Doctoral Thesis

X-ray scattering studies of ordering phenomena in colloids confined in microcavity arrays

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X-Ray Scattering Studies of Ordering Phenomena in Colloids Confined in Microcavity Arrays

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zur Erlangung des Titels

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der


vorgelegt von

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aus Spanien

Angenommen auf Antrag von

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Cover: x-ray scattering measured on a colloidal suspension confined in a microcavity array.
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Summary

The study of liquids in confinement is relevant from a technological point of view, since thin liquid films act as lubricants, preventing damage due to the friction between two surfaces. After a long history of handling lubricants, it is not yet clear how such systems behave on a microscopic scale when the thickness goes down to a few times the size of the fluid’s constituents. Theoretical studies and preliminary measurements of the forces normal to the confining surfaces suggest an arrangement of the molecules in layers parallel to the surfaces, in such a way that an entire number of molecule diameters fits exactly in the confining gap. For the direct determination of the arrangement of the molecules of a fluid in confinement, x-ray diffraction from a brilliant synchrotron source appears to be the most suitable method. This technique can provide atomic resolution and it is optimal for the characterization of periodic systems. However, the experiments carried out in the past found difficulties in dealing with a very small scattering volume and in gaining access to a very thin sample confined between two solid walls.

We have developed a practical method for the study of fluids in confinement which overcomes some limitations of previous experiments. Instead of looking at a single confining slit, we investigate a one-dimensional periodic array of identical slits containing the fluid to be studied. The new container yields a large scattered intensity, since the cross-section of the beam can be taken as large as the whole array. The container consists of an array of narrow cavities etched into a Si wafer by means of electron beam lithography and anisotropic wet etching with KOH, which provides high-aspect-ratio structures with smooth parallel surfaces and cavity widths down to a few hundred nm. Since the width of the cavities is not small enough to induce confinement effects in molecular films, charge-stabilized colloidal suspensions of SiO₂ spheres of ca 100 nm diameter are investigated as scaled-up models of molecular fluids. Apart from yielding an increased intensity, the cavity arrays provide very stable structures, which can be precisely aligned with respect to the x-ray beam. Besides, the design of a microfluidics chamber prevents evaporation and allows the filling of the fluid in the container in an easy and gentle way, very appropriate for data acquisition at a synchrotron beamline. The cavity width can be varied by fabricating several structures on a single Si chip.

The x-ray intensity diffracted from a microcavity array filled with a colloid has
two separate contributions: (a) Bragg scattering from the grating structure formed by the cavities, from which we determine the average density profile of the colloid within the cavities and (b) diffuse scattering arising from short-range correlations within the colloidal fluid. We have developed a simple kinematical theory to describe both contributions.

The ordering/disordering behavior of hard-sphere colloidal suspensions confined in microcavity arrays was investigated in two different experiments. In the first one, high-resolution Bragg scattering measurements were performed on several arrays with different cavity widths. It was found that the colloid profile along the confinement direction is oscillatory, revealing an ordering in layers parallel to the surfaces. The oscillations are found to be strong for cavity widths in which an entire number of hard-sphere diameters fits and weak or absent when this condition is not fulfilled. This behavior is as predicted in theoretical studies and simulations of hard-sphere systems but had not been observed before. In the second experiment, the diffuse scattering from confined hard-sphere colloidal suspensions showed anisotropic structural changes with respect to measurements from bulk suspensions. The observed anisotropy in the structure factor arises from excluded volume effects occurring near the walls of the confining cavity.

Mikrofluidikkammer integriert, welche ein Eintrocknen der Flüssigkeit verhindert, und eine sanfte Befüllung des Probenbehälters ermöglicht, was für die Datenaufnahme am Synchrotron essentiell ist. Die Breite der Schlitze wird variiert, indem auf einem einzelnen Siliziumchip eine Vielzahl verschiedener Gitter realisiert wird.

Die gestreute Röntgenintensität eines solchen mit Kolloid befüllten Gitters hat zwei Beiträge: (a) die Bragg-streuung des Gitters, bestehend aus gefüllten Schlitzen, aus der sich das gemittelte Dichteprofil des Kolloids in den Schlitzen ermitteln lässt, und (b) die diffuse Streuung, welche durch die Nahordnung innerhalb der kolloidalen Flüssigkeit verursacht wird. Es wurde eine kinematische Theorie zur Beschreibung beider Anteile entwickelt.

Chapter 1

Introduction

1.1 Confined liquids

It is known from everyday experience that a liquid film confined between two solid surfaces acts as a lubricant, reducing friction and wear in the surfaces. Friction is sometimes wanted, like in the brakes of a car, and it is sometimes unwanted, like in the moving parts of an engine, where a thin film of oil is used to reduce friction. Sometimes friction needs to be carefully controlled, like when playing a string instrument. The existence of a thin water film on an ice surface makes it slippery, which can be wanted for example in ice-skating, but it can become extremely dangerous when driving a car. These previous examples illustrate how important it is to study thin liquid films confined between two solid surfaces. It is especially interesting to understand thin liquid films on a molecular scale, in order to be able to explain the observable macroscopic phenomena. But the experimental investigation of such systems is a challenge because it is difficult to gain access to a very thin liquid film confined between two solid surfaces.

Two opposing surfaces at nanometer distance, with a liquid in between, serve as a model for a lubricated contact. From studies of friction it is well known that the lubricating properties of liquid films change drastically if the distance between the surfaces becomes less than a few molecular diameters $[1]$. The change is thought to be due to a solid-like ordering of the fluid’s molecules in the small gap between the plates $[2]$. On the left side of Fig. 1.1, the structure of a hard-sphere liquid is illustrated for different confining wall separations with their corresponding density profile below. When the separation between the walls is large (a), the hard spheres layer close to the walls, but in the center they show a structure like in a bulk liquid. When the distance between the walls decreases to a few times the size of the spheres (b, c, d), the oscillations of the density profile $\rho(x)$ close to each wall interfere in the center, yielding oscillatory profiles across the whole gap. These oscillations are stronger when an entire number of layers fit in the gap, like for example in (b) and (d). Theoretical calculations and simulations with hard-sphere liquids revealed such behavior in very
Figure 1.1: Structure of a confined hard-sphere fluid for different confining wall separations (left). Stick-slip behavior for two sliding surfaces with a thin liquid film in between (right). From M. J. Zwanenburg [3].

Confined liquid films [4] [5] [6].

Confinement-induced ordering of the molecules of a liquid would explain experimental phenomena like the stick-slip behavior observed in thin lubricant films. A sketch of this behavior is shown on the right side of Fig. 1.1. When the molecules of a thin liquid film are ordered within the space between the two surfaces, the system is thought to exhibit large friction and the upper surface will resist movement under a sliding force (a). When the sliding force is large enough, the system will slide producing a disorder in the molecules (melting), until they order again (freezing) and the movement stops. The stick-slip behavior has been discussed in numerous friction studies [7] [8].

Experimentally, ordering phenomena in confined liquids have been studied on a molecular scale with the surface force apparatus (SFA). With the SFA it is possible to confine fluids between two atomically smooth surfaces which can be set at distances down to only a few nanometers. One of the surfaces is attached to a spring that allows measurement of the normal force acting on it. It has been found that the normal force oscillates as a function of the distance between the surfaces with a period corresponding to the thickness of a layer and with an amplitude becoming larger as the separation decreases [9] [10]. This suggests an arrangement of the fluid’s constituents in layers parallel to the surfaces, in agreement with the theoretical studies mentioned above. But the question of how exactly the molecules arrange in the narrow space between the surfaces has not yet been answered.
For the determination of the periodical arrangement of molecules, x-ray diffraction is the most used tool. At the interface with a single solid wall, x-ray reflectivity studies revealed layering on the molecular scale at the interface between liquid gallium and diamond [11]. X-ray diffraction was used to determine a five-fold local symmetry in liquid lead adjacent to a silicon wall [12]. But problems arise when a thin liquid film is confined by two solid surfaces due to the difficult accessibility of the system.

Previously, x-ray waveguiding experiments were performed through a small tunable gap between two smooth parallel surfaces [13]. The setup was designed to direct an x-ray beam at the entrance of the small gap and to let it propagate all along the gap, which acted as a waveguide for the x-rays (Fig. 1.2, left). The diffracted intensity at the end of the waveguide was then analyzed in the far field. The waveguiding technique and the waviness of the surfaces restricted the gap sizes between the surfaces to be larger than a few hundreds of nanometers, and therefore colloidal solutions were used as a scaled-up molecular model. Using this method, a clear confinement-induced layering of the colloid parallel to the surfaces was detected [14]. Although the method proved to be capable of detecting ordering phenomena, it also revealed problems such as evaporation of the liquid sample. More importantly, the waveguiding technique limits the spatial resolution in the determination of the arrangement of the colloidal particles to $\Delta x \sim \lambda/(4\alpha_c)$, with $\lambda$ the x-ray wavelength and $\alpha_c$ the critical angle for total reflection from the confining surfaces. In principle, a much better spatial resolution is provided by specular x-ray reflectivity at larger angles. Such a study has been performed by Seeck et al [15] on a confined molecular fluid, but a unique density profile for the fluid was not obtained.

An alternative geometrical configuration consisting of two crossed cylindrical surfaces was designed for waveguiding and specular reflectivity experiments, as shown on the right side of Fig. 1.2 [16]. This geometry allowed a flat contact point between the two surfaces over a few tens of micrometers, overcoming the limitation of the size of the gap due to the waviness of the surfaces. This apparatus was designed for the study of confinement-induced ordering phenomena in liquids on a molecular scale, the only
limit to the minimum size of the gap being the atomic-scale roughness of the surfaces. Preliminary studies with synchrotron radiation succeeded in the characterization of the contact between both surfaces in the absence of liquid [16], but they were difficult due to the extremely small intensity. Besides, the cylindrical geometry considerably complicated the data analysis. X-ray scattering experiments on molecular liquids confined by crossed cylinders have so far been unsuccessful because of radiation damage, despite a single very promising attempt [17]. However, a single x-ray study carried out on liquid crystals confined between two crossed cylindrical surfaces at micrometer distance has been reported [18].

1.2 A new approach to the study of confined fluids

The previously discussed experiments on fluids confined between two opposing surfaces have a common problem: the use of a single tiny slit for the confinement of the fluid results in a very small scattering volume and detected intensity. The aim of this thesis is to introduce a new approach to the investigation of confined fluids which overcomes this problem and simplifies both measurements and analysis.

Figure 1.3: Sketch of the new experimental setup for the investigation of confined fluids. The Si wafer, into which the cavities have been etched, is much thicker than drawn (250 \( \mu \)m). The covering glass slide is 420 nm thick.

For the confinement of the fluid, a set of identical slits is used instead of a single one, and the diffracted intensity from the array is detected in the far field [19]. A sketch of the experiment is shown in Fig. 1.3. The slits are etched into a Si wafer and covered with a glass slide. The main advantage of this method is that the multitude of slits enlarges the scattered intensity. Besides, the etching technique used for the fabrication
of the structures provides slits with smooth and parallel surfaces, solving the problem of the alignment of the surfaces. The solid Si structure provides more stability than in the previous experiments and finally, the glass slide prevents evaporation of the fluid.

On the other hand, the new method also has some disadvantages. The fabrication technique limits the minimum gap size of the slits to a few hundreds of nanometers and therefore the method does not allow experiments on a molecular scale. Instead, solutions of colloidal particles with a diameter of approximately 100 nm are used as a model of a molecular fluid. In such a colloidal solution, the particles are large enough to induce ordering phenomena within the available gap sizes of the slits, but they are still small enough to have a Brownian motion in the solvent, in the same way as molecules do in a fluid. Finally, the new method does not allow normal-force or shear-force measurements on the confined fluid, unlike the SFA.

In the following, the confining slits will be referred to as microcavities and the whole structure as microcavity array. The parameters shown in Fig. 1.3 are the period \( p \) of the array (typically 1 \( \mu \)m), the height \( h \) of the structures (typically a few micrometers) and the width \( w \) of the microcavities. The optimization of these parameters, which is explained in detail in chapter 4, results in high-aspect-ratio structures whose fabrication proved to be a challenge.

The new method described above enabled the determination of the arrangement of the colloidal particles in layers parallel to the confinement walls, as well as the determination of the short-range particle-particle correlations. It was found that the confinement-induced layering of the colloidal particles varied as a function of the gap width according to the integer-fractional layering shown on the left side of Fig. 1.1. Regarding the inter-particle correlations, it was found that the short-range structure of colloidal suspensions in confinement differs substantially from that in bulk liquids.

Our microcavity arrays have been previously used for the confinement of a micellar solution of 30 nm particle diameter in cavity widths of approximately 300 nm \[17\]. The Bragg scattering showed a dense layering of the micelles close to the confining cavity walls.

### 1.3 Synchrotron radiation as a source of x rays

#### 1.3.1 Hard x rays and soft condensed matter

Electromagnetic radiation with wavelengths around 1 Å is referred to as hard x rays. The small wavelength of hard x rays makes them useful for two reasons: their penetration depth, used for example in medical radiography, and their ability to diffract from objects on the atomic scale, used for example in crystallography. In the latter field, x-ray scattering is used as a tool for the determination of the arrangement of atoms in space. Hard x rays are also used in the field of soft condensed matter, for the
determination of the structure of complex fluids such as colloids and emulsions and the
determination of the size and shape of their constituent particles.

In the research on soft condensed matter, x-ray scattering presents some advantages
in comparison to other techniques. Let us consider a colloidal suspension in which
colloidal particles float in the solvent, performing a Brownian movement on a timescale
$\tau \sim \text{ms}$. With microscopy techniques such as transmission electron microscopy (TEM)
or scanning electron microscopy (SEM) one can get access to a small part of the system
at a specific time, but this is not enough for the determination of the structure of the
fluid. Moreover, integration over times $t \gg \tau$ would provide blurred images due to
the movement of the particles. For the determination of the structure of a fluid with
microscopy it is necessary to perform video microscopy by taking several consecutive
2D-images with an exposure time smaller than $\tau$. Video microscopy can be used
for the determination of the structure of colloids in space and time [20]. However,
this technique has some limitations due to the overlap of images over a volume [21].
Scattering, on the other hand, determines the time-averaged structure of the fluid in
a single measurement integrated over a time $t \gg \tau$ and covering a large volume of
sample.

For particles of approximately 100 nm diameter, dynamical light scattering (DLS)
is in principle suitable for the determination of the structure of the fluid and the size
of the colloidal particles. Nevertheless, this technique has the disadvantage of multiple
scattering. For hard x rays, on the other hand, the refractive index contrast between
the particles and the solvent is very low, and therefore multiple scattering effects can
be neglected.

As will be shown later in chapter 2, the angular range of the intensity scattered
from an object scales inversely with the size of the object and proportionally with the
wavelength. For 100 nm-diameter particles and 1 Å wavelength, the scattered radiation
in the far field oscillates with a periodicity of 1.3 mrad. Measuring such a scattering
signal requires a special setup for small angle x-ray scattering (SAXS) at a synchrotron
radiation facility. Synchrotron radiation is x-ray radiation with extraordinary proper-
ties such as low divergence and high flux, which allows fast scattering measurements
over a large dynamical range.

Finally, we make use of the penetration properties of x rays in matter. As shown in
Fig. 1.3 a Si container consisting of microcavity arrays is used to confine the colloidal
solution. The incident x rays have to penetrate the Si wafer to reach the sample under
study. The transmission of a 250 µm-thick Si wafer is 37% for $\lambda = 1$ Å. Additionally,
the transmission through the 420 µm-thick glass slide for the same wavelength is 41%,
making a total transmission of 15%. This might seem a very low transmission, but
working with a synchrotron source one can perfectly afford a 85% intensity loss, as will
be shown below.
1.3.2 Interaction of X-rays with matter

X-ray photons interact with the atoms of matter in two different ways: scattering and absorption. In the classical approach, scattering is produced when the incident radiation exerts a force on the electrons of the atoms, which are accelerated and radiate the so-called scattered wave. The other way of interaction of X-rays with matter is by photoelectric absorption, in which a X-ray photon is absorbed by an atom and the energy is transferred to one electron, which is expelled from an inner atomic shell. If \( I_0 \) is the incident intensity on a sample, the intensity at a depth \( t \) from the sample is

\[
I(t) = I_0 e^{-\mu t},
\]

with \( \mu \) being the so-called attenuation coefficient, which strongly depends on the energy of the incident wave and has abrupt edges at the ionization energies of the atom. One speaks of the absorption edges of a determined material to refer to this discontinuous behavior of X-ray absorption. The attenuation coefficient varies with the atomic number \( Z \) approximately as \( Z^4 \) \[22\]. This results in an enormous contrast between different elements, which makes X-rays very useful in imaging.

So far X-ray interaction with matter has been considered at the atomic level. X-ray scattering phenomena can be regarded as reflection and refraction at the interfaces between two materials, when each of them is considered as a continuous medium having a locally constant electron density. In general, the refractive index of X-rays can be written as

\[
n = 1 - \delta + i\beta.\]

The real part of the refractive index, \( 1 - \delta \), is responsible for the phase shift experienced by a wave when propagating through the medium. For energies far away from an absorption edge,

\[
\delta = \frac{\lambda^2 r_e n_e}{2\pi},
\]

with \( \lambda \) the wavelength, \( r_e \) the classical electron radius and \( n_e \) the electron density of the material. The imaginary part in Eq. 1.2 introduces an attenuation of the wave amplitude and it is related to the attenuation coefficient via

\[
\beta = \frac{\lambda \mu}{4\pi}.
\]

For hard X-rays, one finds that \( \beta \ll \delta \) and therefore absorption can be neglected in refraction phenomena.

When X-rays propagate from a medium with refractive index \( n_1 \) to another medium with refractive index \( n_2 \), they are refracted according to Snell’s law. If \( n_2 > n_1 \), the fact that \( n < 1 \) implies that below a certain incident grazing angle \( \alpha_c \) X-rays are totally reflected. The critical angle for total reflection is \( \alpha_c \approx \sqrt{2\delta} \), neglecting absorption.

The concept of coherence is also very important in X-ray experiments. The wave front of a real beam deviates from that of a plane or spherical wave in two ways:
1. The beam is not perfectly monochromatic and, after a certain propagation length, there will be a phase shift of \( \pi \) between two waves with wavelengths \( \lambda \) and \( \Delta \lambda \). This length is called \textit{longitudinal coherence length} and it can be defined as \[ \xi_l = \frac{\lambda^2}{2 \Delta \lambda}. \] (1.5)

2. The x-ray source has a finite size and waves are emitted from every point of the source. For this reason, an object downstream of the source receives the x rays from different angles. At a certain distance from the source, the different waves are no longer in phase. One way to define the \textit{transversal coherence length} is by the visibility of interference fringes from a double slit, as reported in \cite{23}:

\[ \xi_t = \frac{\lambda D}{\sigma}, \] (1.6)

where \( \sigma \) is the size of the source and \( D \) the distance to the source.

With a rectangular source of size \( \sigma_v \) and \( \sigma_h \) in the vertical and horizontal directions, respectively, the vertical and horizontal coherence lengths \( \xi_v \) and \( \xi_h \) are defined according to Eq.\[1.6\]. The volume determined by \( \xi_l \cdot \xi_v \cdot \xi_h \) is the \textit{coherence volume}, and scattering experiments for which the sample lies within the coherence volume are said to be coherent.

Diffraction occurs when the x rays scattered from an object interfere, yielding maxima and minima at constructive and destructive interferences. For our periodic array, a transversal coherence length of the order of a few periods is enough for interference phenomena to be visible. This is the technique used in our experiments to investigate the ordering of the colloidal suspension in layers parallel to the cavity walls. Similarly, the interaction between the colloidal particles can be investigated because \( \xi_t \) is large enough to cover the interaction range between the particles.

The \textit{divergence} \( \sigma' \) of the source is another relevant quantity in diffraction experiments. It is defined as the angular spread of the x-ray beam when exiting the source. The \textit{emittance} of a source is defined as the product of the size of the source with the divergence \cite{22}:

\[ \epsilon = \sigma \cdot \sigma'. \] (1.7)

In a diffraction experiment it is desirable to have a source with low emittance.

1.3.3 Synchrotron radiation

The source of choice for our diffraction experiments is synchrotron radiation. Several experiments were performed at the Swiss Light Source (SLS) at the Paul Scherrer Institute in Villigen and at the European Synchrotron Radiation Facility (ESRF) in
Grenoble. At the SLS, all measurements were performed at the Material Science beamline, and at ESRF two different experiments were carried out at the beamlines BM05 and ID02. Three different beamlines in two different synchrotron machines obviously yield different experimental conditions. In this section, specifications for the three different measurement stations are given.

![Diagram of a typical x-ray beamline with an undulator source at a synchrotron](from [22]).

Synchrotron radiation is produced when charged particles travel at relativistic speeds in a curved path. Electrons are stored in a large ring, where bending magnets make them orbit around. At the position of the bending magnets, the trajectory of the electrons is curved and the electrons emit a cone of electromagnetic radiation within a wide spectral range extending from the far infrared to the hard x-ray region. At other places of the ring where the trajectory of the electrons is straight, so-called insertion devices can be installed. They consist of a periodic magnetic field which make the electrons oscillate several times in the plane transverse to the e-beam, making them radiate at every oscillation. A beamline is built downstream of the source, where the beam is passed through a monochromator to select a specific wavelength. It is collimated using mirrors and slits, and finally it is used for the experiment (see Fig. 1.4).
An important property of the source is the brilliance, defined as \[22\]

\[
\text{Brilliance} = \frac{\text{Nr of photons/second}}{\epsilon [\text{mrad}^2\text{mm}^2](0.1\% \text{ bandwidth})},
\]

where \(\epsilon\) is the emittance defined in Eq. [1.7]. The brilliance is a figure of merit for the source. The best 3\textsuperscript{rd} generation synchrotron source is typically 10\textsuperscript{10} times brighter than a standard x-ray tube. This explains why synchrotron radiation is so appreciated in experiments performed with x rays.

An electron orbiting in the storage ring at relativistic speed \(v\) has an energy \(\varepsilon_e = mc^2/\sqrt{1 - (v/c)^2}\). The radiation produced by a bending magnet depends on the frequency \(\omega\) of the orbiting electrons and the electron energy \(\gamma = \varepsilon_e/mc^2\) in units of its rest mass energy. The opening angle of the radiated cone in the vertical direction is \(\gamma^{-1}\), which is typically \(10^{-4}\) rad, while, in the horizontal direction, a wide fan of radiation is produced. The radiated power of a bending magnet in practical units is

\[
P[kW] = 1.266 \varepsilon_e^2[\text{GeV}] B^2[T] L[m] I[A],
\]

where \(B\) is the magnetic field, \(L\) the length of the curved electron path as viewed through an aperture at some distance from the source (typically a few mm) and \(I\) the electron current in the ring. The radiated power of a bending magnet is usually a few Watt.

Insertion devices produce x rays more efficiently. There are two types of insertion devices: wigglers and undulators. A wiggler is a set of alternating up- and down-oriented magnetic fields which make the electrons oscillate several times, emitting radiation at every curved part of the path. For the same field strength, the intensity is increased \(2N\) with respect to a bending magnet, with \(N\) being the number of oscillations. The radiated power from a wiggler is

\[
P[kW] = 0.633 \varepsilon_e^2[\text{GeV}] B_0^2[T] L[m] I[A],
\]

with \(B_0\) being the maximum magnetic field and \(L\) length of the device. Because insertion devices have a length of the order of 1 to 2 m, the radiated power is about 1000 times larger than in bending magnets. This produces a huge heat load on the first optical components of the beamline.

The parameter characterizing an insertion device is \(K = \theta_{max}\gamma\), where \(\theta_{max}\) is the maximum angular deviation of the electron oscillations in the insertion device with respect to the electron trajectory in the storage ring. Wigglers typically have \(K \sim 20\). The opening angle of the radiation in a wiggler is \(K\gamma^{-1}\) in the horizontal direction and \(\gamma^{-1}\) in the vertical direction.

An undulator is an insertion device like a wiggler, but with the important difference that the radiation emission cones along the electron trajectory strongly overlap in their
angular range. This results in a coherent addition of the radiation amplitudes at a particular wavelength and its higher harmonics. The coherent addition of amplitudes requires that the oscillation amplitude of the electron in the insertion device is small, i.e., $K \lesssim 1$. The emitted radiation is quasi-monochromatic. The wavelength and its harmonics can be changed by changing the strength of the magnetic fields, i.e., by varying the gap between the upper and lower magnets. The opening angle of the radiation in an undulator is $N^{-1/2}\gamma^{-1}$ in both directions, much smaller than in a wiggler. For this reason, undulators are more brilliant sources than wigglers.

<table>
<thead>
<tr>
<th>source</th>
<th>MS wiggler</th>
<th>ID2 undulator</th>
<th>BM05 bending magnet</th>
</tr>
</thead>
<tbody>
<tr>
<td>machine</td>
<td>SLS</td>
<td>ESRF</td>
<td>ESRF</td>
</tr>
<tr>
<td>$\varepsilon_e$ [GeV]</td>
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<td>6.0</td>
<td>6.0</td>
</tr>
<tr>
<td>$I$ [mA]</td>
<td>300</td>
<td>200</td>
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<tr>
<td>$P$ [kW]</td>
<td>5.7</td>
<td>1.6</td>
<td>$1.4 \times 10^{-3}$</td>
</tr>
<tr>
<td>$\epsilon_h$ [mm mrad]</td>
<td>$6.10 \times 10^4$</td>
<td>$2.36 \times 10^{-2}$</td>
<td>$6.48 \times 10^{-1}$</td>
</tr>
<tr>
<td>$\epsilon_v$ [mm mrad]</td>
<td>$5.06 \times 10^{-1}$</td>
<td>$1.39 \times 10^{-4}$</td>
<td>$1.44 \times 10^{-2}$</td>
</tr>
<tr>
<td>brilliance*</td>
<td>$10^{14}$</td>
<td>$10^{10}$</td>
<td>$10^{10}$</td>
</tr>
<tr>
<td>flux at sample [ph/s]</td>
<td>$10^{13}$</td>
<td>$10^{13}$</td>
<td>$10^{10}$</td>
</tr>
</tbody>
</table>

Table 1.1: Main characteristics of the sources used in our experiments. (*[ph/s/mrad$^2$/mm$^2$/0.1%BW])

In table 1.1, the main characteristics of the sources used for the experiments are shown. A very important characteristic for our experiments is the flux of photons. At the MB05 beamline at ESRF some preliminary experiments took place, where the flux was an important limitation. The emittance is always low in the vertical direction, enabling diffraction with high angular resolution in the vertical plane. This is why the microcavity arrays are oriented such that the direction of confinement is in the vertical plane (cavity ribs horizontal). At the ID2 beamline at the ESRF, the low vertical and horizontal emittances make this station more suitable for 2D SAXS experiments in which the inter-particle correlations in colloidal suspensions are investigated.

At both stations at the ESRF, the x-ray beam was defined by slits, which determined the resolution of the diffraction pattern. At the Materials Science beamline, the beam was vertically focused onto the detector plane in order to resolve the diffraction orders from the microcavity array. In all these experiments, the detector was placed as far as possible behind the sample in order to increase the angular resolution.

1.4 Outline of the thesis

This thesis presents a new method for the measurement of confinement-induced effects in fluids. An array of microcavities is used as a container, which provides a large
scattering signal in comparison with previous methods, where only one single cavity was available.

The second chapter of the thesis deals with theory of x-ray scattering. A kinematical approach is used to derive the scattered signal from an array of cavities filled with a colloidal suspension. The total scattered intensity has two contributions: one is Bragg scattering resulting from the periodic array and the oscillating colloid profile, which act as a grating, and the other one is diffuse scattering, originating from the short-range particle-particle correlations within the colloidal suspension. For the analysis of Bragg scattering, the Patterson function is introduced. For the diffuse scattering part, a new approach is taken which properly deals with the structure factor of a fluid in confinement. Also, dynamical scattering effects are studied, which have to be taken into account in order to explain our experimental results. Finally, we introduce a 1D phase retrieval algorithm for a direct determination of the average density profile of the colloid from the Bragg scattering signal.

In the third chapter we present an overview of colloidal suspensions, focusing on the systems that have been investigated: charge-stabilized SiO$_2$ colloidal particles suspended in a mixture of benzyl-alcohol and ethanol. The technique used for the measurement of the diffuse scattering signal, SAXS, is here described, as well as the determination of the particle size and polydispersity and the determination of the structure factor of bulk colloidal suspensions.

Chapter 4 is concerned with the fabrication of the microcavity arrays for the confinement of the colloidal solutions and their characterization with x rays. The fabrication process is one of the most important parts of the thesis, since it describes a new method with which one achieves high-aspect-ratio structures with adequate characteristics for confinement-induced ordering of colloidal particles. Such microcavity arrays are not exclusively used for the study of confinement-induced ordering of fluids, but also for hard x-ray interferometry, more specifically for phase contrast imaging and tomography, a promising new technique in medical radiography. In this chapter we also describe the design of a microfluidics chamber to fill the microcavities during the measurements and to keep the system sealed, preventing evaporation. Finally, we present a characterization of the cavity arrays by means of x-ray diffraction, using simple kinematical calculations to fit the data.

The fifth chapter shows experimental results from SiO$_2$ colloidal suspensions confined within microcavity arrays. Two main experiments are here presented. In the first one, the confinement-induced oscillating density profile of the colloid in the cavity is determined from measurements of the Bragg scattering intensities from the array. Patterson analysis and kinematical model-dependent calculations give hints regarding the arrangement of the colloidal particles across the cavity as a consequence of the confinement. The use of a phase retrieval algorithm provided a unique reconstruction of the density profile under certain boundary conditions. The results show that
hard-sphere solutions tend to order in layers parallel to the confining walls according to the integer-fractional layer model shown on the left side of Fig. 1.1. In the second experiment, the diffuse scattering from hard-sphere colloidal suspensions revealed an anisotropic structure factor of the fluid due to confinement. The results are compared to a model of hard spheres confined within a narrow gap obtained from the theory in chapter 2. Additionally, we show how a qualitative study of the dynamical scattering effects in the diffuse scattering revealed hints about order/disorder transitions as a function of the cavity width.
Chapter 2

X-ray scattering

2.1 Introduction to x-ray scattering

Scattering is one of the possible interactions of x rays with matter. In the classical description of x-ray scattering, the incoming wave interacts with the electrons in matter, which start oscillating and radiating with the wavelength of the incident radiation. It can be shown that this description is valid for electrons bound to the atom when the energy of the incident beam is far from the absorption edges of the material [24]. The momentum transfer of a photon in a scattering event is

\[ q = k' - k, \]

(2.1)

where \( k \) and \( k' \) are the initial and final wavevectors of the photons, respectively. The quantity \( q \) has units of \([\text{nm}^{-1}]\) or \([\text{Å}^{-1}]\) and it is the natural variable to describe scattering processes.

In a scattering process from an object with an electron density distribution \( \rho(r) \), the different phase shifts of the incoming wave as it passes through different parts of the object have to be considered. In Fig. 2.1 it can be seen that the phase shift of the wave through one particular path is \( \Delta \phi(r) = (k' - k) \cdot r = q \cdot r \). A volume element \( d^3r \) at the position \( r \) contributes with \( \rho(r)d^3r \) to the scattered field with a phase factor of \( e^{iqr} \). The total scattered amplitude is an integration over the whole density distribution:

\[ F(q) = \int \rho(r)e^{iqr}d^3r. \]

(2.2)

Mathematically, Eq. 2.2 can be regarded as the Fourier transform of the electron density of the scatterer, the momentum transfer \( q \) being the reciprocal space coordinate (see Eq. A.6). Experimentally, one measures the intensity function

\[ I(q) \propto |F(q)|^2, \]

(2.3)

which is real and from which all phase information from the object has been lost. More precisely, the scattered intensity measured in number of photons per second in a solid
angle $\Delta \Omega$ centered around the momentum transfer $\mathbf{q}$ equals [22]:

$$I(\mathbf{q}) = r_e^2 \cdot |F(\mathbf{q})|^2 \Delta \Omega \cdot \frac{I_0}{A_0}$$

(2.4)

where $I_0$ [nr of photons/s] is the intensity of the incident beam, $A_0$ is its cross-sectional area and $r_e = \frac{e^2}{4\pi\epsilon_0 mc^2} = 2.82 \times 10^{-15}$ m is the Thomson scattering length.

If the electron density $\rho(\mathbf{r})$ is a real quantity (no absorption), according to Eq. 2.2 we obtain Friedel’s law:

$$F(\mathbf{q}) = F^*(-\mathbf{q}).$$

(2.5)

As a consequence, the intensity patterns from real objects are symmetric and the phases are antisymmetric with respect to the origin.

The scattered intensity is not always enough to determine the real object in a unique way, but it serves for the determination of the arrangement of periodical structures, measurement of the interactions in an ensemble of particles, characterization of small particles (size and shape), etc. In coherent scattering experiments from a non-periodic object, where one oversamples reciprocal space by at least a factor of two compared to Bragg sampling, it is possible to reconstruct the phase object in a unique way using phase retrieval algorithms, at least in two- and three-dimensional systems [25].

![Figure 2.1: Scattering from an object with electron density distribution $\rho(\mathbf{r})$.](image)

In the derivation of Eq. 2.2, the possibility of multiple scattering of the beam through the object has been neglected. This is the so-called kinematic approximation and it is only valid if the interaction of x-rays with the object is small. If the interaction is strong, it is necessary to take multiple scattering into account and one speaks of dynamical scattering.

The scattered amplitude $F(\mathbf{q})$ from an object can be expressed as an operator on the density:

$$F(\mathbf{q}) = \mathcal{F}[\rho(\mathbf{r})],$$

(2.6)
where $\mathcal{F}$ denotes the Fourier transform operator. The inverse operation is called inverse Fourier transform and it gives the electron density distribution:

$$\mathcal{F}^{-1}[F(q)] = \frac{1}{2\pi} \rho(r). \tag{2.7}$$

In a scattering experiment one measures the scattered intensity (see Eq. 2.4), where the complex function $F(q)$ is not known. Instead, the following Fourier transform can be performed:

$$\mathcal{F}^{-1}[|F(q)|^2] = \mathcal{F}^{-1}[F(q) \cdot F(q)^*] = \frac{1}{4\pi^2} \rho(r) \otimes \rho(-r), \tag{2.8}$$

where $\otimes$ denotes the convolution operator (see Eq. A.5) and the multiplication theorem in Eq. A.8 has been used. The right-hand side of Eq. 2.8 is the autocorrelation function of the density or the Patterson function:

$$P(r) = \rho(r) \otimes \rho(-r) = \int \rho(R) \rho(R + r) \, d^3R. \tag{2.9}$$

The Patterson function provides the length scales over which the electron distribution varies, weighted in accordance to their frequency of occurrence. For example, in a set of particles, the Patterson function gives the positions of each particle relative to the others, indicating the weight of a particular inter-particle distance.

### 2.2 X-ray scattering from a linear array of cavities filled with colloid - a kinematical theory

#### 2.2.1 The problem

We consider a linear microcavity array filled with a colloidal suspension, as shown in Fig. 2.2a. The array and the oscillating density profile of the colloid act as a diffraction grating with a period $p$. Scattering of a plane wave from the filled array results in two contributions. One contribution consists of Bragg scattering peaks arising from the grating and the other contribution is diffuse scattering originating from short-range spatial variations in the colloid density. In the following, we present a kinematic scattering theory which yields the Bragg and diffusely scattered intensities [26]. It is our goal to extract from the scattering patterns the structural rearrangements within the colloid as a result of its confinement.

In Fig. 2.2, the scattering geometry is shown. A cartesian coordinate system is chosen such that the cavity array is periodic in the $x$-direction and the incident plane wave propagates along the $z$-direction. The origin of the coordinate system is chosen in the center of a cavity. The array has a periodicity $p$ and the cavities have a height $h$ and a wall separation $w$. The microcavity array has a length $L$ along the $y$-direction.
2.2.2 Total scattered intensity

In this section, a general expression is derived for the total scattered intensity of a linear array of microcavities filled with a colloidal suspension. Let the electron density distribution of the whole system be $\rho(\mathbf{r})$. If the cavities were empty, the density distribution of each period would be the same. Filling with a colloidal suspension, however, causes local density variations which are at different locations for each array period. We express the total electron density distribution as a sum of two contributions:

$$\rho(\mathbf{r}) = \bar{\rho}(\mathbf{r}) + \Delta \rho(\mathbf{r}),$$

(2.10)

where $\bar{\rho}$ is the average density describing the shape of the cavities and the average density distribution of the colloid, and $\Delta \rho(\mathbf{r})$ is the local density variation associated with the presence or the absence of a single particle. Since $\bar{\rho}$ is the same in each period, we can write

$$\bar{\rho}(\mathbf{r}) = \bar{\rho}_p(\mathbf{r}) \otimes \sum_n \delta(x - np),$$

(2.11)

where $\bar{\rho}_p(\mathbf{r})$ is the density within a single period. For ease of notation we define the grating function

$$t(x) = \sum_n \delta(x - np),$$

(2.12)

and the total density of the system results in

$$\rho(\mathbf{r}) = \bar{\rho}_p(\mathbf{r}) \otimes t(x) + \Delta \rho(\mathbf{r}).$$

(2.13)
For the derivation of the scattered intensity from $\rho(\mathbf{r})$, we make use of Eq. 2.4, where

$$
|F(\mathbf{q})|^2 = \mathcal{F}[\rho(\mathbf{r}) \otimes \rho(-\mathbf{r})].
$$

(2.14)

The reason for taking this expression instead of the definition in Eq. 2.2 is that the convolution allows an easier handling of the operations in the following steps. Fourier transform of the grating function $t(x)$ yields

$$
\mathcal{F}[t(x)] = T(q_x) = \frac{2\pi}{p} \sum_m \delta(q_x - \frac{2\pi m}{p})
$$

(2.15)

and Fourier transform of its autocorrelation function gives

$$
\mathcal{F}[t(x) \otimes t(-x)] = \mathcal{F}\left[\sum_{n,m} \delta(x - np) \otimes \delta(-x - mp)\right]
$$

$$
= \mathcal{F}\left[\sum_{n,m} \delta(x - np + mp)\right]
$$

$$
= N_g \cdot \mathcal{F}\left[\sum_n \delta(x - np)\right]
$$

$$
= N_g \cdot T(q_x),
$$

(2.16)

in which $N_g$ is the number of grating periods. Substituting Eq. 2.13 in Eq. 2.14 and applying the convolution theorem of Fourier theory in Eq. A.9, we obtain the following expression for the total scattered amplitude:

$$
|F(\mathbf{q})|^2 = \mathcal{F}[\bar{\rho}_p(\mathbf{r}) \otimes \bar{\rho}_p(-\mathbf{r})] \cdot N_g T(q_x) + \mathcal{F} [\Delta \rho(\mathbf{r}) \otimes \Delta \rho(-\mathbf{r})] + 2\Re\left\{\mathcal{F}[\bar{\rho}(\mathbf{r}) \otimes \Delta \rho(-\mathbf{r})]\right\},
$$

(2.17)

where $\Re\{\}$ is the real part of the complex quantity in brackets. The first term in Eq. 2.17 yields the intensities of the diffraction orders of the colloid-filled grating at the momentum transfer values $q_{x,m} = \frac{2\pi m}{p}$, with $m$ an integer number. Knowing the density profile of the empty grating and using phase retrieval algorithms one can reconstruct from this term the confinement-induced density profile of the colloid. The second term gives the diffusely scattered intensity arising from short-range particle-particle correlations. As a result of the confinement, it is expected to be anisotropic in the $(q_x, q_y)$-plane. The third term is zero, as will be shown.

Using Eq. 2.4, the following expression for the total scattered intensity is obtained:

$$
I(\mathbf{q}) = \nu_e^2 \cdot \left\{ \mathcal{F}[\bar{\rho}_p(\mathbf{r}) \otimes \bar{\rho}_p(-\mathbf{r})] \cdot N_g T(q_x) + \mathcal{F}[\Delta \rho(\mathbf{r}) \otimes \Delta \rho(-\mathbf{r})] \right\} \cdot \Delta\Omega \cdot \frac{I_0}{A_0},
$$

(2.18)

In the following sections the different terms are calculated for specific models of the grating profile and the particle-particle correlations.
Bragg scattering from the array

In this section, the first term of Eq. 2.18, which yields the Bragg scattering, is worked out in detail. This term describes the diffraction orders arising from the cavity array and from the oscillating average density of the colloid due to confinement. Within the interval $-h/2 < z < h/2$, the average density $\bar{\rho}_p(r)$ is a function of $x$ only and outside this interval $\bar{\rho}_p(r) = 0$. We denote the average electron density jump across the silicon-colloid interface as $\Delta n_{e,g}$ and express the density modulation $c(x)$ due to the colloid in the cavity as a fraction of $\Delta n_{e,g}$ (see Fig. 2.3a):

$$\bar{\rho}_p(r) = \begin{cases} 
\Delta n_{e,g} & \text{if } -p/2 < x < -w/2 \text{ and } w/2 < x < p/2, \\
\Delta n_{e,g} \cdot c(x) & \text{if } -w/2 < x < w/2.
\end{cases} \quad (2.19)$$

![Figure 2.3: Electron average density profile within one period of the cavity array in two different cases: cavity with rectangular shape (a) and tapered cavity (b).]

The Fourier transform of the average density within one period of the array is

$$\mathcal{F}[\bar{\rho}_p(r)] = \tilde{\bar{\rho}}_p(\mathbf{q}) = \int \bar{\rho}_p(r) e^{i\mathbf{q} \cdot \mathbf{r}} d^3 \mathbf{r}$$

$$= \Delta n_{e,g} \cdot \left\{ \int_{-p/2}^{p/2} e^{i\mathbf{q} \cdot \mathbf{x}} dx + \int_{-w/2}^{w/2} [c(x) - 1] e^{i\mathbf{q} \cdot \mathbf{x}} dx \right\}$$

$$\cdot \int_{-L/2}^{L/2} e^{i\mathbf{q} \cdot \mathbf{y}} dy \cdot \int_{-h/2}^{h/2} e^{i\mathbf{q} \cdot \mathbf{z}} dz$$

$$= \Delta n_{e,g} \frac{2}{q_x} \left\{ \sin(q_x p/2) - \sin(q_x w/2) + C(q_x) \right\}$$

$$\cdot \frac{\sin(q_y L/2)}{q_y/2} \cdot \frac{\sin(q_z h/2)}{q_z/2}, \quad (2.20)$$

with

$$C(q_x) \equiv \frac{q_x}{2} \int_{-w/2}^{w/2} c(x) e^{i q_x x} dx. \quad (2.21)$$
Since, according to Eq. 2.15, $q_x$ can only have the values $2\pi m/p$, the first sinus in Eq. 2.20 vanishes and the second sinus becomes $\sin(m\pi w/p)$. Since the size of the beam in the $y$-direction $L$ is very large, $\tilde{F}_p(\mathbf{q})$ has nonzero intensity only close to $q_y = 0$. In conclusion, the Bragg scattered intensity from the grating consists of diffraction orders along the $q_x$-direction at $q_y = 0$, as sketched in the detector plane of Fig. 2.2.

From the autocorrelation function $\mathcal{F}[\tilde{\rho}_p(\mathbf{r}) \otimes \tilde{\rho}_p(-\mathbf{r})] = |\mathcal{F}[\tilde{\rho}_p(\mathbf{r})]|^2$ it is possible to derive the scattered intensity from the grating in diffraction order $m$:

$$I_g^m = r_e^2 \cdot \left\{ \int |\mathcal{F}[\tilde{\rho}_p(\mathbf{r})]|^2 \cdot N_g \cdot T(q_x) \, d^2\Omega \right\} \cdot \frac{I_0}{A_0},$$

(2.22)

where the integration over the solid angle $d^2\Omega = (dq_x \cdot dq_y)/k^2 = (dq_x \cdot dq_y)\lambda^2/(4\pi^2)$ in the detector plane is performed around the $m^{th}$ order. Substituting Eq. 2.20 in Eq. 2.22 and carrying out the integration over the solid angle $d^2\Omega$ we obtain

$$I_g^m = r_e^2 \cdot (\Delta n_{e,g})^2 \cdot \left\{ \int \sin^2(qyL/2) \, dq_y \right\} \cdot \sin^2(qzh/2) \cdot \frac{\lambda^2}{4\pi^2} \cdot \frac{I_0}{A_0}.$$

(2.23)

The integral in $\{\}$ equals $2\pi L$. For our case of the incident wavevector being parallel to the $z$-direction, the momentum transfer component $q_z$ at the $m^{th}$ order has the value $q_{z,m} = -q_x^2/(2k) \approx -q_{x,m}^2/(2k) = -\pi m^2 \lambda/p^2$. In addition, we realize that $A_0 = N_g L p$. Eq. 2.23 can now be rewritten as

$$I_g^m = \frac{4(\Delta \delta_g)^2}{\lambda^2} \cdot \left[ \frac{C(2\pi m/p) - \sin(m\pi w/p)}{m \pi m} \right]^2 \cdot \frac{\sin^2(q_{z,m}h/2)}{(q_{z,m}/2)^2} \cdot \frac{\lambda^2}{4\pi^2} \cdot \frac{I_0}{A_0}.$$

(2.24)

in which $\Delta \delta$ is the jump in the average x-ray refractive index across the silicon-colloid interface, given by

$$\Delta \delta_g = \frac{\lambda^2 r_e \Delta n_{e,g}}{2\pi}.$$

(2.25)

If $q_{z,m}/2 \ll 1$ we can approximate $\sin^2(q_{z,m}h/2)/(q_{z,m}/2) \approx h^2$ and obtain for the diffraction efficiency in order $m$:

$$\eta_m = \frac{I_g^m}{I_0} \approx (\Delta \phi)^2 \cdot \left[ \frac{C(2\pi m/p) - \sin(m\pi w/p)}{\pi m} \right]^2.$$

(2.26)

Here,

$$\Delta \phi = \frac{2\pi h \Delta \delta_g}{\lambda}$$

(2.27)

is the phase shift along the rib height $h$, which should fulfill the condition $\Delta \phi \ll 1$ for the kinematic approximation to be valid. If the grating is a thick phase object,
(\Delta \phi)^2$ should in fact be replaced by $4 \sin^2(\pi h \Delta \delta / \lambda)$. When we choose the grating height such that the total phase shift equals $\pi$, i.e. if $h = \lambda / (2 \Delta \delta)$, then this term equals 4. Assuming no colloid ordering ($c(x) = 0$) and choosing a duty cycle of the array of $w/p = 0.5$, we obtain the well-known result $\eta_m \simeq 4/(\pi^2 m^2)$ for odd values of $m$ and $\eta_m = 0$ for even values of $m$ \[27\]. If one adds now a colloidal suspension with an oscillating profile $c(x)$, we have $\eta_m = (\Delta \phi)^2 \cdot |C(2\pi m/p)/(\pi m)|^2$ for even $m$. This provides high sensitivity in the detection of confinement-induced ordering phenomena in these gratings.

Eq. 2.26 gives the diffraction efficiencies for an array of rectangular microcavities filled with a colloid. As we will show in chapter 4, the microcavities used in the experiments do not have a perfect rectangular shape, but they have slightly tapered walls as shown in Fig. 2.3. Also, the smoothness of the Si edges and the thickness of a native SiO$_2$ layer can play an important role in the calculation of diffraction efficiencies. Therefore, in order to work with an appropriate model to evaluate the experiments, one would prefer to assume a general shape $s(x)$ of the grating and the colloid profile which can be easily modelled in a computer program. We express the density of the filled array within a period as:

$$\bar{\rho}_p(r) = \Delta n_{e,g} \cdot s(x), \quad \text{for} \quad -p/2 < x < p/2.$$ \hspace{1cm} (2.28)

Following the same procedure as before, we obtain the following expressions for the scattered intensity in order $m$

$$I^m = (\Delta \phi)^2 \cdot \left| \frac{1}{p} \int_{-p/2}^{p/2} s(x) e^{2\pi imx/p} dx \right|^2 \cdot I_0$$ \hspace{1cm} (2.29)

and for the diffraction efficiency of order $m$

$$\eta_m \simeq (\Delta \phi)^2 \cdot \left| \frac{1}{p} \int_{-p/2}^{p/2} s(x) e^{2\pi imx/p} dx \right|^2.$$ \hspace{1cm} (2.30)

In Fig. 2.4a we show calculated diffraction efficiencies up to the 20$^{th}$ order according to Eq. 2.30 for two different microcavity profiles $s(x)$. In the inset of the plot we show the phase shift of the x rays corresponding to $s(x)$ for an empty cavity (blue line) and the same cavity filled with a layered fluid (red line). The efficiencies from the empty array have been scaled with the factor $(\Delta \phi/\Delta \phi')^2$, with $\Delta \phi'$ the (larger) phase shift or the empty grating structure, in order to compare both cases. In the calculations, the following parameters were taken: $p = 1 \mu m$, $w = 400 \text{ nm}$, $h = 6 \mu m$ and $\theta = 0.14^\circ$. For the layered colloid, a period $s = 130 \text{ nm}$ was assumed. The effect of the tapering parameter $\theta$ is that the efficiencies decrease slightly faster at high orders. However, the diffraction efficiencies are mainly influenced by $h$, $w/p$ and the oscillating profile within the cavity, and they can be qualitatively explained by Eq. 2.26. The height of
Figure 2.4: (a) Calculated diffraction efficiencies for an empty Si microcavity array and the same array filled with a layered colloid. The efficiencies from the empty array have been scaled with the factor $(\Delta \phi / \Delta \phi')^2$. The plot in the inset shows the respective phase profiles. In the calculation, the following parameters were assumed: $p = 1 \mu m$, $w = 400 \text{ nm}$, $h = 6 \mu m$, $\theta = 0.14^\circ$ and $\lambda = 1 \text{ A}$. The period of the oscillating colloid profile is $s = 130 \text{ nm}$. (b) Patterson functions obtained from the calculated diffraction efficiencies shown in (a). (c) Difference $\Delta P(x)$ between the Patterson functions shown in (b).
Chapter 2  

X-ray scattering

the cavities \( h \) only contributes to a constant phase shift. When there is no layering within the colloid (\( c(x) = 0 \)), the efficiencies oscillate according to the sinus function in Eq. 2.26, depending only on \( w/p \). Now we introduce a layered colloid within the cavity given by an oscillating function

\[
c(x) = A \cos \left( \frac{2\pi x}{s} \right),
\]

(2.31)

with \( A \) being the amplitude and \( s \) the period of the oscillation. The diffraction efficiencies have now an additional dependence on \( C(2\pi m/p) \), with the first maximum at \( q_x = 2\pi/s \), i.e. for \( m = p/s \). This corresponds to the 8th diffraction order in our example.

The expression between \([\ldots]\) in Eq. 2.30 is the \( m \)th Fourier coefficient of the shape function \( s(x) \) in the Fourier series

\[
s(x) = \frac{1}{\Delta \phi} \sum_{n=-\infty}^{+\infty} e^{i\varphi_n} \eta_{1/2} e^{-2\pi i n x/p} \quad \text{for} \quad -p/2 \leq x \leq p/2.
\]

(2.32)

Note, the phases \( \varphi_n \) cannot be determined from the measured diffraction efficiencies. Due to the 'phase problem', the direct determination of the shape function \( s(x) \) from the measured diffraction efficiencies is not possible. A hint for the shape of \( s(x) \), however, is provided by the normalized one-dimensional Patterson function:

\[
P(x) = \frac{(\Delta \phi)^2}{p} s(x) \otimes s(-x).
\]

(2.33)

From Eqs. 2.32 and 2.33 we derive the following expression for the Patterson function of one period of the microcavity array:

\[
P(x) = \frac{(\Delta \phi)^2}{p} \int_{-p/2}^{p/2} s(X) \cdot s(x+X) dX
\]

\[= \sum_{n,m} e^{i(\varphi_n+\varphi_m)} \eta_n^{1/2} \eta_m^{1/2} e^{-2\pi i n x/p} \delta_{n,-m},
\]

(2.34)

with

\[
\delta_{n,m} = \frac{1}{p} \int_{-p/2}^{p/2} e^{2\pi i (m-n) x/p} dx
\]

(2.35)

being the Kronecker delta function. As a consequence of Friedel’s law in Eq. 2.5, \( \eta_n = \eta_{-n} \) and \( \varphi_n = -\varphi_{-n} \). Hence the phases drop out and we find

\[
P(x) = \sum_{n=-\infty}^{+\infty} \eta_n \cos(2\pi n x/p).
\]

(2.36)

Eq. 2.36 is the Patterson function of a 1D lattice of period \( p \) [24]. In Fig. 2.4b we show the Patterson functions calculated with Eq. 2.36 and using the diffraction efficiencies in
Fig. 2.4a. Both curves have a triangular shape as a consequence of the self-convolution of one cavity with a rectangular shape. The size of the base of the triangle is given by $2w$. In order to see the small differences between the two functions, we introduce the difference Patterson function

$$\Delta P(x) = P(x) - P'(x) = \sum_{n=-\infty}^{+\infty} (\eta_n - \eta'_n) \cos(2\pi nx/p), \quad (2.37)$$

where $P(x)$ and $P'(x)$ denote the Patterson functions of the colloid-filled and (scaled) empty gratings, respectively. Here the efficiencies $\eta'_n$ from the empty array have been scaled with the factor $(\Delta \phi / \Delta \phi')^2$, with $\Delta \phi'$ the (larger) phase shift or the empty grating structure. $\Delta P(x)$ is shown in Fig. 2.4c, where clear oscillations within the region $-w < x < w$ arise as a consequence of the oscillating colloid profile. The period of the oscillations in $\Delta P(x)$ is very close to $s$. This example illustrates how Patterson functions reveal confinement effects in colloids.

Patterson functions are useful but do not yield the structure. For the reconstruction of the exact electron density profile, one needs to know the phases $\phi_n$, which are lost in the measurement of the diffraction efficiencies. To retrieve the phase information, iterative algorithms have proven to be very helpful. However, it has been shown that phase retrieval in 1D problems generally is non-unique (with the exception of one special case [28]), while in two-dimensional systems multiple solutions are less abundant [29]. For the present case of 1D density profiles to be retrieved from Bragg scattering data we tried a combination of standard iterative phase retrieval algorithms, namely Gerchberg-Saxton’s error reduction, and Fienup’s hybrid input-output algorithm [30] [31] [32]. By including physical constraints in the algorithm we succeeded in retrieving complex objects, i.e., both amplitude and phase, for a 1D problem [33]. In chapter 5 we show the results from this algorithm.

### 2.2.4 Diffuse scattering from confined colloid

In this section, we consider the second term in Eq. 2.17, which gives rise to diffuse scattering. It is our aim to rewrite this term in a way that simplifies calculations for models of particle-particle correlations. For this purpose we write the particle density within the cavities as a convolution of the density distribution $f_c(r)$ within a single particle with the number density $n(r)$ of particles:

$$\rho(r) = f_c(r) \otimes n(r), \quad (2.38)$$

with

$$n(r) = \sum_j \delta(r - r_j) \quad (2.39)$$
and the positions of the colloidal particles in the cavities. We express the local variation in the density as

\[ \Delta \rho(r) = f_c(r) \otimes \Delta n(r). \] (2.40)

Here,

\[ \Delta n(r) = \sum_j \delta(r - r_j) - \bar{n}(r), \] (2.41)

where \( \bar{n}(r) \) is to be understood as a slowly varying function of \( r \). The definition of \( \Delta n(r) \) is such that

\[ \int \Delta n(r) d^3r = 0. \] (2.42)

The diffuse term in Eq. 2.17 can be rewritten as

\[ F[\Delta \rho(r) \otimes \Delta \rho(-r)] = F[f_c(r) \otimes f_c(-r) \otimes \Delta n(r) \otimes \Delta n(-r)] \]

\[ = |F_c(q)|^2 \cdot F[\Delta n(r) \otimes \Delta n(-r)], \] (2.43)

where the convolution theorem in Eq. A.9 has been used and the Fourier transform of \( f_c(r) \) has been denoted by \( F_c(q) \). For the evaluation of \( F[\Delta n(r) \otimes \Delta n(-r)] \), the following approach is taken. First, we apply the convolution theorem and work out the different factors:

\[ F[\Delta n(r) \otimes \Delta n(-r)] = F[\Delta n(r)] \cdot F[\Delta n(-r)] = \left( \sum_j e^{i \mathbf{q} \cdot \mathbf{r}_j} - \int \bar{n}(r)e^{i \mathbf{q} \cdot \mathbf{r}}d^3r \right) \]

\[ \cdot \left( \sum_i e^{-i \mathbf{q} \cdot \mathbf{r}_i} - \int \bar{n}(-r')e^{i \mathbf{q} \cdot \mathbf{r}'d^3r'} \right) \]

\[ = \sum_{i,j} e^{i \mathbf{q} \cdot (\mathbf{r}_j - \mathbf{r}_i)} + \left| \int \bar{n}(r)e^{i \mathbf{q} \cdot \mathbf{r}}d^3r \right|^2 + \text{cross terms}. \] (2.44)

Having singled out the important first term describing the particle correlations, we now approximate the sums over the particles in the cross terms by integrals:

\[ \sum_j e^{i \mathbf{q} \cdot \mathbf{r}_j} = \int \bar{n}(r)e^{i \mathbf{q} \cdot \mathbf{r}}d^3r; \quad \sum_i e^{-i \mathbf{q} \cdot \mathbf{r}_i} = \int \bar{n}(r)e^{-i \mathbf{q} \cdot \mathbf{r}}d^3r. \] (2.45)

As a consequence, the inter-particle correlations are described by the following expression:

\[ F[\Delta n(r) \otimes \Delta n(-r)] = \sum_{i,j} e^{i \mathbf{q} \cdot (\mathbf{r}_j - \mathbf{r}_i)} - \left| \int \bar{n}(r)e^{i \mathbf{q} \cdot \mathbf{r}}d^3r \right|^2. \] (2.46)

We separate the sum over particle pairs in Eq. 2.46 in diagonal and non-diagonal terms and replace the sum by an ensemble average:

\[ \sum_{i,j} e^{i \mathbf{q} \cdot (\mathbf{r}_j - \mathbf{r}_i)} = N + \iint n^{(2)}(\mathbf{r}_1, \mathbf{r}_2)e^{i \mathbf{q} \cdot (\mathbf{r}_2 - \mathbf{r}_1)}d^3\mathbf{r}_1d^3\mathbf{r}_2, \] (2.47)
where $N$ is the total number of particles and $n^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ is the joint probability density to find a particle at $\mathbf{r}_2$, given a particle at $\mathbf{r}_1$. The second term in Eq. 2.46 can be rewritten as

$$\left| \int \tilde{n}(\mathbf{r}) e^{i\mathbf{q} \cdot \mathbf{r}} d^3 \mathbf{r} \right|^2 = \int \tilde{n}(\mathbf{r}_1) \tilde{n}(\mathbf{r}_2) e^{i\mathbf{q} \cdot (\mathbf{r}_2 - \mathbf{r}_1)} d^3 \mathbf{r}_1 d^3 \mathbf{r}_2. \quad (2.48)$$

Finally, combining Eqs. 2.43, 2.46, 2.47 and 2.48 we obtain the following form for the diffuse term:

$$\mathcal{F}[\Delta \rho(\mathbf{r}) \otimes \Delta \rho(-\mathbf{r})] = N |F_c(q)|^2 \cdot S(q), \quad (2.49)$$

where $S(q)$ is the liquid structure factor, defined as

$$S(q) \equiv 1 + \frac{1}{N} \int \int [n^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - \tilde{n}(\mathbf{r}_1) \tilde{n}(\mathbf{r}_2)] e^{i\mathbf{q} \cdot (\mathbf{r}_2 - \mathbf{r}_1)} d^3 \mathbf{r}_1 d^3 \mathbf{r}_2. \quad (2.50)$$

The cross term in the total scattered amplitude (third term in Eq. 2.17) vanishes after considering the approximations in Eq. 2.45. In analogy with the preceding steps, we write this term as

$$\mathcal{F}[\bar{\rho}(\mathbf{r}) \otimes \Delta \rho(-\mathbf{r})] = |F_c(q)|^2 \cdot \mathcal{F}[\tilde{n}(\mathbf{r}) \otimes \Delta n(-\mathbf{r})] = \mathcal{F}[\tilde{n}(\mathbf{r}) \otimes \left\{ \sum_i \delta(-\mathbf{r} - \mathbf{r}_i) - \bar{n}(-\mathbf{r}) \right\}] = \int \tilde{n}(\mathbf{r}) e^{i\mathbf{q} \cdot \mathbf{r}} d^3 \mathbf{r} \cdot \sum_i e^{-i\mathbf{q} \cdot \mathbf{r}_i} - \left| \int \tilde{n}(\mathbf{r}) e^{i\mathbf{q} \cdot \mathbf{r}} d^3 \mathbf{r} \right|^2. \quad (2.51)$$

Using the second relation in Eq. 2.45 we conclude that

$$\mathcal{F}[\bar{\rho}(\mathbf{r}) \otimes \Delta \rho(-\mathbf{r})] = 0. \quad (2.52)$$

**Form factor of colloidal particle**

The Fourier transform $F_c(q)$ of the electron density distribution $f_c(\mathbf{r})$ within a single colloidal particle is readily obtained. For a spherical particle of radius $R$ and uniform density, the electron density distribution is given by

$$f_c(r) = \begin{cases} \Delta n_{e,c} & \text{for } r \leq R \\ 0 & \text{for } r > R, \end{cases} \quad (2.53)$$

where $\Delta n_{e,c}$ is the difference in the average electron density of the particle and the solvent. The Fourier transform of the radial function $f_c(r)$ can be easily performed using spherical coordinates:

$$F_c(q) = V_c \cdot \Delta n_{e,c} \cdot \frac{3}{(qR)^3} (\sin qR - qR \cos qR), \quad (2.54)$$
with $V_c = 4\pi R^3/3$ being the volume of the colloidal particle. It is convenient to define the dimensionless form factor of the particle:

$$\tilde{F}(q) = \frac{3}{(qR)^3} (\sin qR - qR \cos qR).$$  \hspace{1cm} (2.55)

The scattered intensity from a single colloidal particle is proportional to $|\tilde{F}(q)|^2$, which is plotted in Fig. 2.5 as a function of $qR$. It is an oscillating function with its first zero at $qR = 4.4934$. It is studied in more detail in chapter 3.

**Structure factor of confined colloid**

Confinement of the colloidal suspension is expected to induce short-range structural rearrangements which will lead to characteristic changes in the structure factor in comparison with the one for a bulk colloid. The determination of a pair correlation function for the confined colloid by direct Fourier inversion of $S(q)$ is difficult, as will be shown. But it is possible to calculate the structure factor for simple confinement models and to compare this with the measured structure factor.

In Eq. 2.50 we replace the integration variable $\mathbf{r}_2$ by $\mathbf{r}_1 + \mathbf{r}$, where $\mathbf{r}$ is a running variable at fixed $\mathbf{r}_1$. With this change, the structure factor can be written as

$$S(q) \equiv 1 + \frac{1}{N} \iiint [n^{(2)}(\mathbf{r}_1, \mathbf{r}) - \bar{n}(\mathbf{r}_1)\bar{n}(\mathbf{r}_1 + \mathbf{r})] e^{i\mathbf{q} \cdot \mathbf{r}} d^3\mathbf{r}_1 d^3\mathbf{r}. \hspace{1cm} (2.56)$$

This equation can be further simplified by factorizing the joint probability function $n^{(2)}(\mathbf{r}_1, \mathbf{r})$ as follows:

$$n^{(2)}(\mathbf{r}_1, \mathbf{r}) = \bar{n}(\mathbf{r}_1)\bar{n}(\mathbf{r}_1 + \mathbf{r})g(\mathbf{r}_1, \mathbf{r}), \hspace{1cm} (2.57)$$
where \( n(r_1) \) is the number density of particles at position \( r_1 \) and \( \bar{n}(r_1 + r)g(r_1, r) \) the number density at a position which is translated by \( r \) with respect to \( r_1 \). Here, \( g(r_1, r) \) is the pair distribution function. In our case \( \bar{n} \) within the cavity is a function of \( x \) only. Additionally, we assume that the pair distribution function \( g \) depends only on the difference vector \( r \) between the positions of two particles. We thus write \( n^{(2)}(r_1, r) \) as

\[
n^{(2)}(r_1, r) = \bar{n}(x_1)\bar{n}(x_1 + x)g(r) \quad \text{for} \quad x \in [-w/2, w/2],
\]

and \( x + x_1 \in [-w/2, w/2] \). \( (2.58) \)

Substituting Eq. \( 2.58 \) in Eq. \( 2.56 \), we find the following simplified expression for the structure factor of a colloid confined in the \( x \)-direction:

\[
S(q) \simeq 1 + \frac{1}{N} \int \int \bar{n}(x_1)\bar{n}(x_1 + x)[g(r) - 1]e^{iq \cdot r}d^3r_1d^3r.
\] \( (2.59) \)

The confinement effect on the structure factor is expressed by the functions \( \bar{n}(x_1) \) and \( \bar{n}(x_1 + x) \), which are nonzero over a limited interval.

We can retrieve the well-known expression for the structure factor \( S_b \) of a bulk liquid (see for example [34]) by putting in Eq. \( 2.59 \) a constant density \( \bar{n}(x_1) = \bar{n}(x_1 + x) = \bar{n} \), integrating over \( r_1 \) and using \( N/V = \bar{n} \):

\[
S_b(q) = 1 + \bar{n} \int [g(r) - 1]e^{iq \cdot r}d^3r.
\] \( (2.60) \)

Since a bulk liquid is isotropic, this expression can be simplified further to

\[
S_b(q) = 1 + \frac{4\pi \bar{n}}{q} \int r[g(r) - 1]\sin(qr)dr.
\] \( (2.61) \)

The bulk liquid’s pair distribution function \( g(r) \) in Eq. \( 2.61 \) can be obtained from \( S_b(q) \) by direct inverse Fourier transform, but this is impossible for the confined liquid, since even the simplified integrand of Eq. \( 2.59 \) is a two-point function.

Theoretically, the pair distribution function of a uniform fluid in which the particles interact through pairwise-additive forces can be calculated from approximative integral equations. In the Percus-Yevick (PY) approximation [35], the so-called direct correlation function of the system is approximated by a series of powers of \( \Delta n_{e,c} \), which makes the integral equations soluble. It has been shown that the PY approximation is a good approximation when the inter-particle interactions are short-ranged [36]. It is particularly suitable for hard-sphere systems, for which \( g(r) \) can be obtained analytically [37]. Fig. \( 2.6a \) displays the analytically calculated \( g(r) \) for 100 nm-diameter hard-sphere systems with different volume fractions \( \phi = N V_c/V \), where \( V \) is the total volume of the system. The \( g(r) \) of hard-sphere fluids equals zero for distances \( r < 2R \), has a maximum at \( r = 2R \), oscillates with a frequency equal to \( 2R \) for \( r > 2R \) and
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Figure 2.6: (a) Analytical calculation of the pair distribution function \( g(r) \) in the PY approximation for bulk hard-sphere systems with different volume fraction \( \phi \). (b) Calculated bulk structure factor \( S_b(q) \) from the \( g(r) \) plotted in (a).

rapidly decays to 1. The maximum value of \( g(r) \) and the amplitude of its oscillations depends on \( \phi \).

The theoretical structure factor of the bulk fluid \( S_b(q) \) can be obtained from Eq. 2.61 using the \( g(r) \) calculated in the PY approximation (see Fig. 2.6b). The structure factor of a hard-sphere fluid has its first maximum at \( q \simeq 2\pi/(2R) \).

**Diffusely scattered intensity from colloid**

The diffusely scattered intensity from the confined colloid is given by

\[
I_c(q) = r_c^2 \cdot (V_c \cdot \Delta n_{e,c})^2 \cdot |\tilde{F}(q)|^2 \cdot N S(q) \cdot \Delta \Omega \cdot I_0 / A_0, \tag{2.62}
\]

with \( S(q) \) the structure factor given, for example, by Eq. 2.59. Eq. 2.62 can be written in a more convenient way by introducing the volume concentration \( \phi \) of particles, which is the number of particles per unit volume of the cavities multiplied by the volume \( V_c \) of a single particle:

\[
\phi = \frac{p}{w} \cdot \frac{N}{A_0h} \cdot V_c. \tag{2.63}
\]

The ratio \( p/w \) is the ratio of the total illuminated area to the area covered by all cavities. Introducing

\[
\Delta \delta_c = \frac{\lambda^2 r_c \Delta n_{e,c}}{2\pi} \tag{2.64}
\]

as the jump in the x-ray refractive index across the particle-solvent interface and writing \( \Delta \Omega = \lambda^2 (\Delta q_x \Delta q_y)/(4\pi^2) \), the following expression is obtained for the diffusely
scattered intensity from the confined colloid:

$$\frac{I_c(q)}{I_0} = \frac{(\Delta \delta_c)^2}{\lambda^2} \cdot \frac{wh}{p} \cdot \phi \cdot V_c \cdot |\tilde{F}(q)|^2 \cdot S(q) \cdot \Delta q_x \Delta q_y.$$  \hspace{1cm} (2.65)

In a typical experiment we have silica colloidal particles of radius $R \approx 60$ nm in an alcohol mixture with $\phi = 0.1$, $\Delta \delta_c = 1.24 \times 10^{-6}$, $\lambda = 1 \text{Å}$, $p = 1 \mu m$, $w = 400$ nm and $h = 6 \mu m$. Taking $S(q) \simeq 1$ and $\tilde{F}(q) \simeq 1$, we have in one pixel of a 2D detector spanning a solid angle of $6.75 \times 10^{-11}$ rad$^2$ an intensity ratio $I_c(q)/I_0 = 8.83 \times 10^{-9}$, which illustrates the importance of a high-flux source. At the Materials Science beamline, a flux of approximately $10^{13}$ ph/s (see table 1.1) results in a counting rate of $10^5$ ph/s. In Fig. 2.5 we observe that this is enough to cover a large range of $|\tilde{F}(q)|^2$, which is modulating the intensity pattern. At the BM05 beamline at the ESRF the flux is approximately 3 orders of magnitudes smaller, and the diffuse scattering could only be measured up to the first minimum of the form factor.

### 2.2.5 Structural models for a colloidal suspension in confinement

In the following, we apply Eq. 2.59 to two simple models for the structural arrangement of the colloidal particles with respect to the confining walls. In both cases we assume the cavity width $w$ to be comparable to the particle-particle distance. Additionally, we assume that the pair distribution function is a function of the inter-particle distance only, i.e. $g(r) = g(r)$. Anisotropy of $S(q)$ then only arises from the anisotropic density distributions $\bar{n}(x_1)$ and $\bar{n}(x_1 + x)$ in Eq. 2.59. Finally, we make the usual assumption that $g(r) - 1$ is non-zero over a limited volume, so that the integrals to be considered all exist.

By assuming an isotropic pair distribution function, we state that the interaction between the particles is independent of the direction in 3D space despite the confinement. This assumption is valid in the case of a hard-sphere system, but it is likely to be wrong in systems with charged particles. Therefore, in the following we focus on hard-sphere fluids only. The structure factor of a confined fluid in which $g(r)$ is isotropic essentially accounts for excluded volume effects \cite{38}, i.e. for the confinement-induced changes in the packing of the particles.

#### Uniform filling of cavity with colloid

The simplest of all models is one in which the number density $\bar{n}(x)$ is constant across the cavity. Particles with radius $R$ can occupy the space in the cavity with their centers within the width $w - 2R$, $w$ being the total width of the cavity. Calling $b \equiv (w - 2R)/2$ and $P(x)$ the probability for a particle to be at position $x$, we have

$$\bar{n} = \frac{N}{O} \cdot P(x),$$  \hspace{1cm} (2.66)
with $\mathcal{O}$ the area of the cavity wall and

$$P(x) = \begin{cases} 
\frac{1}{2b} & \text{for } -b \leq x \leq b, \\
0 & \text{for } x < -b \text{ and } x > b.
\end{cases} \quad (2.67)$$

Figure 2.7: Two particles inside a cavity uniformly filled with colloid. The structure factor $S(q)$ is obtained by integrating over all allowed positions $x_1$ and inter-particle vectors $r$.

Substituting into Eq. 2.59 we obtain

$$S(q) = 1 + \bar{n} \int_{-b}^{b} dx_1 \int d^3r P(x_1 + x)[g(r) - 1]e^{iq \cdot r}, \quad (2.68)$$

where $\bar{n} = N/(2b\mathcal{O})$ is the constant average density in the cavity. For the integration over $r$ in Eq. 2.68, polar coordinates are chosen (see Fig. 2.7):

$$\begin{align*}
  r &= r(\cos \theta, \sin \theta \cos \phi, \sin \theta \sin \phi), \\
  d^3r &= r^2 \sin \theta \, dr \, d\theta \, d\phi \quad \text{and} \\
  q \cdot r &\simeq q_x r \cos \theta + q_y r \sin \theta \cos \phi. \quad (2.69)
\end{align*}$$

In the last equation, the term $q_z r \sin \theta \sin \phi$ has been neglected, since it is nearly zero over the integration volume. The condition in Eq. 2.67 on $P(x + x_1)$ can be rewritten as

$$P(r \cos \theta + x_1) = \begin{cases} 
1/(2b) & \text{for } (-b - x_1)/r \leq \cos \theta \leq (b - x_1)/r, \\
0 & \text{for } \cos \theta < (-b - x_1)/r \text{ and } \cos \theta > (b - x_1)/r.
\end{cases} \quad (2.70)$$

Calling

$$\begin{align*}
  \cos \theta_1 &= \max[(-b - x_1)/r, -1] \quad \text{and} \\
  \cos \theta_2 &= \min[(b - x_1)/r, 1],
\end{align*} \quad (2.71)$$
we obtain for Eq. 2.68

\[ S(q) = 1 + \bar{n} \frac{1}{2b} \int_{-b}^{b} dx_1 \int_{0}^{\infty} dr \int_{\theta_1(x_1,r)}^{\theta_2(x_1,r)} d\theta \sin \theta e^{iq_x r \cos \theta} \int_{0}^{2\pi} d\phi e^{iq_y \sin \theta \cos \phi}, \]  

(2.72)

where the angles \( \theta_1 \) and \( \theta_2 \) are expressed as functions of \( x_1 \) and \( r \). The integration over \( \phi \) yields

\[ \int_{0}^{2\pi} d\phi e^{iq_y \sin \theta \cos \phi} = 2\pi J_0(q_y r \sin \theta), \]  

(2.73)

where \( J_0 \) denotes the Bessel function of zeroth order. Defining the anisotropic packing function \( G(r, q) \) as

\[ G(r, q) \equiv \pi b \int_{-b}^{b} dx_1 \int_{\theta_1(x_1,r)}^{\theta_2(x_1,r)} d\theta \sin \theta e^{iq_x r \cos \theta} J_0(q_y r \sin \theta), \]  

(2.74)

we write the structure factor in Eq. 2.72 as

\[ S(q) = 1 + \bar{n} \int_{0}^{\infty} dr \int_{\theta_1(x_1,r)}^{\theta_2(x_1,r)} d\theta \sin \theta e^{iq_x r \cos \theta} J_0(q_y r \sin \theta), \]  

(2.75)

To the extent that our previous assumptions are valid, the effect of confinement is completely contained in the anisotropic packing function, independent of the form of \( g(r) \). Therefore, an analysis of \( G(r, q) \) brings out the difference compared with the fluid’s bulk structure. To our knowledge, there exists no analytical expression for the double integral in Eq. 2.74. By substituting \( \cos \theta = t \) we can write this integral in a more convenient form:

\[ G(r, q) = \frac{\pi}{b} \int_{-b}^{b} dx_1 \int_{t_1}^{t_2} dt e^{iq_x r t} J_0(q_y r \sqrt{1 - t^2}), \]  

(2.76)

with \( t_1 = \cos \theta_1 \) and \( t_2 = \cos \theta_2 \).

If \( b \) is much larger than the largest \( r \)-value, \( r_{max} \), for which \( g(r) - 1 \) is non-zero, the anisotropy due to confinement should disappear. In this bulk limit, \( t_1 = -1 \) and \( t_2 = 1 \), and we find

\[ G_b(r, q) = 4\pi \int_{0}^{1} dt \cos(q_x r t) J_0(q_y r \sqrt{1 - t^2}). \]  

(2.77)

The latter integral is known [39]:

\[ G_b(r, q) = 4\pi \sin(q r) \frac{q}{qr}, \]  

(2.78)

where \( q = \sqrt{q_x^2 + q_y^2} \). Substituting Eq. 2.78 in Eq. 2.72 we regain the expression for the bulk structure factor \( S_b(q) \) in Eq. 2.61. Whereas for a given \( r \)-value the function
Figure 2.8: Numerical calculation of $G(r, q)$ for a cavity uniformly filled with colloid. The following parameters were assumed: $r = 150\,\text{nm}$, $w = 300\,\text{nm}$ and $R = 50\,\text{nm}$. Top: 2D calculation. Bottom: sections along the $q_y$-direction at $q_x = 0$ and along the $q_z$-direction at $q_y = 0$. 
Figure 2.9: Numerical calculation of $S(q)$ for a cavity uniformly filled with colloid. The following parameters were assumed: $R = 50\text{ nm}$, $\phi = 0.2$ and $\psi = 300\text{ nm}$. For the pair distribution function $g(r)$, the Percus-Yevick hard-sphere approximation has been taken (see Fig. 2.6). Top: 2D calculation. Bottom: sections along the $q_x$-direction at $q_x = 0$ and along the $q_y$-direction at $q_y = 0$. 
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$G_b(r, q)$ is constant along circles $q_x^2 + q_y^2 = C(r)$ in reciprocal space, the function $G(r, q)$ for the confined fluid is expected to be constant along contours elongated along the direction of confinement (ellipses).

As an example, the integral in Eq. (2.76) has been calculated numerically for $r = 150 \text{ nm}$, $w = 300 \text{ nm}$ and $R = 50 \text{ nm}$ (see Fig. 2.8). Sections along the $q_x$- and $q_y$-directions, at $q_y = 0$ and $q_x = 0$ respectively, show the expected elongation of $G(r, q)$ along the confinement direction, but it also shows stronger peaks in the non-confinement direction. This is due to the absence of close neighbor particles in the confinement direction. Obviously, a packing of particles at a distance $r = 150 \text{ nm}$ to each other confined in a cavity of width $w = 300 \text{ nm}$ cannot give a strong correlation in the confinement direction, simply because at most two particles can be accommodated along this direction.

The structure factor in Eq. (2.72) can be obtained numerically from the $G(r, q)$ in Eq. (2.76) using the Percus-Yevick pair distribution function for a hard-sphere model (see Fig. 2.6). Fig. 2.9 shows the calculated $S(q)$ for a hard-sphere model of 50 nm radius colloidal particles with volume concentration $\phi = 0.2$ confined in a cavity of width $w = 300 \text{ nm}$. A section along the $q_y$-direction at $q_x = 0$ (non-confinement direction) shows a structure factor almost identical to the one corresponding to the bulk hard-sphere model in Fig. 2.6. The maximum of $S(q)$ in this direction depends on the volume concentration of particles and its position is given by $q_{max} \approx 2\pi/(2R)$. By contrast, the structure factor peak in the confinement direction is much weaker. This can be understood by considering the smaller amount of neighboring particles along the confinement direction in comparison to the other direction (excluded volume effect). In addition, one notices that the position of the structure factor peak in the non-confinement direction is slightly shifted to higher $q$-values. This might seem meaningless from a physical point of view, since it would correspond to distances smaller than a particle diameter. The shift is a consequence of the smearing of the peak and can be interpreted as a compression of the structure in the confinement direction.

Gaussian density distribution of colloid within the cavity

We now consider a Gaussian distribution for the number density which is peaked at the center of the cavity. This model corresponds with a single layer in the cavity. The probability $P(x)$ in Eq. (2.66) has the form

$$P(x) = \frac{1}{\sigma \sqrt{2\pi}} e^{-x^2/(2\sigma^2)}$$

(2.79)

The full width at half maximum of the Gaussian, FWHM = $2\sqrt{2 \ln 2} \sigma$, is chosen such that the probability at the walls is close to zero. The integration range for $x$ and $x_1$
Figure 2.10: Numerical calculation of $S(q)$ for a Gaussian distribution of colloid with FWHM = 100 nm, $R = 50$ nm and $\phi = 0.2$. For the pair distribution function $g(r)$, the Percus-Yevick hard-sphere approximation has been taken (see Fig. 2.6). Top: 2D calculation. Bottom: sections along the $q_y$-direction at $q_x = 0$ and along the $q_x$-direction at $q_y = 0$. 

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can then be extended to \([-\infty, +\infty]\). The anisotropic packing function for the Gaussian density distribution is given by

\[
G(r, q) = N \frac{1}{2\pi \sigma^2} \int_{-\infty}^{\infty} dx_1 e^{-x_1^2/(2\sigma^2)} \int_0^{\pi} d\theta \sin \theta e^{-(x_1 + r \cos \theta)^2/(2\sigma^2)} e^{iq_x r \cos \theta} \cdot \int_0^{2\pi} d\phi e^{iq_y r \sin \theta \cos \phi} \\
= N \frac{\sqrt{\pi}}{\sigma} \int_{-1}^{1} dt e^{-t^2/(4\sigma^2)} e^{iq_x t} J_0[q_y \sqrt{1-t^2}],
\]

where we have substituted \(\cos \theta = t\). Eq. 2.80 can be solved numerically in the same way as was done for the uniformly filled colloid. The resulting structure factor \(S(q)\) can be obtained from Eq. 2.75. Fig. 2.10 shows the calculated \(S(q)\) for a Gaussian density of hard spheres of radius \(R = 50\) nm and volume concentration \(\phi = 0.2\). To compare with the uniformly filled colloid, a FWHM of 100 nm was chosen, so that the Gaussian distribution is close to zero at the walls of a cavity of width \(w = 300\) nm. As expected, the \(S(q)\) presents a more pronounced anisotropy than for the uniformly filled cavity.

One could apply the Gaussian distribution model to the case of a colloid distributed in more layers parallel to the cavity walls, namely by considering each layer as a Gaussian distribution of particles. Nevertheless, this model would probably not be realistic, since we know that the inter-layer distance in a hard-sphere liquid is of the order of the particle size, i.e. the FWHM of the Gaussian. Consequently, there exist correlations between particles from neighboring layers which are not taken into account in a model of independent Gaussian distributions.

### 2.3 Dynamical scattering effects

In the problem considered here, one should see a single period of the array as a three-dimensional object in which x rays enter from one side and get reflected and refracted at the interface between Si and colloidal suspension. This dynamical effect, which increases with increasing \(h\), affects the diffraction efficiencies given by Eq. 2.30, which may therefore fail in fitting the data. Additionally, colloidal particles which are very close to the cavity walls may see a wavefront which is modified by the dynamical scattering. This can give rise to anomalies in the diffuse scattering.

The propagation of x rays through one cavity is studied using the wave equation. The Beam Propagation Method (BPM) is a numerical method to calculate the propagation of an electromagnetic field through a medium. In this section it is shown how BPM calculations enable us to evaluate the dynamical effects.
2.3.1 Propagation of x rays through an empty cavity

The propagation of an electromagnetic wavefield $\psi(x,z)$ in the $z$-direction through a single period of the array with refractive index $n(x,z)$ is described by the wave equation

$$\frac{\partial \psi(x,z)}{\partial z} = \frac{i}{2k} \left\{ -\frac{\partial^2 \psi(x,z)}{\partial x^2} - k^2 [n(x,z)^2 - 1] \psi(x,z) \right\}, \tag{2.81}$$

which is derived from the Maxwell equations under the paraxial or parabolical approximation [40]. This approximation is valid in our case because the following conditions are fulfilled:

1. $\Delta n/n \ll 1$, with $\Delta n$ being the variation in the refractive index over a distance of one wavelength. For x rays with $\lambda \sim 1\ \text{Å}$, $n \sim 1$ and $\Delta n \sim 10^{-6}$. Hence this condition is always fulfilled.

2. $\Delta k_x/k_x \ll 1$, where $\Delta k_x$ is the spread in $k_x$. In diffraction from microcavity arrays this condition is satisfied because the scattered angular spread is very small due to the large period $p \gg \lambda$.

The Beam Propagation Method (BPM) solves Eq. 2.81 numerically. For an explanation of how this computational method works we refer to [3].

![Figure 2.11](image)

Figure 2.11: (a) BPM calculation of the propagation in the $z$-direction of x-rays through one period of the array. The absolute value of $\psi(x,z)$ is shown. (b) Phase shift profile at the exit of the cavity, obtained from the field propagation in (a). Parameters used in the calculation are as given in the text.

Fig. 2.11a shows the field amplitude $|\psi(x,z)|$ calculated by the BPM in a single period $p = 1\ \mu m$, with $h = 6\ \mu m$, gap width $w = 500\ \text{nm}$ and tapering angle $\theta = 0.14^\circ$. A plane wave at normal incidence was assumed at the entrance of the medium. Step widths of $\Delta x = 1\ \text{nm}$ in the $x$-direction and $\Delta z = 6\ \text{nm}$ in the $z$-direction were taken.
and a wavelength $\lambda = 1 \text{ Å}$ was assumed. Fig. 2.11b shows the calculated phase shift of the wave front at the exit of the cavity. As a consequence of dynamical scattering, oscillations in the phase profile are present next to the Si/air interface, arising from reflection and refraction of waves.

The dynamical effects arising next to the cavity walls have important consequences for the Bragg scattering from the array when the height $h$ of the structures is large. In the diffuse scattering from the colloidal particles we also see a dynamical effect. This does not arise from propagation effects through the colloidal particles, but from the oscillating field next to the cavity walls, which effectively modifies the form factor of the colloidal particles. Both effects are discussed in the following sections.

### 2.3.2 Dynamical effects in Bragg scattering

In order to evaluate the dynamical effects in our cavities, a comparison with the kinematical theory is needed. In concrete, we are interested in knowing the height $h$ of our structures up to which a kinematical approach is sufficient.

For this purpose, we have calculated the diffraction efficiencies of empty microcavity arrays for three different $h$ values according to the kinematical and the dynamical theory. The results are shown in Fig. 2.12 for (a) $h = 1 \mu\text{m}$, (b) $h = 6 \mu\text{m}$ and (c) $h = 12 \mu\text{m}$. For each case, we plot the amplitude and the phase shift of the wave field over half a period of the grating, as well as the calculated diffraction efficiencies up to the 50th diffraction order. In all cases, a period $p = 1 \mu\text{m}$, a tapering angle $\theta = 0.14^\circ$ and a duty cycle $w/p = 0.43$ were assumed.

For the height $h = 1 \mu\text{m}$, small wiggles in the field amplitude are visible near the walls after propagation through the cavity, as opposed to a simple kinematical field projection. Nonetheless, the diffraction efficiencies calculated in both cases differ only little up to the 50th diffraction order, indicating that, at this height, the kinematical theory is a good approximation. For $h = 6 \mu\text{m}$, the propagated field exhibits stronger wiggles and this results in a larger discrepancy between the kinematical and the dynamical approach. But again, disregarding discrepancies for low efficiency orders, we find a reasonable agreement up to order 40. The problems arise for the height $h = 12 \mu\text{m}$. In this case it is found that the kinematical and dynamical calculations agree only up to the 13th order.

Let us discuss a practical example in which we have a 1 $\mu\text{m}$-period array of microcavities with a height $h = 12 \mu\text{m}$ filled with a suspension containing 100 nm-diameter colloidal particles which order in layers separated by one particle diameter. We neglect propagation effects through the colloidal particles, since they are very thin objects. The ordering effects from the colloid show up at every tenth diffraction order from the microcavity array. Moreover, the number of the diffraction order gives the resolution in real space in terms of particle size: the 10th diffraction order gives a resolution equal
Figure 2.12: Comparison of kinematical and dynamical calculations of diffraction efficiencies of 1 μm-period Si microcavity array with a gap width $w = 430$ nm, i.e. duty cycle $w/p = 0.43$. A tapering angle of $\theta = 0.14^\circ$ has been assumed in all three cases. The structure heights are (a) $h = 1 \mu m$, (b) $h = 6 \mu m$ and (c) $h = 12 \mu m$. A wavelength $\lambda = 1 \AA$ has been used.
to one diameter, the 20th diffraction order gives a resolution of half a diameter, and so on. To study a layered colloid with a resolution of 1/5th of the oscillation period, one needs to measure and fit diffraction efficiencies from the microcavity array up to the 50th order, and then a dynamical approach needs to be considered. If, on the other hand, one only wants to verify whether there is a layering with a periodicity equal to the size particle, then 15 diffraction orders are enough and one can follow a simple kinematical approach to deal with the problem.

2.3.3 Dynamical effects in diffuse scattering

The theoretical form factor of a spherical colloidal particle with radius $R$ has zeros at $q$-values satisfying $\tan(qR) = qR$ (see Eq. 2.55). The propagating field within a cavity shows oscillations in the proximity of the cavity walls, as shown in Fig. 2.11. If a colloidal particle is lying next to the wall, it will no longer be illuminated by a planar wavefront and this will effectively modify the form factor. In the following, we present a calculation of the form factor of a particle illuminated by a wavefront distorted by dynamical effects. This we call the dynamical form factor, to be compared with the kinematical form factor as given by Eq. 2.55.

![Figure 2.13: Oscillatory field, incident on a colloidal particle.](image)

We consider a cavity of width $w$, height $h$ and slightly tapered walls, with one colloidal particle at a distance $x_0$ from the wall of the cavity and at a distance $z_0$ from the entrance of the x rays in the cavity (see Fig. 2.13). The oscillating field at a distance $z_0$ can be calculated with the BPM as described in the previous sections. We can safely assume that the size of the colloidal particle $2R = 100 \text{ nm}$ is too small for dynamical effects to take place. Thus we simply multiply the transmission function of the colloidal particle with the propagated field at $z_0$. Finally, a fast fourier transform
(FFT) of the resulting field in the $x$- and in the $y$-directions is performed. In order to reproduce scattered intensities, the results are squared: $|\text{FFT}|^2$. Fig. 2.14 shows the results of the calculation (red curves), compared with the kinematical expression $|\tilde{F}(q)|^2$ (black curves). In this example, the colloidal particle was placed at position $z_0 = 6 \mu m$ and $x_0 = 50 \text{nm}$, i.e., the particle is touching the wall of the cavity. We observe that the minima of the dynamical form factor are filled considerably more along the confinement direction than along the other direction. The oscillating field incident on the particle is equivalent to scattering from different angles on the particle, which induces angular shifts in the scattered signal. The effect is more pronounced near the minima of the form factor.

Figure 2.14: Calculated squared modulus of the form factor from a colloidal particle of radius $R = 50 \text{nm}$, placed at a distance $z_0 = 6 \mu m$ from the entrance and at a distance $x_0 = 50 \text{nm}$ from the wall. The red curves show the results of the calculation, whereas the black lines indicate the calculated intensity for a planar incident wavefront ($|\tilde{F}|^2$ in Eq. 2.55). Top: scattered intensity along the $q_y$-direction. Bottom: scattered intensity along the $q_x$-direction.

Additional calculations with different values of $x_0$ and $z_0$ show the trends of the dynamical form factor. For increasing $z_0$, the filling of the minima of the form factor in the $q_x$-direction is larger, since the propagation effects next to the cavity walls increase. On the other hand, the effect diminishes fast as the sphere is placed further from the wall, since the field oscillations decrease rapidly toward the center of the cavity. For example, at $x_0 = 75 \text{nm}$ in the previous example, i.e. only $25 \text{nm}$ away from the wall,
there is no dynamical effect at all. Since propagation effects in the cavities take place only next to the walls, the oscillating field in this region does not depend on the width of the cavity. Therefore, the dynamical form factor does not depend on $w$, (provided that $w/h$ is small enough that waveguiding effects are absent).

So far, only the presence of one single colloidal particle next to the wall was discussed. The dynamical effect on the diffuse scattering is expected to increase if many particles are touching the walls at different positions along the $z$-direction. However, the contribution from many more particles which are not close to the cavity weakens the relative importance of the dynamical effect. It should therefore decrease for increasing $w$. 
Chapter 3

Colloidal systems and their characterization

A colloidal suspension can be regarded as a scaled-up model of molecular fluid. For this purpose, a solution of monodisperse colloidal particles with hard-sphere-like interactions is optimal. Small-angle x-ray scattering (SAXS) measures the size and polydispersity of the colloidal particles, as well as the fluid structure factor. In this chapter, we briefly introduce the bulk colloidal suspensions needed in our confinement experiments, namely charged-stabilized silica spheres in an alcohol mixture. We further show SAXS experiments which measured the size and polydispersity of the colloidal particles and the liquid structure factor.

3.1 Colloidal suspensions

Colloidal dispersions are complex fluids in which nanometer- or micrometer-sized particles are dispersed in a solvent. The size of the colloidal particles is larger than the solvent constituent molecules, but still small enough that their movement is determined by thermally activated Brownian motion rather than gravitational settling or sedimentation. Some examples of colloidal dispersions are permanently present in our daily lives (detergents, clays, paints, inks).

Colloidal solutions are frequently seen as scaled-up models of atomic or molecular systems [41] for studying processes like nucleation [42], melting and freezing [43], glass transition [44] and behavior in confining geometries [45]. Due to their Brownian motion, colloidal particles behave like atomic or molecular systems, even if the time scales of the motion and the nature of the inter-particle interactions are not the same. The advantages of working with charge-stabilized colloidal particles are that their size often allows optical microscopy studies, unlike in molecular systems, and that it is possible to control their interactions by simple addition of salt. We work with particles of 100-120 nm diameter, which fit a number of times within a cavity width of a few hundred
nanometer. This size is too small for video microscopy but optimal for SAXS.

Colloidal particles attract each other due to van der Waals forces which make them agglomerate and precipitate with gravitation. One way to avoid this problem is by working with sterically stabilized colloidal particles, in which short polymer chains are adsorbed on the surface of the colloidal particles. In this way, when two particles approach each other, the repulsive interaction between the polymer layers on the two particles prevents them from aggregation. The van der Waals interactions between colloidal particles can be reduced when the solvent has the same optical refractive index as the colloidal particles. Some examples of optical index matching between colloidal particles can be found in the literature: PMMA particles in a mixture of decalin and carbon disulphide 2.66:1 [46], silica particles in a mixture of ethanol and benzyl alcohol 1.22:1 [47] or silica particles in dimethylformamide (DMF) [48].

\[ U_{HS}(r) = \begin{cases} \infty & \text{if } r \leq 2R \\ 0 & \text{if } r > 2R, \end{cases} \]  

where the variable \( r \) denotes the distance between the centers of the two particles and \( R \) is the radius of the spheres (see Fig. 3.1a). One can imagine a hard-sphere colloidal solution like a set of billiard balls dispersed in a liquid with a Brownian motion and moving freely in 3D space, with absolutely no interaction between each other, unless they touch.

Simulations and theoretical studies predict several phases in hard-sphere systems, depending on the volume fraction \( \phi \) of the particles in the solution [49]. As shown in Fig. 3.2 hard spheres behave like a fluid until they reach a volume concentration \( \Phi_F = 0.494 \), and then they enter an intermediate region until they crystallize at \( \Phi_M = 0.535 \). In the intermediate phase between freezing \( (\Phi_F) \) and melting \( (\Phi_M) \), both phases
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coexist. For still increasing volume fraction, the system goes through a heterogeneously nucleated crystal phase and then a glass phase. The random close packing limit is reached at $\Phi_{RCP} = 0.64$. Experimentally, these results have been obtained for sterically stabilized PMMA spheres, in which the effective hard sphere radius is slightly larger than the radius of the particles [46].

Figure 3.2: Predicted phases of a hard-sphere colloidal system as a function of the volume fraction of particles in solution (from Pusey [49]).

In some colloidal systems, charged particles interact through a strong, long-ranged Coulombic potential. Ionic groups present at the surface of colloidal particles can dissociate when dissolved in a polar liquid like water, resulting in a nett charge at the surface of the particles. The counterions are dispersed in the liquid, but they surround the particles due to charge attractions, forming an electrical double layer. The screened repulsive Coulomb potential produced by the charges keeps the particles away from each other, preventing aggregation. Such suspensions are far away from hard-sphere models.

When ions are added to a charged-stabilized colloidal suspension, the positive and negative charges flow in the solvent and provide more screening to the Coulomb repulsive interactions between the particles (see Fig. 3.1b). The screened Coulombic or Yukawa potential taken from the Derjaguin, Landau, Verwey and Overbeek theory (DLVO) provides an approximative analytical expression for the effective pair interaction between charged colloidal particles in electrolyte solvents [49]:

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Chapter 3 Colloidal systems and their characterization

\[
\frac{U^{SC}(r)}{k_B T} = \begin{cases} 
\frac{Z^2 e^2}{4\pi\varepsilon_0 \varepsilon_r k_B T} \left( \frac{\infty}{(1+\kappa R)} \right)^2 e^{-\kappa r} & \text{if } r \leq 2R \\
\varepsilon_r k_B T \left[ e^{2(\bar{n}|Z|+2n_s)} \right] & \text{if } r > 2R,
\end{cases} \tag{3.2}
\]

where \(\varepsilon_r\) is the dielectric constant of the solvent, \(Z\) is the surface charge of the colloidal particle and \(\kappa^{-1}\) is the so-called Debye screening length:

\[
\kappa^{-1} = \sqrt{\frac{\varepsilon_0 k_B T}{e^2(\bar{n}|Z|+2n_s)}}. \tag{3.3}
\]

In Eq. 3.3, \(\bar{n}\) is the number density of colloidal particles and \(n_s\) the number density of monovalent electrolyte in the solvent. In the absence of ions in the solvent, \(\kappa(r-2R) \to 0\) and the colloidal particles interact through a long-ranged Coulomb potential. If, on the other hand, the amount of ions in the solvent is such that \(\kappa(r-2R) \to \infty\), the potential becomes strongly screened. The screening length \(\kappa^{-1}\) determines the effective radius of the hard spheres. For strongly screened potentials \((\kappa^{-1} \lesssim 1 \text{ nm})\), the van der Waals attraction may dominate in the interactions between colloidal particles, if the optical refractive index of the particles is not matched to that of the solvent. This can result in unstable systems where the particles cluster and, eventually, precipitate due to gravitation.

Charge-stabilized suspensions have a phase behavior different from that of hard spheres, depending on the screening length \(\kappa^{-1}\). Deionized suspensions (large \(\kappa\)) tend to freeze at much lower volume fractions than hard-spheres systems. The crystallization of charge-stabilized colloid suspensions as a function of the range of the interaction potential has been studied with numerical simulations in [50].

Ion exchange resin is a substance which scavenges the ions from the solvent. Ion exchange resins are used in charged-stabilized colloidal suspensions to attract the extra ions of the solvent and prevent them from screening the Coulombic interaction between the colloidal particles. In this way, colloidal suspensions can be stored for a long time without risk of aggregation and precipitation of the particles.

### 3.2 Small angle x-ray scattering from colloidal suspensions

The scattered intensity from a homogeneous, bulk colloidal suspension is

\[
I_b(q) \propto |\bar{F}(q)|^2 \cdot S_b(q), \tag{3.4}
\]

with \(\bar{F}(q)\) the dimensionless form factor defined in Eq. 2.55 and \(S_b(q)\) the structure factor of a bulk liquid, which is related to the pair distribution function \(g(r)\) via Eq. 2.61.

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Figure 3.3: Calculated form factors of spherical colloidal particles of radius $R$ for different polydispersities $\delta$. The plot in the inset shows the Schulz distributions of radii entering the calculations.

The pair distribution function $g(r)$ describes the ensemble average of the inter-particle correlations in the fluid.

The scattered intensity from a single spherical particle is proportional to $|\tilde{F}(q)|^2$ and is plotted in Fig. 3.3 as a function of $qR$ (black solid line). Plotted as a function of the momentum transfer $q$, the positions of the minima of the experimental form factor yield the size of the particles. In practice, the particles of a colloidal suspension do not have the same size, but they are polydisperse. Their size is represented by a distribution function of radii $C(R)$ with a variance $(\Delta R)^2$ and a mean value $R_0$. The degree of polydispersity is defined as $\delta = \Delta R / R_0$. The resulting form factor can be expressed as \[51\]

\[ |\tilde{F}(q, C(R))|^2 = \int_0^\infty C(R) |\tilde{F}(q, R)|^2 \left( \frac{R}{R_0} \right)^6 dR. \]  

(3.5)

The integrand in Eq. 3.5 is weighted by $(R/R_0)^6$ to take into account that the scattered amplitude from a sphere is proportional to its volume. For spherical colloidal particles, a Schulz distribution can be used \[51\]:

\[ C(R) = \frac{R^Z}{\Gamma(Z + 1)} \left( \frac{Z + 1}{R_0} \right)^{Z+1} e^{-(Z+1)R/R_0}, \]  

(3.6)

where $\Gamma$ denotes the gamma function. The parameter $Z$ is related to the polydispersity.
by

$$\delta = \frac{1}{\sqrt{1 + Z}}.$$  \hspace{1cm} (3.7)

Fig. 3.3 displays calculated form factors for colloidal particles having different polydispersities. The effect of the polydispersity is to smear the maxima and minima of the function in Eq. 2.55. In the inset of the figure, the corresponding Schulz distributions are shown. At large polydispersities, the Schulz distribution is asymmetric with respect to $R = R_0$. It becomes a Gaussian when $Z$ (related to $\delta$ via Eq. 3.7) increases and it tends to a Dirac delta function when $Z \to \infty$.

The pair distribution function $g(r)$ can be calculated for different models of the interaction between the colloidal particles. In Fig. 2.6a we showed calculations of the Percus-Yevick pair distribution function for a hard-sphere model with spheres of radius $R = 50$ nm. The correspondent structure factors are plotted in Fig. 2.6b as a function of $q$. They have a maximum at $q = 2\pi/(2R)$, and they oscillate with an amplitude dependent on the volume fraction $\phi$. Note that $S_b(q) \to 1$ as $q \to \infty$, indicating the absence of inter-particle correlations when the particles are far from each other.

In charge-stabilized colloidal solutions, the structure factor has a stronger peak in comparison with the structure factor from hard-sphere suspensions \cite{52}. The reason for this is that the inter-particle correlations are stronger due to the Coulombic potential and the fluid presents a more pronounced order. In these systems, the position of the first maxima of the structure factor is situated at $q_{\text{max}} = 2\pi/(2R_{\text{eff}})$, with $R_{\text{eff}}$ being the effective radius of the colloidal particles, determined by the screening length: $R_{\text{eff}} = R + \kappa^{-1}$.

Experimentally, the structure factor from a colloidal suspension is obtained by dividing the scattered intensity from the sample by $|\tilde{F}(q)|^2$, which can be measured for a diluted sample or calculated via Eq. 2.55. The result is scaled in such a way that $S_b(q) \to 1$ when $q \to \infty$, the scaling factor being the ratio of the number of particles in the concentrated sample to that in the diluted sample.

![Figure 3.4: Experimental setup for small-angle x-ray scattering (SAXS).](image-url)
The experimental setup for small-angle x-ray scattering is schematically shown in Fig. 3.4. The momentum transfer $q$ is related to the scattering angle $\theta$ through:

$$q = \frac{4\pi}{\lambda} \sin(\theta/2) \approx \frac{2\pi \theta}{\lambda}. \quad (3.8)$$

For particles of radius $R = 50 \text{nm}$ and x rays with wavelength of $\lambda = 1 \text{Å}$ the first minimum of the form factor corresponds to a scattered angle $\theta \sim 1 \text{mrad}$ and the first maximum of the structure factor would be at even smaller angles. In order to separate at these small angles the scattered beam from the direct beam, two slits are used: the first one to define the incident beam and the second one, placed right in front of the sample, to block any intensity diffracted from the first one. The detector is placed at a large distance (typically $\sim 10 \text{m}$) from the sample in order to increase the angular resolution. Over such large paths of the x rays, air scattering and absorption are a problem. For this reason, flight tubes filled with He or evacuated are placed between the sample and the detector.

### 3.3 Silica suspensions as molecular models for studies of ordering phenomena

We have chosen suspensions of charge-stabilized silica spheres as models of a molecular fluid. The required characteristics for such suspensions are monodispersity of the colloidal particles and minimal inter-particle interaction. The latter is controlled by screening the Coulomb potential of the charged particles with extra ions dissolved in the solution. To avoid aggregation of the particles, the attractive van der Waals interactions between the particles are minimized by matching the optical refractive index of the solvent to that of the colloidal particles.

Silica spheres of different mean sizes ($R = 55$ and $59 \text{nm}$) were fabricated with a very low polydispersity ($\delta < 0.05$) in the Debye Institute of Utrecht University. The density of the spheres is $\rho_c = (1.93 \pm 0.03) \text{ g/cm}^3$ and they have an optical refractive index $n_c = 1.463$. The colloidal suspensions were prepared at the Van der Waals-Zeeman Insititute in Amsterdam in collaboration with the group of Dr. G. H. Wegdam. The same colloidal particles have previously been used in a number of experiments, e.g. [14] [17], where they showed good stability when suspended in an index-matched mixture of benzyl-alcohol/ethanol or water/glycerol. The first solvent was chosen, since it has the appropriate viscosity for our purpose.

The colloidal particles were stored as an aqueous solution of low volume concentration. In order to prepare the suspensions, we needed to centrifuge the stock solutions at $5000 \text{ rpm}$ for sedimentation and extraction from the original solvent. This process was repeated several times while adding an amount of ethanol after every step in order to make sure that the largest possible amount of particles precipitate and that the original
solvent is completely removed. It is recommended to centrifuge in several short cycles of few minutes each rather than in a very long single cycle. In this way one avoids the sedimentation to be so strong that the particles do not dissolve again. Afterwards, the process is repeated a few times using the final solvent. A mixture of 55% benzyl alcohol and 45% ethanol is estimated to have an optical refractive index identical to that of the colloidal particles \((n_c = 1.463)\). If the solvent does not match exactly the refractive index of the colloidal particles, the solution looks turbid due to multiple light scattering. By adding small drops of either one component of the solvent mixture, we achieve an exact match, and then the sample suddenly becomes transparent.

Initially, suspensions with a high volume concentration were prepared. To obtain lower concentrations the sample was diluted by adding specific amounts of the same solvent. The maximum concentration recommended is around \(\phi = 0.18\), above which aggregation and precipitation of colloidal particles can occur. To measure the concentration of the initial suspension, a large and precisely known amount is weighed in a closed scale with a high precision (error \(\pm 10^{-5}\) g) and then the volume concentration of colloids in the solution is determined from the size of the colloidal spheres. In order to keep highly concentrated colloidal suspensions stable for a long time, very pure benzyl alcohol and ethanol (pa. 99.8%) were used in the solvent. Additionally, an ion-exchange resin was deposited at the bottom of the bottle containing the suspension in order to scavenge counter ions from the solvent and keep a strong Coulomb interaction between the charged colloidal spheres. In this way, colloidal suspensions can be kept stable for several months.

We characterized our colloidal sample by means of SAXS. As an example, let us consider a suspension of silica spheres of 55 nm radius silica in an index-matched mixture of benzyl alcohol and ethanol. The suspension had a relatively high volume concentration of approximately \(\phi = 0.1\). It was kept for several months with ion-exchange resin and therefore it was deionized. The SAXS measurements were performed at the ID02 beamline at ESRF using the setup shown in Fig. 3.4. The photon energy was 12.46 keV and the distance between the sample and the detector was 10.064 m. For the determination of the size and polydispersity of the sample, a small amount of the suspension was diluted in an index-matched mixture of benzyl alcohol and ethanol and introduced in a 2 mm-diameter glass capillary, whose sides were sealed afterwards with a bit of wax. The scattered intensity from the sample was recorded with a 2D detector.

The red curve in Fig. 3.5 shows the measured intensity averaged over all angles in a cone corresponding to a given \(q\)-value as a function of \(q\). The data have been background corrected by subtracting a similar measurement through a capillary filled with solvent only. The black line is a fit to the data using the theoretical form factor of a sphere in Eq. 2.55 convoluted with the size distribution given by the Schulz function in Eq. 3.6. The measurement is scaled in such a way that both curves overlap at large \(q\) values. The best fit-values for the radius of the sphere and the polydispersity are
Figure 3.5: Form factor fit for the characterization of a diluted colloidal suspension. The red curve is the measured scattered intensity from the sample and the black curve is a fit of the theoretical form factor of a sphere. The plots are scaled in such a way that they coincide at large $q$ values.

Figure 3.6: (a) Comparison of the measured scattered intensity from a colloid with a volume concentration $\phi = 0.1$ and the calculated form factor. (b) Measured structure factor of the same colloid.
Chapter 3 Colloidal systems and their characterization

\[ R_0 = (54.6 \pm 0.2) \text{nm} \text{ and } \delta = (0.030 \pm 0.005) \text{.} \] The measurement and the calculation differ significantly at small \( q \) values due to the structure of the fluid. Even if the sample is very diluted (\( \phi < 0.005 \)), the strong Coulomb repulsion between the particles in the deionized suspension is responsible for a structure factor peak which is probably showing at very small \( q \) values, where no data points are available due to the presence of a beamstop in front of the detector. Nevertheless, the data at large \( q \)-values gives a precise measurement of the radius and the polydispersity of the colloidal spheres.

The same solution but with volume concentration \( \phi = 0.1 \) was prepared in a capillary in a similar way. The measured scattered intensity after background correction is shown in the blue curve of Fig. 3.6b, together with the calculated form factor. The structure factor is obtained by dividing the measured intensity by the calculated form factor, as shown in Fig. 3.6b. The result shows a hard sphere-like structure factor, with a faint peak at approximately \( q = 0.035 \text{nm}^{-1} \), indicating an effective radius \( R_{\text{eff}} = 180 \text{nm} \). For a sample which was kept for months with ion-exchange resin, the structure factor from such a concentrated suspension is expected to be much stronger. Nevertheless, if the sample was contaminated with extra ions in the solvent during the preparation process by, for example, touching with a dirty pipette or by handling the instruments without gloves, the repulsive interactions between the particles can be drastically screened, providing an almost perfect hard-sphere system like the one observed here.

This shows how delicate the systems are and how much care must be taken in handling the samples properly. In the confinement-induced experiments, microcavities are used as containers. As explained in section 4.3, a microchannel system is used for the on-line filling of the suspensions in the microcavities, and this process could affect the structure of the fluid due to contamination with extra ions in the solvent. Therefore, it is extremely important to perform in-situ measurements on the bulk fluid after filling of the microcavity array. For this end, a special container for bulk fluid is etched into the array (see section 4.3).

In conclusion, charge-stabilized silica suspensions with volume concentrations up to \( \phi = 0.1 \) can serve as good models of hard-sphere systems. The low polydispersity and the possibility to screen the Coulomb interaction between the particles have been demonstrated with SAXS. Experiments show drastic changes of the screening length of the Coulomb potential even without adding salt in the system, revealing the importance of a proper handling of the samples and of on-line measurements on bulk suspensions during the experiments with confined fluids.
Chapter 4

Fabrication and characterization of microcavity arrays

4.1 Introduction

The confinement-induced ordering phenomena in colloidal suspensions are investigated in cavities with wall separations ranging from 300 nm to 1000 nm. The fabrication of such structures requires lithography and etching techniques in order to achieve periodical and identical cavities within a precision of a few nanometers. Another requirement for the experiment is the filling of the cavities with the colloidal solution, which has to be fast and gentle in order to be performed on-line without losing the alignment of the sample with respect to the x-ray beam. For this purpose, microfluidic channels were etched to connect the microcavity arrays to an external microfluidic system. In the next two sections of this chapter, the fabrication process of microcavity arrays and the design of the microfluidic channels are described.

The size of the resulting structures is obviously large enough that scanning electron microscopy (SEM) can be used for their characterization. Nevertheless, because the experiments with colloidal solutions are to be performed with synchrotron radiation, it is important that the microcavity arrays are characterized by x-ray diffraction, which involves determining their shape, size and alignment before the filling process. In addition, the x-ray diffraction measurements are affected by roughness of the cavity walls and dynamical scattering effects. These aspects will be discussed in the fourth section of this chapter.

The main characteristics of the microcavity arrays are summarized in the last section. Also other applications of these structures are mentioned here.
4.2 Fabrication process

The main parameters of the microcavity arrays are indicated in Fig. 2.2: the period $p$, the wall separation $w$, the height $h$ and the length of the grating $L$. The parameter $w$ is to be varied from approximately 300 nm to 1000 nm. The parameter $p$ is minimized as much as possible for two reasons: (a) it increases the angular resolution required for resolving the Bragg scattering peaks and (b) it increases the scattering volume. The latter point would also be a good argument for making $h$ and $L$ as large as possible. However, if $h$ is so large that strong dynamical scattering effects occur, the analysis of the diffracted signal becomes considerably more difficult. Moreover, as shown below, the fabrication process causes an unavoidable tapering of the walls of the cavities and one has to keep $h$ as small as possible in order to keep $w$ constant all along the cavity.

A third parameter in the optimization of $h$ arises from the phase shift difference $\Delta \phi$ between the optical path of x rays through Si and the optical path of the cavity filled with the colloidal solution. As a compromise, we choose values of $h$ in the range of 6 to 10 $\mu$m. This requires the fabrication of solid high-aspect-ratio microstructures. There is no limitation for the length $L$ of the grating in the fabrication process apart from exposure time with e-beam lithography.

The structures were fabricated using anisotropic wet etching of Si $<110>$ with KOH. This technique has previously been used for the fabrication of hard x-ray diffractive lenses [53] and other diffractive devices, such as partial decoherer gratings [54] and beam splitters for x-ray interferometry [55] [56]. The method used to fabricate the microstructures for these applications is described in [53]. In brief, the patterns are defined by electron beam lithography and transferred into chromium structures by a lift-off process, which results in a negative patterned structure, i.e. the lines written become the lines that serve as a mask for the wet Si etching (see Fig. 4.1). The lines were aligned to the $<112>$ crystallographic direction of the Si $<110>$ wafer with a precision of 0.1° to achieve a vertical etching of the structures with KOH. The resulting structures had an aspect ratio of up to 40, limited by capillary forces during the drying process, which made thin lines collapse. In addition, the interface between the chromium mask and the Si was not well sealed, and some small amount of KOH was penetrating this interface causing several small defects at the walls and on the top of the structures.

Therefore, a new approach to the fabrication was developed (see Fig. 4.2), resulting in high-quality microcavity arrays for the confinement of colloidal solutions [19]. Instead of a Cr lift-off, the PMMA structures resulting from the electron-beam lithography are used as a mask to etch the Cr from a layer previously grown on the substrate. In this way, a direct transfer of the pattern into the Cr is obtained, and the same later on into the Si wafer. The positive pattern transfer results in cavities etched into the Si (Fig. 4.2) rather than Si lines sticking out of the Si (Fig. 4.1). Additionally, another layer of SiO$_2$ between the Si and the Cr is used to create a double layer mask for the wet
etching of the Si. The SiO$_2$ layer is obtained by thermal oxidation of the Si substrate. For this reason, the SiO$_2$-Si interface is better sealed than the Cr-Si interface existing in the previous method. The use of the double Cr and SiO$_2$ mask has considerably improved the quality of the resulting structures, since the KOH does not penetrate the SiO$_2$-Si interface during the etching process.

### 4.2.1 Substrate preparation and alignment

For the preparation of the substrate, a <110>-oriented Si wafer of 250 $\mu$m thickness is first thermally oxidized to give an oxide thickness of about 50 nm and then coated by thermal evaporation with a layer of Cr of 40 to 100 nm thickness, depending on how deep the Si cavities have to be etched. For the electron-beam lithography, a layer of PMMA of 100 to 150 nm is spin-coated on the substrate. As sketched in Fig. 4.2d, the lines are patterned along the <112> crystallographic direction of the Si wafer, in order to obtain the most efficient anisotropic etching into the Si with KOH. This is achieved when the walls of the cavities are perpendicular to the <111> direction, since this crystallographic plane has a much slower etching rate than the <110> direction. Due to the small size of the structures, the precision of the alignment of the patterned lines needs to be within 0.1°.
The flat of the Si <110>-oriented wafers provided by suppliers is frequently not precisely aligned along the <112> direction. Therefore, every lot of wafers needs to be tested in advance in order to determine the misalignment of the flat within an accuracy of 0.1°. For this purpose, a 'star' profile consisting of lines with all possible orientations with an interval of 0.1° (see Fig. 4.3a) is transferred to a double-layer mask of SiO$_2$ and Cr and then the Si is etched with KOH. For the lines with an orientation far from <112>, the Si is etched under the mask until, at a certain point, the wall is completely etched away and the structures disappear. Only when the orientation of the lines is close to the <112> direction is the etching almost vertical and do the structures survive, reaching a high aspect ratio. Fig. 4.3b shows a microscope image of a test sample after a 15 µm deep wet Si etch. In this figure, the flat of the wafer and the <112> crystallographic direction are indicated with red lines. The latter was known from the optimal vertical etching achieved, resulting in the cavity with the smallest wall separation. The misalignment angle with respect to the flat is in this case $\Delta \theta = 1.1°$. Also other structures at -54.74° survive, where the <111> planes cross a <100> plane. These structures are not cavities, but they have tapered walls. At 70.5°, another <111> plane is crossing which also gives high-aspect-ratio structures, but this cannot be seen because it is out of the range of the picture. In principle one
could also choose this direction to fabricate high-aspect-ratio structures.

![Figure 4.3: (a) 'Star' profile for the determination of the <112> crystallographic direction on a <110> Si wafer. Lines with all possible orientations are patterned with electron-beam lithography in steps of 0.1° (not resolved in the picture). Inhomogeneities observed in some of the short lines are optical effects of the software used to visualize the exposed lines. (b) Lines far from the <112> direction disappear after wet etching of Si due to under-etching: the longest surviving line has the optimal orientation.]

Once the exact misalignment angle $\Delta \theta$ of the wafer flat is known, there are two possible ways to align the wafer in the electron-beam holder. The first possibility is to align the flat of the wafer to the holder and to pattern lines which are tilted by an angle $\Delta \theta$. Another possibility is to align the wafer with a misalignment of $-\Delta \theta$ with respect of the holder and then pattern vertical lines with the electron-beam. Both ways give equally good results in the electron-beam exposure of the structures.

### 4.2.2 Electron-beam lithography

Electron-beam lithography is a technique commonly used to pattern small structures on electron-sensitive resist materials such as polymers (e.g. polymethylmethacrylat or PMMA). Solutions of the resist are spin-coated onto the substrate of the sample and baked to leave a hardened thin film on the surface of the substrate. A focused electron beam is swept along the parts of the resist which are to be patterned. The electrons scatter in the exposed part of the resist, changing its properties, and then a developer dissolves the exposed regions (positive resist).

For the patterning of the lines in the fabrication of microcavity arrays, the LION-LV1 e-beam lithography system from Leica Lithographiesysteme Jena was used. This machine is operated in a continuous path mode, which allows us to expose curved and straight lines by moving the sample stage continuously under the beam. The line width can be increased continuously from 50 nm to many microns by changing the
defocus of the beam and the line dose. The e-beam has a very low energy (2.5 keV), which avoids proximity effects [58] and therefore the system is especially suited for the fabrication of diffractive optical elements, which usually requires a high precision of the width of the structures. Several apertures after the electron source of 10, 17, 30, 60 and 120 µm can select different currents for an optimization of the exposure times according to the size of the structures.

The pattern of the microcavity arrays consists of a set of parallel straight lines with the desired periodicity and line width, taking into account that the width increases after the anisotropic etch step with KOH due to a minor etching of the walls under the mask. This is explained in more detail in section (4.2.3). The width of the lines can be controlled to an accuracy of few nanometers as described in [57]. Line widths ranging from 70 nm until several hundreds of nanometers can be achieved using an aperture for the electron beam of 30 µm for thin lines and of 60 µm for thick lines. The lines are developed using a standard 1:3 mixture of MIBK (methyl isobutyl ketone) and IPA (isopropyl alcohol).

![Figure 4.4: Measured wall separation of microcavities after the whole fabrication process as a function of the defocus of the electron beam (left) and the line dose (right). All structures were etched simultaneously to a depth \( h = 8 \mu m \). The measurements were performed with a SEM having a resolution of approximately 10 nm.](image)

Fig. 4.4 shows the resulting wall separation \( w \) of several microcavities after the whole fabrication process as a function of the defocus of the e-beam defocus and the line dose used in the exposure. The line dose is the charge deposited into the resist per length unit, which is related to the speed of the sample stage under the beam and to the e-beam current. For the data shown here, the 30 µm aperture and a current of approximately 50 pA was used.
4.2.3 Plasma etching

After electron-beam exposure and development, plasma etching is used to etch the double-layer mask of SiO₂ and Cr. In this technique, a plasma is generated by applying a radio-frequency (RF) electromagnetic field to the electrodes of a chamber containing a low-pressure gas. Under these conditions, the plasma contains different gaseous species including atoms, ions, free radicals and electrons, which can be used to etch different materials, depending on the gas chosen.

For the etching of Cr (Fig. 4.2c), the BMP from Plasma Technology GMBH with a 1:1 mixture of Cl₂ and CO₂ is used (see table 4.1). The two electrodes of the BMP machine have the same size, leading to a negligible bias voltage which results in an almost isotropic etching of the material. In this process, the patterned PMMA is used as a mask for the Cr. The etching ratio between the PMMA and the Cr is about 1:2 and the experimental etching rate of Cr is shown in Fig. 4.5a, obtained from height measurements of the structures with a profilometer (Tencor Alpha Step) after the Cr is completely removed. Special care must be taken with narrow lines (below 150 nm), where the Cr etching is generally slower. The etching rates shown in the plot are optimized for the etching of narrow lines. One would need 20 to 30 seconds less to etch the same thickness of Cr if the patterned lines have a width larger than 150 nm.

Figure 4.5: (a) Experimental etched depths of chromium with Cl₂ plasma, tested for lines narrower than 150 nm. (b) Proposed etching profile of Cr with plasma. (c) Proposed etching profile of SiO₂ with RIE.

In Fig. 4.5b a schematic of the profile of the sample after plasma etching is shown. Due to the anisotropic etching with this machine, the plasma does not etch the Cr vertically, but forms a tapered edge as shown in the picture, which would explain the slower etching rate in thin lines. When the etching time is prolonged after reaching the Cr, the plasma starts attacking the tapered borders of Cr, making the line wider. A proper control of the etching time of the Cr can help to increase or decrease the width of the lines even after exposure and development. The remaining PMMA is etched by
means of O$_2$ plasma using the same machine with the parameters indicated in table 4.1.

For the etching of the SiO$_2$ layer (Fig. 4.2c), reactive ion etching (RIE) with the Plasmafab 100 from Oxford Instruments is used. This machine enables vertical etching because it produces self-bias voltages using high RF input powers at low chamber pressures of the order of mTorr. A 1:1 mixture of CHF$_3$ and O$_2$ is used according to the steps given in table 4.2. A first step of oxygen cleans the sample of possible PMMA remaining from the previous process. In a second step, a mixture of CHF$_3$ and O$_2$ plasma is used to etch the SiO$_2$ using the Cr as a mask. The use of CHF$_3$ RIE for dry etching of SiO$_2$ is a well established technique in micro- and nanotechnology [59].

The CHF$_3$ plasma produces a polymer which is deposited on the sample during the process and this slows down progressively the etching rate at fixed conditions. For this reason, O$_2$ plasma is mixed with the CHF$_3$. The oxygen helps to remove the polymer created during the process to stabilize the etching rate. Finally, a third step of O$_2$ plasma is used to clean the sample from any possible rests of polymer remaining from the second step. The parameters used in the RIE process, which were experimentally optimized, are shown in table 4.2.

<table>
<thead>
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<th>pressure (mTorr)</th>
<th>temperature (K)</th>
<th>DC-bias (V)</th>
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<td></td>
<td>CO$_2$</td>
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<td></td>
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<tr>
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<td>250</td>
<td>300</td>
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</tr>
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Table 4.1: Recipes used for the etching of Cr and PMMA with plasma.

<table>
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<th>flow (sccm)</th>
<th>pressure (mTorr)</th>
<th>temperature (K)</th>
<th>power (W)</th>
<th>DC-bias (V)</th>
</tr>
</thead>
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<td>100</td>
<td>300</td>
<td>100</td>
<td>415</td>
</tr>
<tr>
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<td>3</td>
<td>CHF$_3$</td>
<td>10</td>
<td>100</td>
<td>300</td>
<td>100</td>
<td>368</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O$_2$</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>O$_2$</td>
<td>20</td>
<td>100</td>
<td>300</td>
<td>100</td>
<td>400</td>
</tr>
</tbody>
</table>

Table 4.2: Recipe used for the etching of the SiO$_2$ layer with RIE. The first and the third steps only have a cleaning purpose, while the etching process takes place during the second step.

Height measurements of the profile of the sample after RIE suggest that part of the Si wafer is also etched during the process described above. Fig. 4.5c, shows a schematic of the profile of the sample before and after RIE. It is well known that this etching
technique provides vertical walls under the mask, unlike the previous plasma etching step, which results in tapered edges of the Cr (see Fig. 4.3).

### 4.2.4 Anisotropic etching of Si with KOH

Anisotropic wet etching of Si with alkali metal hydroxide etchant such as KOH or NaOH dissolved in water or isopropanol is a well understood phenomenon (see [60], [61] and [62]). The reaction taking place in this process is

\[
Si + 2OH^- + 2H_2O \rightarrow SiO_2(OH)_2^{2-} + 2H_2 \text{(gas)}.
\]

Etching with these substances is known to be anisotropic or selective because different crystallographic planes have different etching rates, the \(<111>\) planes being the slowest ones. The type of etchant and its temperature affect the etching rate and the surface smoothness. KOH is known to produce very smooth \(<111>\) planes with an etching rate of few microns per minute, depending on the temperature.

In this process the high selectivity between Si \(<111>\) and SiO\(_2\) and between \(<111>\) and \(<110>\) is used to achieve high-aspect-ratio structures. A 10 vol. % solution of KOH in water at 72°C is chosen to etch microcavity arrays using the double layer of Cr and SiO\(_2\) as a mask. Previously, the lines transferred to the mask have been aligned with the \(<112>\) direction in order to achieve an almost vertical etching into the Si, as described in section 4.2.1.

At this point of the process, the samples have just been treated with CHF\(_3\) RIE to etch the SiO\(_2\) mask. Nevertheless, the growth of a native oxide layer of 0.5 to 1 nm is relatively fast and this can delay the KOH etching into the Si. Therefore, a buffer oxide etch\(^1\) (BOE 7:1) of 10 to 13 seconds is necessary prior to the etching with KOH. After a quick rinse in water, the sample is introduced immediately in a recipient of about 5 liters of 10% KOH solution in water at 72°C with a magnetic stirring system, which helps to maintain an homogeneous temperature and concentration of KOH all over the recipient. It is to be noted that, due to the stirring system, the etchant flows with different speeds at different parts of the recipient. It is observed that the etching rates of Si depend on the part of the recipient where the sample is placed. For reproducibility, the samples are always kept fixed at the same position within the recipient with the help of tweezers, with the Si wafer oriented perpendicular to the surface of the KOH solution. After the KOH wet etching treatment, the sample is immediately rinsed repeatedly with water in different water containers and washed with a pressure shower to completely remove any possible rests of KOH and of etched Si. In a last step, the structures must be rinsed in alcohol before letting the water dry up. The sample is

\(^1\)Buffer oxide etch is a mixture of HF and water with a buffer agent like for example NH\(_4\)F. The HF is a SiO\(_2\) etchant and the buffer agent is added to maintain the HF concentration and to control the pH.
then dried by flushing with N\textsubscript{2} until all alcohol droplets have disappeared. Drying of water would increase the surface tension between the Si lamella, which would make them collapse.

It is possible to measure the etching rate of the KOH in Si \textsubscript{<110>} by performing height measurements of the structures after the process. For this purpose, one channel perpendicular to the direction of the lines is written with the e-beam at both sides of each array and transferred to the mask in the same steps as the structures. The channel is also etched with KOH at the same time as the structures, and its walls are rapidly wide etched because they have a crystallographic direction far from the \textsubscript{<111>}.

These wide channels allow height measurements next to the structured region using a profilometer as well as viewing the structure by SEM. Otherwise, the profile of the microcavities would not be observable, since they are etched into the Si several microns deep. Height measurements at different etching times are presented in the graph of Fig. 4.6a. The slope of the linear regression gives an etching rate of 1.5 $\mu$m/min for 20% KOH in water and 1.4 $\mu$m/min for 10% KOH, both at a temperature of 72 °C.

![Figure 4.6: (a) Experimental etched depths of Si \textsubscript{<110>} in 10% and 20% KOH in water at 72 °C. The slopes of the linear regressions indicate the etching rates. (b) SEM picture of the corner of a microcavity array after KOH etch. A wide channel etched perpendicular to the lines of the array allows the height measurements on the structures as well as this view of the sample with the holder of the SEM tilted by 45°.](image)

After KOH wet etching, the mask is still remaining on top of the structures, as seen in the SEM picture of Fig. 4.6b. The double layer of Cr and SiO\textsubscript{2} remains on the sample after KOH etching and it curls up at the end of the lines, where the Si has been etched faster for having another crystallographic orientation. The distance etched under the mask is usually called under-cut or under-etch. In the \textsubscript{<111>} direction, i.e. perpendicular to the cavity walls, there is also an under-etch, but much smaller compared to the other directions. This under-etch has been experimentally estimated to be about 13 nm per 1$\mu$m depth, giving an etching ratio between the \textsubscript{<110>} and the
<111> directions of 77. In [63] an etching ratio of 290 at 70° and 30% KOH in water is given. The large disagreement is probably due to the limited selectivity of our etching mask. The under-etch needs to be taken into account when writing the width of the lines in the e-beam lithography process. Probably as a consequence of the under-etch, the resulting cavities have slightly tapered walls, which can become a problem if the width difference from the top to the bottom of the cavity is too large. This is discussed later in more detail.

The remaining Cr mask can be removed using a Cr wet etchant (15 g Fe(CN)₆ and 5 g KOH in 100 ml water) at a rate of approximately 20 nm/min. The effect of the KOH on the Si is now completely negligible at room temperature. Nonetheless, a careful rinse with water after the process makes sure that the solution is completely washed out. Finally, the SiO₂ mask is removed in a bath of a few minutes in BOE 1:7.

In Fig. 4.7 SEM pictures of the microcavity arrays after the whole process are shown. Fig. 4.7a shows the cross section of a 0.5 µm-period microcavity array with a height of 4.5 µm and a wall separation of 330 nm. Such a cross section of the sample is achieved by cleavage of the <110> oriented wafer along the edge with a <111> plane, which happens to occur at 54.74° with respect to the flat side of the wafer. The aspect ratio, defined as the height of the lines divided by its width, is in this case 26, but aspect ratios up to 40 were achieved with this technique. Important is that the cavities are identical to each other to within a few nanometers, which is required for our studies of confinement-induced ordering in colloidal solutions. Note that the walls of the cavities are not exactly vertical, but slightly tapered. This may be a problem if the wall separation difference between the top and the low part of the cavities is a substantial fraction of the size of the colloidal particles. This is not the case in the sample shown here, but it can happen in structures that are deeper etched into the Si. Also a bad alignment of the array lines along the <112> direction can increase the tapering of the cavity walls. Characterization of the cavities is thus extremely important. This point will be considered later in section 4.4. Panels (b) and (c) of Fig. 4.7 show close-ups of the top and bottom parts of the cavities from other arrays, in which details such as the shape of the cavities and the roughness of the Si walls are observed with high resolution. These images reveal the high quality of the micro-containers. In Fig. 4.7c, an oxide layer of 50 nm thickness can be observed. Thermal oxidation was performed on some structures with the purpose of decreasing interactions between the cavities and the colloidal particles, but this complicated x-ray diffraction characterization and it was never used in the experiments. The structures acquire a native oxide layer of 1 or 2 nm, which proved to be thick enough to prevent the colloidal particles to get stuck to the cavity walls. However, the thin oxide layer could be negatively charged and this would interact with the negatively charged colloidal particles.

There are few delicate steps concerning the fabrication of high-aspect-ratio microcavity arrays that need to be mentioned. First of all, the step between the BOE etch
Figure 4.7: SEM images of high-aspect-ratio microcavity arrays after the fabrication process. (a) Cross section of a 0.5 period structure with a height of 4.5 µm and a wall separation of 330 nm (aspect ratio = 26). In this image the homogeneity of the cavities can be appreciated. Close-up of the top part (b) and bottom part (c) of other microcavity arrays. In these images, the well defined structures and the smoothness of the vertical walls are remarkable. (d) Example of successful KOH etching on a 1 µm array which was carefully rinsed with water after the BOE process previous to the KOH etch. In contrast, (e): a similar sample which was not rinsed with water after the BOE step.
and the KOH etch, in which the structures are rinsed with water, has to be short and thorough. It is recommended to flush the sample with a water shower rather than just rinsing it in a water bath, since the flushing seems to help removing rests of etched SiO$_2$ between the lines. This is evident from the samples which have not been flushed during this step, because the Si in between the lines starts etching later, resulting in a height at the structured region which is different from that of the transverse channel. Moreover, the etching between the lines can be inhomogeneous, resulting in cavities with different heights. An example of this situation is shown in figure 4.7e. For comparison, figure 4.7d shows the case of a similar microcavity array which was carefully flushed with water at this point. Finally, it is worthwhile to recall the importance of a bath of the samples in isopropanol before drying, with the effect that the surface tension in the cavities is reduced and collapse of the cavity walls is prevented. Of course, at very high aspect ratios and for very thin lines, a collapse cannot be avoided, and freeze drying eg in cyclo-hexane or critical point drying (CPD) in CO$_2$ has to be applied.

4.3 Design of a microfluidics filling system

Our experimental approach to studies of colloids in confinement is to measure the intensity diffracted from an empty system and to compare it with the diffracted intensity from a filled system. Thus the structures need to be filled in such a way that the alignment of the sample with respect to the beam is kept. As will be shown in section 4.4, the alignment requires a precision of millidegrees, which means that the cavities need to be filled very gently. At the same time, the system has to be sealed in order to prevent fast evaporation of the colloid solvent (benzyl alcohol and ethanol mixture).

A microfluidic channel system was designed to facilitate the insertion of the liquid in the microcavities (see Fig. 4.8b). Microchannels are etched into the Si chip simultaneously with the microcavity arrays. These channels connect different arrays with different characteristics (period and cavity wall separation) to each other, and they are further connected to other channels designed to collect the liquid to be inserted. The fabrication of these channels follows exactly the same steps as explained in the previous section and they are processed simultaneously with the microcavity arrays. The width of the channels is a few hundreds of microns, much larger than the typical lines written with e-beam lithography. In order to write these lines efficiently, the largest aperture of the e-beam (120 $\mu$m) is used and, for the channels which are perpendicular to the microcavity array lines, the large under-etch during the KOH anisotropic etching is taken into account.

Fig. 4.8a shows a picture of one Si chip after processing. In the chip, 31 microcavity arrays and several connecting microchannels were etched. One of the microcavities is completely etched away intentionally in order to obtain a container for scattering from bulk colloid. Such a container has the same size as an array and it is called a hole. The
Figure 4.8: (a) Photograph of a $2 \times 2$ cm$^2$ Si chip with several $1 \times 2$ mm$^2$ microcavity arrays connected by microfluidic channels. The light is diffracted in the microcavity arrays at different wavelengths of the visible spectrum. (b) SEM picture with low magnification showing several arrays in dark and the connecting microfluidic channels. (c) The microcavity arrays are covered with a glass slide. Two channels cut in the glass allow the insertion of needles. (d) Sketch of the microfluidics setup for the filling of microcavity arrays with a colloid.
size of a single array in the picture is $1 \times 2 \text{mm}^2$, which is sufficiently large to cover the cross section of the x-ray beam.

The filling system is sketched in Figs. 4.8c and d. A 420 $\mu$m-thick glass slide with a surface slightly larger than the Si chip is prepared as follows. First two channels of ca $300 \mu$m depth are sawed in the glass. The channels are parallel to each other and their length reaches the border of the glass on one side. Two steel needles of 130 $\mu$m inner and 260 $\mu$m outer diameter are fixed in the channels by a glue droplet. Then the Si chip is placed onto the glass in such a way that the top of the microcavity structures and the face of the glass in which the channels are sawed are touching each other, and then the edges are sealed with glue. In Fig. 4.8c it is shown how the spacing between the needles matches the position of the horizontal microfluidics channels etched into the Si. The needles are attached to flexible teflon tubes of 300 $\mu$m inner and 800 $\mu$m outer diameter. One of the tubes is attached to a 500 $\mu$l empty syringe on one side, while the second tube is lowered into the colloidal suspension on the other side. The needles, tubes and syringe were acquired from Hamilton.

Now, by sucking air out with the syringe, the liquid flows through the tube and the microfluidics system, and the microcavities are immediately filled by capillary forces. Besides, a native oxide layer grown on the Si makes the wetting easier. The flexibility of the teflon tubes damps any sudden movement produced during the filling process.

4.4 Characterization with x rays

X-ray diffraction from empty microcavity arrays serves to determine the shape and dimensions of the cavities by means of fits to model-dependent calculations of diffraction efficiencies. The characterization of empty samples is necessary for the analysis of the diffracted signal from filled arrays, since it reduces the number of fitting parameters in the calculations of the diffraction efficiencies and it provides accurate real-space constraints needed in phase retrieval algorithms. The experimental strategy in the data acquisition is to first align and measure a set of empty arrays, then insert the fluid in the cavities, without losing the alignment, and finally repeat the set of measurements with the confined colloid. In addition, diffuse scattering of empty arrays provides information about the roughness of the cavity walls. This measurement is not needed for every sample, since the etching process with KOH is expected to give reproducible results concerning the roughness of the Si $<111>$-planes. In this section, diffraction efficiency calculations are used to characterize the shape and dimensions of the cavities, assuming that they are identical within each array.
4.4.1 Experimental setup and data acquisition

Small-angle x-ray diffraction measurements were performed at the Materials Science Beamline at the *Swiss Light Source* in Villigen, Switzerland. Fig. 4.9 shows a sketch of the experiment, which required a special setup in the first hutch of the beamline. The sample was mounted on the tomography stage, situated at the beginning of the hutch, at 5 m distance from the detector. Two helium flight tubes, each of approximately 2 m length, were placed in between in order to reduce air scattering. The detector is a unique microstrip detector [67] consisting of 15000 Si elements of 50 µm size which records a whole angular spectrum within a few seconds. This detector is currently used in the powder diffraction station of the beamline, which is situated in the back of the hutch. A beam of 11.4 keV energy was focused onto the detector plane so as to increase the angular resolution. Two pairs of slits were carefully set to define and clean the focused beam, as shown in the figure. Finally, a beamstop was situated in front of the detector to block the primary beam. The motorized beamstop could be removed so as to allow for measurements of the zeroth diffraction order using attenuation filters.

![Experimental setup](image)

Figure 4.9: Experimental setup for small-angle x-ray diffraction at the Material Science beamline of the SLS. The dashed line indicates the trajectory of the primary beam, which was focused onto the detector. For simplicity, only the zeroth, +1\textsuperscript{st} and −1\textsuperscript{st} diffraction orders are drawn. A beamstop situated in front of the detector blocks the intensity from the zeroth order.

In order to obtain a symmetric diffraction pattern, the sample needs to be aligned in all three rotations around the \(x\)-, \(y\)- and \(z\)-axes with a precision of about 5 mdeg. For this purpose, the sample is mounted on a holder fixed to a goniometer with two angular stages motorized around the \(y\)- and \(z\)-axes. The goniometer is mounted on a rotational stage motorized around the \(x\)-axis. The most efficient way to achieve a precise alignment is to record diffraction patterns at different incident angles and to check in a \(\theta_{\text{in}}-\theta_{\text{out}}\) plot which is the angle of incidence that gives the highest symmetry. In theory, all the arrays in one silicon chip should have the same alignment angles. However, the tension introduced in the chip after gluing the glass slide causes alignment...
differences up to 3 mdeg. Even such small misalignments lead to an asymmetry of the diffraction pattern. Nonetheless, this error is allowed for ease of data acquisition and is corrected by symmetrization of the data.

The microstrip detector provides fast measurements of diffraction patterns, but some problems needed to be considered. Above 3000 cts per pixel, the detected intensity was no longer reliable (overexposure). Even for this counting rate, there existed erratic pixels which sometimes behaved as if they were overexposed. In addition, the detector is made of several modules, which yields dead regions at the positions where two modules join. Finally, about 15% of the pixels were dead from previous usage of the detector. In order to overcome these limitations, nine different exposures (three exposures at three different filter settings) from the whole angular spectrum were recorded. Three different attenuation filter settings were chosen in such a way that the different regions of the spectrum were recorded with the appropriate counting rate. One of these settings included a large attenuation of the beam, allowing for recording the zeroth order of the pattern without the beamstop. For each attenuation filter setting, three exposures were recorded in order to eliminate accidental overexposed pixels. At the time of writing, a greatly improved version of the microstrip detector becomes available.

4.4.2 Data treatment

In order to extract the diffraction efficiencies of the grating orders from the data, the following steps are carried out:

1. For every attenuation setting, a median filter is applied to the three exposures, which chooses the intermediate value recorded by each pixel. This helps to eliminate possible erratic pixels in case of overexposure.

2. Exposures with different attenuators settings are corrected according to the attenuation values.

3. Data points are selected according to the number of counts that they have. All data points from the low-attenuation exposure are included if they have less than 3000 cts, and if not, they are replaced by the data from the medium attenuation exposure. The same is applied to the medium and the high-attenuation exposures.

4. The data are symmetrized with respect to the zeroth order. This helps to correct for the misalignment of the sample, but it also allows to cover the dead regions of the detector where the modules join each other, in which no data points are recorded.

5. A series of Gauss functions with the same full-width-at-half maximum (FWHM) are fitted to the measured grating orders. The fitting parameters are the period of
the array, the FWHM of the Gaussian and the amplitude of the Gaussian for each peak. The points where consecutive Gaussian functions cross each other are significantly lower than the measured intensity minima. The difference is considered as background and it is subtracted from the data in a few iterations. Calling $I^m$ the integrated intensity under the Gaussian fitting order $m$, the diffraction efficiencies are derived from

$$\eta_m = \frac{I^m}{I_0}, \quad (4.1)$$

with $I_0$ the total intensity incident on the array after attenuation through the wafer thickness. $I_0$ can be determined experimentally as

$$I_0 = \sum_m I^m, \quad (4.2)$$

neglecting absorption through the Si ribs of the microcavity array.

Fig. 4.10a shows a diffraction pattern from a microcavity array after scaling three exposures with different attenuations and after symmetrization. Only one half of the spectrum is shown, since the pattern is symmetric with respect to the zeroth order at $q_x = 0$. Note that the microstrip detector is curved, as shown in Fig. 4.9, and therefore the reciprocal space coordinate is not exactly $q_x$. However, the diffraction angles are so small (7.8 mrad angular range) that $q \simeq q_x$. The width of every diffraction peak indicates the resolution of the measurement, which is determined by the divergence of the beam and by the detector opening angle. The full width at half maximum (FWHM) of each peak is $\delta q = 0.0013 \text{ nm}^{-1}$. Apart from the excellent resolution in reciprocal space, the combination of three measurements with different attenuations of the intensity allows the recording of the signal over more than 6 orders of magnitude with a very low noise rate up to the 80th diffraction order. The large momentum range of the measurement $\Delta q = 0.5 \text{ nm}^{-1}$ corresponds to a resolution in real space of $\Delta x = 12.5 \text{ nm}$. The spacing between the diffraction peaks, which equals $6.3 \times 10^{-3} \text{ nm}^{-1}$, corresponds to an array period $p = 996 \text{ nm}$, in good agreement with the line spacing of 1 $\mu$m written by the e-beam.

Fig. 4.10b shows the efficiencies of the diffraction orders on a logarithmic scale. Diffraction efficiencies were obtained from the diffraction pattern by fitting a Gaussian function to all diffraction peaks, following the 5th step of the data treatment.

### 4.4.3 A simple calculation for the characterization

In the following, we want to show that an analysis of the first 20 diffraction orders using a simple kinematical theory is enough to describe the average shape of the array cavities and the height $h$ of the structure. For this purpose, diffraction efficiencies are calculated from Eq. 2.30. In this approach, the grating profile is projected onto the
Figure 4.10: a) Diffraction pattern measured from an empty microcavity array after attenuators correction and symmetrization. b) Diffraction efficiencies extracted from (a) after fitting a Gauss function to all diffraction peaks and subtracting background.
(x, y)-plane perpendicular to the beam propagation direction. This neglects dynamical (volume) scattering effects, which is justified if the height h of the structures is small: $q_z h/2 \ll 1$.

In Fig. 4.11, a fit to the measured diffraction efficiencies from an empty microcavity array is shown. In the inset of the plot the phase profile projection at the exit of the cavity assumed for the calculation is shown. The best-fit parameters are a wall separation of $w = 292$ nm, a structure height of $h = 6.4$ $\mu$m and a tapering angle of the cavity walls of $\theta = 0.18^\circ$. Note that both measurement and calculation are on an absolute scale. The period $p = 996$ nm was deduced from the separation between the diffraction peaks in Fig. 4.10. A SEM inspection of the cavities of the same array cleaved after the experiment showed a complete agreement with the model. Only the walls of the cavity were not so straight as assumed in the model: the tapering was more pronounced at the bottom than at the top of the cavity. Nonetheless, the difference between the wall separation on top and at the bottom of the cavity coincided within the resolution of the SEM.

Characterization of microcavity arrays with x-ray diffraction has two main advantages in comparison to SEM imaging: (1) the sample does not need to be broken for inspection and (2) x-ray diffraction provides the average cavity shape over the area illuminated by the x-ray beam. The x-ray characterization method, however, has an important disadvantage, namely the ambiguity between a duty cycle $w/p$ and $1 - w/p$. In both cases, the diffraction efficiencies look exactly the same. Since the absorption through Si lines in these gratings is very small ($\simeq 0.98\%$), the measurement is usually
not sensitive to this change. It is known from the parameters used in the fabrication process whether the DC is larger or smaller than 0.5. Also a SEM inspection with a top view of the structures is in most cases enough to decide. But for duty cycles very close to 0.5, one needs to inspect the cross section of the cavities after the experiment by SEM, so as to be sure about the exact width of the cavity.

4.5 Conclusions

In this chapter it was shown that the fabrication of microcavity arrays using electron beam lithography and anisotropic wet etching of Si with KOH provides a periodic set of identical cavities with smooth walls. The resulting structures appear appropriate for the confinement of colloidal suspensions, except for the fact of not having perfectly parallel walls. Indeed, if the tapering of the confining walls is such that the change in wall separation $w$ along the beam propagation direction becomes as large as a particle diameter, confinement-induced modulation of the density profile of the colloid in the $x$-direction will be smeared out. This is an important point to consider in the design of the samples: in order to prevent this problem, the structures should not have a too large height $h$. The microcavity array analyzed in the previous section revealed a height $h = 6.4 \mu m$ and a tapering angle of the walls of $\theta = 0.18^\circ$, which means a 20 nm difference in wall separation from $z = -h/2$ to $z = h/2$. For 110 nm-diameter particles, this is already at the limit of what we can afford. Fortunately, SEM inspections show that the tapering of the walls is not so dramatic along most of the cavity; it is mostly concentrated at the bottom of the structures. Nevertheless, it is concluded that $h \approx 6 \mu m$ is the maximum height that can be afforded.

The etching technique used for the fabrication of the microcavity arrays can also be exploited for applications within x-ray optics. For example, it has been used to improve the quality of phase gratings for hard x-ray interferometry (12-24 keV), requiring high-aspect-ratio structures with a period of about 4 $\mu$m, a duty cycle of $w/p = 0.5$ and a height $h$ ranging from 15 to 30 $\mu$m. Such phase gratings were successfully used for x-ray wavefront analysis [56], coherence measurements [68] and phase-contrast imaging and tomography [69] [70].

The smoothness of the Si $<111>$ crystallographic planes after anisotropic wet etching with KOH makes it possible to fabricate one single Si lamella between two separate parallel Si walls (Fig. 4.12). Such a structure can be used as an interferometer. The idea is to split and recombine an x-ray beam incident at a small angle with respect to the walls of the structure. The single lamella would need a length of a few mm, a thickness as small as possible in order to allow a large transmission of the beam and a height $h$ as large as possible so as to allow the x-ray beam to fit in the interferometer. The lamella was fabricated following the same steps as in the fabrication of the microcavity arrays. Fig. 4.12 shows a SEM picture of the cross section of one Si lamella between
two Si walls etched into a $<110>$-Si wafer. The height of the structure is $h = 50 \mu m$, which is limited by the Cr/SiO$_2$ double mask used during the wet etching with KOH. The structure stands upright over a length of 1 mm. The holder of the SEM was tilted an angle $\approx 45^\circ$ and therefore the image gets out of focus far from the focused region of the sample.

Figure 4.12: SEM picture of a single Si lamella of $\sim 1 \mu m$ thickness fabricated using anisotropic etching with KOH. The height of the structure, which could be used as a x-ray interferometer, is $h = 50 \mu m$ and it is standing over a length of 1 mm. This example demonstrates the extreme selectivity of the etching process.
Chapter 5

Ordering phenomena in confined SiO$_2$ colloidal suspensions

The Bragg and diffuse contributions to the x-ray scattering from SiO$_2$ colloidal suspensions confined in microcavity arrays (see Fig. 5.1) were measured in two different experiments. The Bragg scattering experiment took place at the Material Science beamline of the SLS. Small-angle x-ray diffraction along the confinement direction revealed, as we will show below, an oscillatory ordered-disordered density profile of the colloid as a function of the size of the cavities and of the screening length of the Coulombic interaction potential between the particles. The broad fan in the horizontal direction at this wiggler beamline made it impossible to measure the 2D diffusely scattered intensity arising from the short-ranged inter-particle correlations. Therefore, a second experiment was carried out at the ID2 beamline at ESRF, where a sufficiently collimated beam in both directions allowed 2D SAXS measurements on confined colloidal suspensions. The diffuse scattering revealed an anisotropic structure factor of the colloid as well as a dynamically modified form factor, the latter being due to propagation effects next to the cavity walls.

This chapter consists of two parts, which are concerned with the Bragg scattering and the diffuse scattering experiments, respectively. In each of them, the measurements, analysis methods and results are explained in detail.

5.1 Bragg scattering along the confinement direction

The Bragg scattering intensities from a 1D microcavity array are given by the diffraction efficiencies in Eq. 2.30. In this equation, $s(x)$ is a general function which describes the shape of the cavities and the density profile of the confined colloidal solution. The function $s(x)$ is partly known from previous diffraction experiments from empty arrays. In concrete, the shape and size of the cavities has already been determined from
model-dependent kinematical calculations, as shown in section 4.4. In the following, it is shown how diffraction experiments from microcavity arrays filled with a colloidal solution served to determine the colloid’s density profile as a function of the separation between the confining walls. For this purpose, different microcavity arrays with varying periods and cavity widths, and a colloidal suspension of 55 nm-radius silica particles with two different salt concentrations were used.

For the interpretation of the data, several analysis methods have been used. A Patterson analysis revealed the spatial frequencies in the oscillating density profile. Different frequencies and amplitudes were obtained depending on the width of the cavities, but also depending on the salt concentration in the colloidal suspension. For the determination of the exact density profile of the colloid, model-dependent fits of the diffraction efficiencies have been performed based on the hints provided by the Patterson analysis. In order to keep a small number of parameters, a simple model of sinusoidal oscillations was assumed, which however did not provide a satisfactory fit to the data. Finally, a phase retrieval algorithm succeeded in the unique reconstruction of the phase profile, which is equivalent to reconstructing the density profile. This approach results in a good fit to the data when comparing the diffraction efficiencies from the reconstructed profile with the measured ones, and has the advantage to be a model-independent method. However, the phase retrieval analysis method uses tight constraints in real space, without which the solution cannot converge in a unique way.

5.1.1 Experimental

Small-angle x-ray diffraction measurements were performed at the Materials Science beamline at the SLS. The experimental setup and data treatment were explained in
detail in sections 4.4.1 and 4.4.2, where it was shown how diffraction efficiencies can be extracted from diffraction patterns. In the present experiment, several microcavity arrays were investigated in a systematic way, measuring first diffraction patterns from all empty structures and repeating the measurements after filling them with a SiO<sub>2</sub> colloidal suspension. The arrays were etched into the Si chip following the steps described in section 4.2 with periods ranging from 0.5 to 1.25 µm and cavity widths ranging from 260 to 600 nm. Two of the arrays were completely etched away to create containers (holes) for measurements on the bulk colloidal solution. The sample is a suspension of charge-stabilized colloidal SiO<sub>2</sub> spheres of 54.6 nm radius in a 55%/45% mixture of benzyl-alcohol and ethanol, index-matched to the colloidal particles. The volume concentration of particles in the suspension was ϕ = 0.1. The characteristics of such colloidal suspensions were explained in detail in section 3.3.

In order to investigate the influence of the inter-particle interactions, LiCl was added to the colloidal solution. Adding salt screens the Coulomb interactions between the charged particles. Initially, the solution was considered to be deionized, since it had been kept for months in a bottle with ion-exchange resin. Then, after diffraction measurements on filled arrays had been performed, a second solution with LiCl 0.4M was flushed through the gratings several times, in order to assure that the deionized solution was completely replaced by the new one. It was impossible to verify that the colloid inside the cavities was actually replaced during this process. Nevertheless, even if the colloid in the microcavities was not replaced, the ions should rapidly diffuse into the suspension.

Fig. 2.9a shows the measured diffraction efficiencies from an empty array of microcavities (blue) and from the same array filled with the colloidal suspension (red) up to the 50<sup>th</sup> diffraction order. The empty array was already analyzed in section 4.4, yielding a period \( p = 1 \) µm, an average cavity width \( w = 292 \) nm and an average height \( h = 6.4 \) µm. In comparison, the data for the filled array show a higher efficiency in the zeroth order and, in general, lower efficiencies in the other orders. The diffraction efficiencies are proportional to \((\Delta \phi')^2\) (see Eq. 2.30), \(\Delta \phi'\) being the phase shift caused by the difference optical path between the Si lines and the empty cavities. When the cavities are filled with a fluid, \(\Delta \phi\) is smaller, and therefore all diffraction efficiencies decrease. The total intensity transmitted through the structure is almost the same through empty or filled cavities, since the transmission through 6.4 µm of colloid is very high \((T = 0.998\) for \(\lambda = 1.05\) Å), which means that the total normalized transmitted intensity should be very similar in both cases. This results in an increase of the zeroth diffraction order, as observed in the data. The relevant changes in the diffraction orders due to the modulation of \(s(x)\) inside the cavities arise from relative differences between empty and filled diffraction efficiencies. For example, in Fig. 5.2a, it is evident that the 8<sup>th</sup> order from the filled array is much higher than the others, and that the 10<sup>th</sup> is a bit lower. Such small changes in the diffraction efficiencies will reveal the
confinement effect in the colloidal solution.

![Graphs showing measured diffraction efficiencies and Patterson functions](image)

Figure 5.2: (a) Measured diffraction efficiencies from an empty microcavity array (blue) and the same array filled with a colloidal suspension (red). The cavity parameters are \( p = 1 \, \mu \text{m}, w = 290 \, \text{nm} \) and \( h = 6.4 \, \mu \text{m} \). (b) Patterson functions obtained from the measured diffraction efficiencies shown in (a). The diffraction efficiencies from the empty cavity were first scaled to the data for the filled cavity (see text). (c) Difference \( \Delta P(x) \) between the Patterson functions for the filled and empty cavities shown in (b).

### 5.1.2 Data analysis

#### Patterson functions

The Patterson function of a microcavity array, given by Eq. [2.36], can be readily obtained from the measured diffraction efficiencies \( \eta_n \). In order to compare data from empty and filled microcavity arrays, the data from the empty arrays needs to be scaled with the factor \( (\Delta \phi / \Delta \phi')^2 \). In an equivalent way, one can scale the data in such a way that \( \eta'_1 = \eta_1 \) for empty and filled measurements, since the efficiency of the first diffraction order is not affected by the ordering of the colloid.

Fig. [5.2] shows the Patterson functions corresponding to the diffraction efficiencies...
shown in Fig. 5.2a, in which the diffraction efficiencies from the empty array were previously scaled for comparison. Both curves have a triangular shape with its base equal to $2w$ as a consequence of the auto-convolution of cavities with a rectangular shape and a width $w = 293\text{ nm}$. The Patterson function is therefore dominated by the shape of the cavities for both empty and filled arrays. By contrast, the difference Patterson function $\Delta P(x)$, as defined in Eq. 2.37, shows the relevant changes between empty and filled microcavity arrays due to confinement effects (see Fig. 5.2c). $\Delta P(x)$ shows oscillations with a frequency of $\Delta x \approx 130\text{ nm}$, close to the diameter of the colloidal particles $2R = 109\text{ nm}$. The oscillations are clear evidence of a modulated density profile.

Contrary to what it was found in the theoretical calculation of Fig. 2.4, the experimental difference Patterson shown in Fig. 5.2c has a large peak in the center and features near $\pm w$ which arise from the shape of the cavity imprinted in the confined colloid. The confinement between two parallel walls induces a deep minimum of the shape function $s(x)$ in the proximity of the walls, even when the cavity is uniformly filled, which arises simply because particles cannot penetrate the wall. This ‘excluded volume’ effect was not considered in the theoretical example shown in Fig. 2.4, where the oscillations within the colloid profile were all assumed to have equally pronounced minima.

Fig. 5.3 shows the difference Patterson functions obtained for all arrays. Each plot corresponds to a different array and the plots are placed in the figure at the positions in which they were etched into the chip. Each row corresponds to a different period $p = 0.5, 0.75, 1$ and $1.25\text{ µm}$ from top to bottom. The $x$-values of the Patterson functions range from $-p/2$ to $p/2$. In each plot, the name of the array and the width of the cavity are indicated. The name of the array consists of a number equal to the period in microns and a letter from A to F corresponding to the column. In principle, the fabrication of the arrays was thought to have an increasing cavity width from A to F, but this was not quite achieved, as shown by the values of $w$, which were obtained from a fit to the diffraction efficiencies from empty arrays. The plots show difference Patterson functions for cavities filled with charge-stabilized colloid (red lines) and the same colloid with LiCl added (green lines).

The difference Patterson function shown in Fig. 5.2c is plotted in Fig. 5.3 under the name ‘1C’. It is one of the functions having stronger oscillations arising from the cavity imprint. Also other arrays with narrow cavities feature such strong oscillations, like ‘0.5A’, ‘0.5D’, ‘1B’ and ‘1.25B’. As expected, samples with larger $w$ show a weaker cavity imprint.

The oscillations with frequency smaller than $w$ are attributed to correlations within the colloid profile. Strong short-range oscillations with a frequency of the order of the particle size (or effective size due to Coulombic screened interactions) indicate a layered colloid profile. For example, the difference Patterson from the array ‘1C’, previously
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Figure 5.3: Difference Patterson functions obtained from diffraction efficiencies from different cavity arrays etched into the same Si chip. The red lines correspond to data from arrays filled with a charge-stabilized colloidal solution of SiO$_2$ spheres with radius $R=54.6$ nm. The green lines correspond to the same colloid in which LiCl was added to achieve a 0.4 M concentration. See also next page.
Ordering phenomena in confined SiO₂ colloidal suspensions

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studied in Fig. 5.2, shows strong oscillations in the deionized suspension (red line) with a frequency of approximately 130 nm. The same occurs in the case of the array '1B' for the suspension with LiCl. For cavity widths of \( w = 284 \) nm and \( w = 290 \) nm, this can be interpreted as ordering of the confined colloid in two layers. A similar pronounced colloid ordering of the same frequency is found in the array '1.25D' and in '1E', where respectively 3 and 4 layers can just fit. This happens in both cases with the suspension with screened Coulomb interactions (green lines). On the other hand, arrays with a similar cavity width \( w \) as the two previous ones, like for example '1D' and '1.25E', exhibit non-periodic and weaker oscillations. The other arrays present even weaker short-ranged oscillations, sometimes at frequencies smaller than the particles size, especially when \( w \) is small. This can be explained if different layered arrangements of the particles coexist within the same array.

One generally finds that the deionized colloid shows less pronounced and more irregular oscillations, whereas the hard-sphere solution shows a more clear structure. This can be explained arguing that in the deionized solution, local charge differences induce a variation of the correlation distances within the same arrays. On the other hand, one finds that clear, periodic oscillations appear for the hard-sphere solutions at gap sizes which are a multiple of approximately 142 nm. As an exception, in the array '1C' it is the deionized solution which presents more clear oscillations. In '0.5D', one can also observe very clear oscillations, but with a frequency smaller than the particle size, indicating a superposition of layered profiles.

The analysis described above by means of difference Patterson functions can lead to ambiguities in the interpretation. Indeed, a spatial frequency detected in the colloid profile does not necessarily indicate layering of the colloid across the entire gap. It can also mean that only two layers of colloid exist in the center of the gap, even when the gap is large enough to fit one or two layers more. This ambiguity may only be resolved through a direct structural analysis as presented below.

### Fits to the measured efficiencies using kinematical calculations

Using Eq. 2.30 we have attempted to fit the measured diffraction efficiencies with calculations assuming a model for the shape function \( s(x) \). The height \( h \), the cavity width \( w \) and the tapering angle \( \theta \) of the walls are taken as fixed parameters from the analysis of the empty arrays shown in section 4.4. For the shape of the colloid density profile, a combination of sinusoidal functions of half a period each is taken, in which each half-sinus is modelling a layer within the colloidal suspension. The parameters used are the half-period of the sinus function \( s \) and the distance \( d \) between consecutive layers. The parameter \( s \) is typically chosen to be close to the size of the colloidal particles, and \( d \) as given by the previous Patterson analysis.

Fig. 5.4 shows the best fit to the data for the array '1C' filled with a deionized
suspension, which was achieved for $s = 120 \text{ nm}$ and $d = 125 \text{ nm}$. Both values are in reasonable agreement with the expected inter-layer distance and the size of the colloidal particles. The model brings out the most relevant trend in the diffraction efficiencies, namely an increase in the 8th diffraction order. Even if the fit is not perfect, the increase of the efficiency in the 8th order explains the frequency of approximately 130 nm observed in the difference Patterson function. Discrepancies at orders with low efficiencies, like at the 7th and the 10th orders, are less relevant considering the logarithmic scale of the plot.

Beyond the 20th diffraction order, the kinematical approximation is longer accurate. This is equivalent to the statement that the colloid profile is modelled with a resolution of $p/20 = 50 \text{ nm}$, close to the radius of the colloidal particle. This resolution is just enough to detect ordering/disordering effects within the colloid profile.

In conclusion, model dependent calculations of the diffraction efficiencies from microcavity arrays with a shape $s(x)$ provide good fits to the measured efficiencies up to the 20th diffraction order. The best-fit parameters for $s$ and $d$ are consistent with the Patterson analysis. Different shapes of the colloid profile model might improve the fits at the expense of increasing the number of fitting parameters.
Phase retrieval

A model-independent determination of the density profile was achieved by means of a phase retrieval algorithm (see Figs. 5.5 and 5.6 [33]). The algorithm converged to unique solutions when the following constraints were applied:

1. The phase was assumed to be constant in the regions of the silicon lines. This is known from the shape of the cavities.

2. Since the phase modulations within the cavities are small, the phase was restricted to vary within an interval of ±0.1 rad relative to the average value, whereas the average value and thereby the height \( h \) was not restricted.

3. Within the Si lines and the cavity region, the amplitude and the phase are coupled by the known real part \( \delta \) and imaginary part \( \beta \) of the refractive indices.

In the narrow regions near the walls, the phase was unconstrained so as to allow for dynamical scattering effects (see section 2.3). For further details about the algorithm we refer to [33]. The total \( q \)-range of the measured diffraction patterns and the constraints implemented in the algorithm yield a resolution in the reconstruction of \( \delta x \approx 6 \text{ nm} \). The retrieved phase profiles gave the same values for \( h \) and \( w \) as obtained in model-dependent calculations within 0.1 \( \mu \text{m} \) and 4 nm, respectively.

A comparison of the retrieved phase profiles in Figs. 5.5 and 5.6 with the Patterson functions in Fig. 5.3 shows a complete analogy. The imprint of the cavity in the colloid profile can be seen in the reconstructed phase profile as a significant decrease of the phase next to the cavity walls. Besides, oscillations in the phase profiles generally have the same frequency as in the corresponding difference Patterson functions. This coincidence is not surprising, since both analysis methods are performed on the same data set in a model-independent way, and therefore they must agree in their interpretation. The phase retrieval, however, resolves the ambiguity introduced in the Patterson analysis regarding the number of layers existing in the cavities and reconstructs their position relative to the cavity walls.

For the reconstruction, the complete measured \( q \)-range is used, which covers up to 80 diffraction orders in the case of gratings with period \( p = 1 \mu \text{m} \). Unavoidably, dynamical effects are contained in the data, which cause high-frequency oscillations of the phase profile in the proximity of the cavity walls (see Fig. 2.11). In order to decrease this effect, the reconstructed wave profile is back propagated in free space after each iteration of the algorithm in order to apply the real space constraints on a profile with only minimal propagation effects [33]. This approach considerably improved the quality of the reconstructed data without perturbing the colloid profile inside the cavities. The success of the back propagation relies on the small height \( h \) of the structures. For too high structures, the propagation effects are so strong that they dominate over the phase oscillations induced by the colloid.
Figure 5.5: Retrieved phase profile of the microcavities filled with the colloidal suspension before adding LiCl.
Figure 5.6: Retrieved phase profile of the microcavities filled with the colloidal suspension after adding LiCl.
The phase reconstructions for the deionized colloid (Fig. 5.5) show, in general, smooth profiles with weak oscillations. Exceptions are '1C', which exhibits a pronounced oscillation in two layers, and '0.5D', with a strong oscillation of frequency smaller than the particle diameter. The latter cavity, as well as the other cavities filled with deionized colloid, appear to contain a mixture of different density profiles at different $y$- and $z$-values within the cavities.

For the hard-sphere solution (Fig. 5.6), we observe stronger oscillations that change as a function of the cavity width. For very narrow cavities, we see a mixture of one and two layers. Two pronounced layers appear in the arrays '0.75C' and '1B'. For still larger $w$, disorder occurs again, until for '1.25D' three layers have clearly formed. Then disorder progressively occurs until '1E', where four layers have formed. For cavity '1F', five layers are weakly formed, but then, at the largest $w$, disorder takes over again. The cavity widths $w$ in which two, three and four layers are formed, are approximately two, three and four times 142 nm.

In both deionized and screened colloidal suspensions, the measured oscillations are small, as is expected for liquids. If the colloid were crystallized, strong oscillations would result [71], which is not observed here. Moreover, the average volume fraction of particles across the cavities is always equal or smaller than 0.2, below the critical density of the liquid/solid transition in bulk hard-sphere systems (see Fig. 3.2 and [49]).

If we consider that the effective hard-sphere diameter of the colloidal particles due to the screened Coulombic potential is about 140 nm, we have seen confinement-induced ordering of colloidal hard-sphere suspensions in the liquid phase at confinement distances which correspond to integer numbers of the size of the hard spheres. Simulations predict this behavior for hard-sphere systems [5]. In addition, the average density across the cavity is larger when the ordering is more pronounced. This behavior is expected, since a higher degree of order allows for a denser packing of the particles, and it has been recently reported in an optical study of a confined molecular fluid [72].

In summary, Bragg scattering from a charge-stabilized colloidal suspension confined in microcavity arrays showed clear confinement-induced liquid order/disorder behavior in cavities of widths of the order of few times the size of the particles $2R = 109$ nm.

In the hard-sphere solution, the formation of two, three and four layers was observed at cavity widths of $w = 288$ nm, $w = 426$ nm and $w = 561$ nm, corresponding to entire multiples of 142 nm. The oscillations were less pronounced at intermediate cavity widths. Confinement effects were more clearly observable in the hard-sphere suspension than in the deionized suspension.

### 5.2 Diffuse scattering

The diffusely scattered intensity from a colloid confined in an array of microcavities is described by Eq. 2.65, where $S(q)$ is the anisotropic structure factor due to confine-
ment. In the following we report SAXS measurements on confined hard-sphere colloidal suspensions, from which \( S(q) \) was determined. A comparison with the bulk structure factor \( S_b(q) \) of the same colloid revealed differences which can be explained with the structural model for uniformly filled cavities introduced in section 2.2.5. The structural differences between confined and bulk suspensions are anisotropic as predicted and they arise from excluded volume effects.

5.2.1 Experimental

The measurements were performed at the ID2 beamline at the ESRF. Fig. 5.7 shows the experimental setup. The XRII-FReLoN CCD camera [73] at the standard SAXS setup at ID2 served as a detector with a resolution of approximately 200 \( \mu \text{m} \). The distance between the sample and the detector was 10.064 m, with a flight tube in between filled with vacuum. The much stronger Bragg scattering from the grating formed by the microcavity arrays was attenuated by a 5 mm-wide lead strip which acted as a semitransparent beamstop. This still allowed the detection of the diffraction orders for alignment purposes. A thicker central beamstop of lead completely blocked the primary beam and the first four diffraction orders from the array. The photon energy was 12.46 keV and the beam size, defined by the slits, was approximately \( 200 \times 200 \mu \text{m}^2 \).

![Experimental setup](image)

Figure 5.7: Experimental setup used for the measurement of the diffusely scattered intensity from confined colloids.

The colloid was a charge-stabilized solution of \( \text{SiO}_2 \) spheres of radius \( R = 59 \text{ nm} \) and polydispersity \( \delta = 0.045 \) in an index-matched mixture of 55\% benzyl alcohol and
45% ethanol with volume fraction $\phi = 0.11$. Initially, the suspension was deionized after storage with an ion-exchange resin but, for the measurements shown here, a small amount of LiCl was added to the suspension in order to screen the Coulomb potential between the particles. Measurements on the bulk fluid indicated that the suspension was a good approximation to a hard-sphere system. The colloid was confined in cavity arrays of 1 and $1.5 \mu m$ period and with cavity widths ranging from 330 to 1090 nm. The height of the structures was $h = 8 \mu m$.

A typical diffuse scattering measurement from a confined colloid is shown in Fig. 5.8. The exposure time in this measurement was 15 s and the parameters of the array were $p = 1.5 \mu m$ and $w = 340 \mu m$. The lead strip considerably attenuated the diffraction orders from the grating, which were still visible. The sample was aligned with rotations about the three axes in such a way that the diffraction pattern was vertical and symmetric. In order to analyze the scattered intensity from the colloid, a reference measurement through a capillary filled with solvent was subtracted from the data. In the measurements with capillaries, a different beamstop is used with the shape indicated with a thin dashed line in the contour plot of Fig. 5.8. This means that the signal was modified in this region and cannot be included in the analysis.

The second plot in Fig. 5.8 shows intensity curves along the radial direction at different azimuthal angles $\alpha$. The abscissa $q_r$ denotes the momentum transfer in the radial direction. The solid line is a calculated form factor, which was fitted to a measurement of the scattered intensity from a diluted bulk suspension. The calculated form factor is scaled to the data in such a way that they coincide at large $q_r$-values. We see that the minima of the form factor are filled with respect to the theoretical one, most pronounced along the direction given by $\alpha = 65^\circ$, i.e. close to the confinement direction. This is caused, as discussed in section 2.3.3, by dynamical propagation effects close to the cavity walls, which slightly modify the form factor of the particles that are close to the walls.

A measurement through the Si chip and the glass slide at a region where no cavities were etched revealed the presence of bulk colloid between the chip and the glass. This means that, on top of the microcavity arrays, some colloid is present, whose scattering signal is superimposed to that from the confined colloid. From the intensities measured, we know that there is a layer of bulk colloid between the chip and the glass with a thickness varying from approximately 6 to 10 $\mu m$. In order to take this into account for further data analysis, reference measurements through holes and parts of the sample where no arrays exist were performed.

### 5.2.2 Structural changes due to confinement

After recording the diffuse scattering signal from all arrays and holes in the chip, a calculated form factor is manually fitted to each data set as shown in Fig. 5.8. The
Figure 5.8: Diffuse scattering measured on a colloidal suspension confined in a microcavity array. Top: contour plot of the detected intensity on a logarithmic scale. Bottom: integrated intensities along the radial direction over an interval \( \delta \alpha = 8^\circ \) at three different azimuth angles. The solid line is a calculated form factor.
scaling factors used to fit the theoretical form factor serve to estimate the amount of bulk colloid on top of the structures. Calling $I_{\text{grat}}^c$ the intensity recorded from an array and $I_{\text{chip}}^c$ the intensity recorded from a part of the chip without structures, we performed the following correction to the data:

$$I_{\text{corr}}^c = I_{\text{grat}}^c - \frac{F_{\text{grat}}}{F_{\text{next}}} I_{\text{chip}}^c,$$

(5.1)

where $F_{\text{grat}}$ is the scaling factor of the measured array and $F_{\text{next}}$ is the scaling factor of the array situated close to the region where the reference measurement $I_{\text{chip}}^c$ was taken.

In a second step, the corrected data are fitted again to the theoretical form factor, the scaling factor being determined automatically in a routine. Then the data are divided by the form factor in order to obtain the experimental structure factor $S(q)$ of the confined colloid. The confinement-induced changes in the short-range spatial frequencies are contained in the difference structure factor, which we define as

$$\Delta S(q) \equiv S(q) - S_b(q),$$

(5.2)

where $S_b(q)$ is the bulk structure factor. The difference structure factor has previously served for the analysis of structural changes, like for example in [74].

The left panel of Fig. 5.9 shows a measured $\Delta S(q)$, in which the $S(q)$ was obtained from a colloid confined in an array of period $p = 1.5 \mu$m and cavity width $w = 340 \text{ nm}$ and the $S_b(q)$ was measured from a hole. The data show two diffuse minima along the confinement direction. In the right panel of Fig. 5.9 we show a numerical calculation of $\Delta S(q)$ according to the structural model of a colloid uniformly filling the cavity. Here we evaluated $S(q)$ and $S_b(q)$ with the use of Eq. 2.75 and Eq. 2.61 and assumed a Percus-Yevick pair distribution function of a hard-sphere system. The parameters used in the calculations were $w = 340 \text{ nm}$, $R = 59 \text{ nm}$ and $\phi = 0.2$. The diffuse minima along the confinement direction are well explained by this model. They are due to the absence of a structure factor peak along the confinement direction as a consequence of the excluded volume effects.

It is remarkable that experimental and calculated contour plots in Fig. 5.9 agree quantitatively (see false colors). The difference was optimized by taking a volume fraction of particles $\phi = 0.2$ in the calculation of the Percus-Yevick pair distribution function rather than the experimental value of $\phi = 0.11$. The average concentration of particles appears to be higher in confinement than in the bulk solution, in agreement with an enhanced average phase jump across the cavity as seen in our phase reconstructions of strongly layered colloids.

Ideally one would like to have a model describing the short-range inter-particle correlations for a colloid which, apart from being confined in a narrow cavity, has an oscillating density profile, as we found in our previous analysis of the Bragg peaks. The model of a gaussian distribution of particles distributed in a narrow gap (section 2.2.5)
Figure 5.9: Difference structure factor $\Delta S(q)$ between bulk and confined colloid. On the left side, measured $\Delta S(q)$ from an array with $p = 1.5\,\mu\text{m}$ and cavities of width $w = 340\,\text{nm}$ filled with a hard-sphere colloidal suspension ($R = 59\,\text{nm}$ and volume fraction $\phi = 0.11$). On the right side, calculated $\Delta S(q)$ for a uniformly distributed colloidal suspension confined in a cavity of the same width assuming a Percus-Yevick pair distribution function for $\phi = 0.2$ and $R = 59\,\text{nm}$.

would be a simplification of the case in which the cavity is so narrow that only one layer can form, but it cannot be applied to explain the data shown here, in which the cavity has almost three times the size of the particles. However, it seems reasonable that the largest effect in the short-ranged inter-particle correlations is produced by excluded volume effects near the confining walls. This is probably the reason why the model of uniformly filled colloid adequately describes the data.

The large signal in the measured $\Delta S(q)$ at $q_x \simeq 0.07\,\text{nm}^{-1}$ (observe values above the scale maximum) arises from dynamical effects in the diffuse scattering. The enhanced first minimum of the form factor along the confinement direction (see Fig. 5.8) contributes to $S(q)$, while this effect does not exist in bulk suspensions. The dynamical effect in the diffuse scattering can be regarded as an unwanted side effect. On the other hand, it can be exploited to study the behavior of the colloidal particles next to the confining walls, since it is strongly dependent on the distance of the particles to the walls, as we saw in section 2.3.3.

5.2.3 Analysis of the dynamical scattering effects

In Fig. 5.10 we show on the left side $S(q)$ from an array of cavities with $w = 580\,\text{nm}$ on a linear scale over a large range, such as to observe the strong dynamical effect. This manifests itself as a ring at the position of the first minimum of the form factor, which is more intense close to the confinement direction. On the right side, the maximum values of $S(q_r)$ at two different azimuth angles $\alpha = 10^\circ$ and $\alpha = 65^\circ$ are plotted as a function
of the cavity width for all 1.5 µm-period arrays filled with the colloidal suspension with LiCl (hard-spheres system). The maximum values of $S(q_r)$ were determined by fitting Gaussian curves to the large peaks of $S(q_r)$ at the position of the first minimum of the form factor. The peaks have no structural meaning because they are just a consequence of the dynamical scattering effect on the form factor, but fitting them with Gaussians is only a practical way to measure the strength of this effect. In the non-confinement direction, $\alpha = 10^\circ$, the maximum values of $S(q_r)$ stay constant. On the other hand, close to the confinement direction ($\alpha = 65^\circ$) they tend to decrease as the width of the cavities increases.

The increase of dynamical effects for decreasing cavity width can be explained if one takes into account that, for small $w$, a relatively larger proportion of the total number of particles is close to the wall. Since the dynamical scattering effect is localized near the walls, it becomes more prominent for smaller cavities. Moreover, we observe oscillations in the dynamical effect. The green curve in Fig. 5.10 traces out the oscillations of $\text{max}[S(q)]$. The period of the oscillations is approximately 120 nm, very close to the size of the colloidal particles $2R = 118$ nm. One can relate large dynamical effects to the proximity of many particles to the walls and argue as follows. When the particles are perfectly packed in the cavity, the outer layers lie very close to the walls, which enhances the dynamical effect. When the particles are disordered within the cavity, a smaller number or particles lie close to the walls and dynamical effects decrease.

In summary, we have investigated the diffuse scattering from hard-sphere colloidal
suspensions in confinement. The results show anisotropic structural changes with respect to the bulk solution, mainly arising from excluded volume effects in the direction of confinement. Similar effects have been previously studied on liquid benzene confined in cylindrical pores [38].

A qualitative study of the dynamical effects in the diffuse scattering reveals an oscillatory trend which can be associated with the number of particles lying next to the cavity walls. The periodicity of the oscillations is close to the diameter of the particles, which indicates a possible relation to confinement-induced order/disorder phenomena. In order to verify this, a quantitative study of the dynamical effects in the form factor is needed, for which an analytical expression of the propagating field next to the confining walls has to be derived. This would be most efficiently done by decomposing the field in eigenmodes of the array and applying the coupled wave theory, developed for the study of dynamical effects in the diffraction efficiencies of x-ray zone plates [75].
Conclusion and outlook

Confinement-induced phenomena are expected to occur when a fluid is confined within a space of the order of a few times the size of the fluid’s constituents. We investigated charge-stabilized SiO$_2$ colloidal suspensions of ca 100 nm-diameter particles confined in cavity widths ranging from 300 to 1000 nm. Liquid order/disorder was detected in suspensions of nearly hard spheres depending on whether an integer or fractional number of layers fit within the cavity. This integer/fractional layer effect has been predicted by theoretical studies and simulations and also explains force oscillations measured previously in the surface force apparatus. In addition, excluded volume effects were observed, which were explained with a simple model for the structure factor.

We presented a new method for the study of fluids in confinement in which a 1D array of microcavities serves as a container for the fluid. On the one hand, X-ray scattering from the confined fluid yielded the colloid density profile in the confinement direction averaged over many cavities. On the other hand, diffuse scattering measurements revealed the short-range particle-particle correlations within the confined colloid. The possibility to distinguish between these two structural properties is one of the main advantages of having an array of confining containers instead of a single one.

The study of fluids confined in microcavity arrays present several advantages with respect to previous experimental studies. The large scattering volume, the good stability of the structures and the prevention of evaporation of the confined fluid made the measurements simpler than in previous experiments with x-rays in which a single cavity was investigated. The large scattering volume created by many cavities is especially advantageous when radiation damage is a problem, e.g. in micellar solutions, protein solutions and biological fluids in general [76].

Our fabrication technique of the containers limited the confinement gaps to a few hundreds of nm, which is too large to induce confinement effects within simple molecular fluids. However, x-ray lithography currently allows the fabrication of 1D and 2D nanostructures with cavities down to ca 20 nm size over a 500 $\times$ 500 $\mu$m$^2$ area [77], which could serve for confinement of complex fluids with smaller constituents than colloids (micelles, proteins) and even simple fluids with large molecules, such as octamethylcyclotetrasiloxane (OMCTS). Their confinement in nanoholes, in which they
fit an entire number of times, raises questions regarding their structural arrangement, orientation and shape. Finally, coherent illumination over the entire area would allow for studies of the dynamics of fluids in confinement. This would require measurements over time scales typical of the self-diffusion time of the fluid’s constituents. The dynamics of fluids are expected to slow down in confinement, which may enable us to study fluctuations in their positions and even in their molecular shape.
Appendix A

Basic mathematical expressions

A.1 Dirac delta function

The Dirac delta function at \( r = a \) is defined as

\[
\delta(r - a) = \begin{cases} 
0 & \text{for } r \neq a \\
\infty & \text{for } r = a.
\end{cases}
\] (A.1)

with

\[
\int \delta(r - a) d^3r = 1.
\] (A.2)

Mathematically, the Dirac delta function is not a function but a distribution. One can choose the following representation of the delta function:

\[
\delta(r) = \int e^{2\pi i u \cdot r} d^3u.
\] (A.3)

Delta functions only become meaningful when they are applied to a test function \( f(r) \) in the following way:

\[
f(a) = \int \delta(r - a)f(r) d^3r.
\] (A.4)

A.2 Convolution

The convolution between two functions \( f \) and \( g \) is defined as

\[
f(r) \otimes g(r) \equiv \int f(R)g(r - R) d^3R.
\] (A.5)

A.3 Fourier transformations

The Fourier transform of a function \( f \) is defined as

\[
\mathcal{F}[f(r)] = F(u) = \int f(r) e^{2\pi i u \cdot r} d^3r
\] (A.6)
and the inverse Fourier transform is given by

$$\mathcal{F}^{-1}[F(u)] = f(r) = \int F(u)e^{-2\pi i u \cdot r}d^3u.$$  \hspace{1cm} (A.7)

Here, $u = q/2\pi$ with $q$ being the momentum transfer. The variable $u$ is chosen to avoid prefactors in the inverse Fourier transform.

The multiplication theorem in Fourier theory states

$$\mathcal{F}[f(r) \cdot g(r)] = F(u) \otimes G(u),$$  \hspace{1cm} (A.8)

with $F$ and $G$ the Fourier transforms of $f$ and $g$, respectively.

The convolution theorem states

$$\mathcal{F}[f(r) \otimes g(r)] = F(u) \cdot G(u).$$  \hspace{1cm} (A.9)
## Physical constants

<table>
<thead>
<tr>
<th>Constant</th>
<th>symbol</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Classical electron radius</td>
<td>$r_e$</td>
<td>$2.818 \times 10^{-15}$ m</td>
</tr>
<tr>
<td>Electron charge</td>
<td>$e$</td>
<td>$1.602 \times 10^{-19}$ C</td>
</tr>
<tr>
<td>Permittivity of vacuum</td>
<td>$\epsilon_0$</td>
<td>$8.854 \times 10^{-12}$ A s V$^{-1}$ m$^{-1}$</td>
</tr>
<tr>
<td>Speed of light</td>
<td>$c$</td>
<td>$2.998 \times 10^8$ m s$^{-1}$</td>
</tr>
<tr>
<td>Boltzmann’s constant</td>
<td>$k_B$</td>
<td>$1.381 \times 10^{-23}$ J K$^{-1}$</td>
</tr>
</tbody>
</table>
## Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPM</td>
<td>Beam Propagation Method</td>
</tr>
<tr>
<td>BOE</td>
<td>Buffer Oxide Etch</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge-Coupled Device</td>
</tr>
<tr>
<td>DLS</td>
<td>Dynamic Light Scattering</td>
</tr>
<tr>
<td>DLVO</td>
<td>Derjaguin, Landau, Verwey and Overbeck</td>
</tr>
<tr>
<td>ESRF</td>
<td>European Synchrotron Radiation Facility</td>
</tr>
<tr>
<td>FFT</td>
<td>Fast Fourier Transform</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width at Half Maximum</td>
</tr>
<tr>
<td>ID02</td>
<td>2\textsuperscript{nd} undulator beamline at the ESRF</td>
</tr>
<tr>
<td>MS</td>
<td>Materials Science</td>
</tr>
<tr>
<td>PMMA</td>
<td>Polymethylmethacrylate</td>
</tr>
<tr>
<td>RF</td>
<td>Radio Frequency</td>
</tr>
<tr>
<td>RIE</td>
<td>Reactive Ion Etching</td>
</tr>
<tr>
<td>SAXS</td>
<td>Small-Angle X-ray Scattering</td>
</tr>
<tr>
<td>sccm</td>
<td>Standard Cubic Centimeter per Minute</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>SFA</td>
<td>Surface Force Apparatus</td>
</tr>
<tr>
<td>SLS</td>
<td>Swiss Light Source</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscope</td>
</tr>
</tbody>
</table>
### List of symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>azimuthal angle in the detector plane</td>
</tr>
<tr>
<td>$\alpha_c$</td>
<td>critical angle for total reflection</td>
</tr>
<tr>
<td>$\beta$</td>
<td>imaginary part of deviation of refractive index from unity</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>electron energy in storage ring in rest mass energy units</td>
</tr>
<tr>
<td>$\gamma^{-1}$</td>
<td>opening angle of synchrotron radiation cone</td>
</tr>
<tr>
<td>$\delta$</td>
<td>real part of deviation of refractive index from unity (scattering)</td>
</tr>
<tr>
<td>$\delta$</td>
<td>polydispersity (colloidal suspensions)</td>
</tr>
<tr>
<td>$\Delta\theta$</td>
<td>misalignment of wafer flat</td>
</tr>
<tr>
<td>$\Delta\rho$</td>
<td>local electron density variation</td>
</tr>
<tr>
<td>$\Delta\phi$</td>
<td>phase shift along a rib of microcavity array</td>
</tr>
<tr>
<td>$\Delta\phi'$</td>
<td>phase shift along a rib of empty microcavity array</td>
</tr>
<tr>
<td>$\Delta\Omega$</td>
<td>element of solid angle</td>
</tr>
<tr>
<td>$\Delta n$</td>
<td>local number density variation</td>
</tr>
<tr>
<td>$\epsilon_r$</td>
<td>relative dielectric constant</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>emittance</td>
</tr>
<tr>
<td>$\eta_n$</td>
<td>grating diffraction efficiency in order $n$</td>
</tr>
<tr>
<td>$\theta$</td>
<td>scattered angle (scattering)</td>
</tr>
<tr>
<td>$\theta$</td>
<td>tapering angle of microcavity walls (fabrication)</td>
</tr>
<tr>
<td>$\kappa^{-1}$</td>
<td>Debye-Hückel screening length</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>wavelength</td>
</tr>
<tr>
<td>$\lambda_B$</td>
<td>characteristic distance between ions in a solvent</td>
</tr>
<tr>
<td>$\mu$</td>
<td>attenuation coefficient</td>
</tr>
<tr>
<td>$\xi$</td>
<td>coherence length</td>
</tr>
<tr>
<td>$\mathcal{O}$</td>
<td>surface area of cavity wall</td>
</tr>
<tr>
<td>$\rho$</td>
<td>electron density</td>
</tr>
<tr>
<td>$\bar{\rho}(\mathbf{r})$</td>
<td>averaged electron density of microcavity array</td>
</tr>
<tr>
<td>$\bar{\rho}_p(\mathbf{r})$</td>
<td>averaged electron density of one array period</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>source size</td>
</tr>
<tr>
<td>$\sigma'$</td>
<td>source divergence</td>
</tr>
</tbody>
</table>
φ  volume fraction of colloidal particles in solution

φn  scattering of diffraction order n

A  cross sectional area

c(x)  profile of the colloid along the confinement direction

C(R)  Schulz distribution

D  distance sample-source

F(q)  scattered amplitude

Fc(q)  scattered amplitude from single colloidal particle

\( F(q) \)  dimensionless form factor of a sphere

g(r)  pair distribution function

\( G(r, q) \)  anisotropic packing function

h  height of the structures in a microcavity array

I(q)  scattered intensity

I0  incident intensity

J0  Bessel function of zeroth order

k  wave vector

k0  free-space wave number, \( 2\pi/\lambda \)

L  length of microcavity array

n  refractive index (scattering)

n  concentration of ions (colloidal suspensions)

e  electron density

\( n_e(2)(r_1, r_2) \)  joint probability density to find a particle at \( r_2 \), given a particle at \( r_1 \)

n(r)  number density distribution

\( \bar{n} \)  average number density

N  total number of colloidal particles

Ng  number of periods of microcavity array

p  period of microcavity array

P  radiated power of synchrotron source

P(r)  Patterson function

q  momentum transfer

R  particle radius

s  period of oscillating colloid profile

s(x)  microcavity array profile along the confinement direction

S(q)  structure factor of confined colloid

\( S_b(q) \)  structure factor of bulk colloid

T  transmission

w  width of microcavity

\(<hkl>\)  family of planes with Miller indices \( h, k, l \)
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Curriculum vitae

Personal data

Ana Díaz Díaz
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Born 24-07-79 in Oviedo, Spain
Single, mother tongue Spanish

Education

2002-2006 PhD Physics, ETH Zurich
working at the Paul Scherrer Institute, Switzerland

2001-2002 Studies of Physics, University of Tübingen
ERASMUS exchange program
Tübingen, Germany

1997-2002 Licenciature in Physics, University of Oviedo
Oviedo, Spain

Foreign languages

English (fluent)
German (medium)
Research experience

- Nano- and micro-fabrication techniques: electron beam lithography, reactive ion etching, chemical wet etching
- Scanning electron microscopy (SEM)
- Measurements with synchrotron radiation at SLS and ESRF: x-ray diffraction, small angle x-ray scattering (SAXS) on colloid, protein and micelle solutions, phase contrast x-ray imaging, grazing-incidence small angle scattering (GISAXS)
- Beamline commissioning at the Materials Science beamline at SLS: experience with the optical components of a beamline
- Preparation and handling of colloidal suspensions
- Programming skills: IDL for data analysis and calculations

Teaching experience

- Teaching assistant, second year Physics Laboratory at the ETH Zurich

Publications
[16], [19], [20], [33], [56], [68], [69]