of salt ions; in this work $c_i \approx 1$</td>
<td>3.5.1</td>
</tr>
<tr>
<td>$u(r)$</td>
<td>Effective pair potential</td>
<td>3.5.3</td>
</tr>
<tr>
<td>$v^{(2)}(r)$</td>
<td>Two particle potential, in DLVO theory:</td>
<td>5.4</td>
</tr>
<tr>
<td>$w^{(3)}(r)$</td>
<td>Three-body potential</td>
<td>5.4</td>
</tr>
<tr>
<td>$V_0$</td>
<td>Strength or amplitude of the laser potential</td>
<td>3.7.2</td>
</tr>
<tr>
<td>$g^{(2)}(r)$</td>
<td>Pair correlation function</td>
<td>3.1.3</td>
</tr>
<tr>
<td>$g^{(3)}(r)$</td>
<td>Three-body correlation function</td>
<td>3.1.3</td>
</tr>
</tbody>
</table>

### Physical Constants

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning and Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e$</td>
<td>Electron charge; $e = 1.6022 \times 10^{-19}$ C</td>
</tr>
<tr>
<td>$\varepsilon_0$</td>
<td>Dielectric constant; $\varepsilon_0 = 8.8542 \times 10^{-12}$ C/(mol m)</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann constant; $k_B = 1.38066 \times 10^{23}$ J/K</td>
</tr>
<tr>
<td>$k_BT$</td>
<td>Thermal energy, room temperature (22°C); $k_BT = 4.073 \times 10^{-21}$ J = 25.42 meV</td>
</tr>
</tbody>
</table>
Danksagung

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