Structure of confined fluids by x-ray interferometry using diffraction gratings

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Abstract: We develop a novel method for structure determination of confined fluids using diffraction-grating-based x-ray interferometry. Within this approach, diffraction from a microfluidic array, which acts both as confinement and transmission diffraction grating, provides the reference wave, whereas the density modulations of the confined fluid, acting as a weak phase object, generate the object wave. The ensemble-averaged density profile of the fluid perpendicular to the confining channel is then unambiguously obtained from the interference between the reference and object waves by direct Fourier inversion.

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References and links

1. Introduction

Fluids are known to order in layers at the solid-fluid interface [1, 2]. Similarly, confinement of fluids between two solid surfaces has been found to alter their bulk properties, and may even induce solid-like behavior; notably, confinement leads to an increased viscosity, a reduced diffusion of the fluid constituents, and an increased sliding friction between the confining surfaces. Combined with surface force apparatus studies, these observations indirectly imply confinement-induced fluid ordering [3]. However, since the confining geometry imposes strict restrictions on the probe, direct structural information on confined fluids is scarce [4, 5].

An important advance was recently made by the introduction of microfluidic arrays [6], which both provide the confinement and act as hard x-ray transmission diffraction gratings [7] (see Fig. 1 for a schematic representation of the experimental setup). In combination with an iterative phase-retrieval algorithm [8], the ensemble-averaged electron density profile perpendicular to the confining channel could thus be obtained in a model-independent manner [9].

A unique determination of the structure of an object by x-ray diffraction is hampered by the well-known phase problem; the experiment provides information on the diffracted intensities rather than amplitudes, i.e., information on the scattering phases is lost (at least without a priori knowledge [10, 11]). A conceptually simple, yet powerful, method for phase retrieval is provided by holography (see, e.g., [12]), in which the information on the scattering phases is encoded in the interference between the reference and object waves. Such an approach has also been implemented in x-ray crystallography [13], with the reference and object waves being due to x rays scattered from the known and unknown parts of a crystal. This technique has successfully been used, e.g., for completing the crystal structure of biomolecules [14] and determining surface electron densities [15].

Here we propose a method for structure determination of confined fluids by combining microfluidic arrays with the holographic interpretation of x-ray diffraction patterns following
Our novel approach is based on partitioning the sample into a fabricated (and hence known), periodic structure (i.e., the confining microfluidic array filled with a homogeneous fluid) and the unknown, weak phase object under study (i.e., the confinement-induced density modulations of the fluid). This is the first time the technique is applied to an artificially produced periodic structure, allowing structural studies on nano-scale objects rather than atomic systems. Within the present approach, the reference wave is provided by diffraction from the known structure, while the object wave is due to the confined fluid. Since the confinement-induced density modulations of the fluid constitute a weak phase object compared to the homogeneously filled array, the density profile perpendicular to the confining channel can be unambiguously determined from the interference between the reference and object waves by means of direct Fourier inversion. We note that the present method yields the ensemble-averaged fluid density profile (averaged both laterally within a single confining channel and over a set of identical channels) rather than a single realization. The results of the present study can thus be summarized as follows: First, we outline the theoretical framework of our approach. Next, we briefly review the fabrication of microfluidic arrays with reduced dimensions (a factor of \( \sim 1/5 \) compared to the periods \( p \) and channel widths \( w \) reported previously [6]), allowing studies with approximately 4 nm real-space sampling on confinement-induced ordering of fluids with particle diameters below 50 nm. Finally, we demonstrate our diffraction-grating-based x-ray interferometry technique on a confined colloidal fluid.

2. Diffraction-grating-based x-ray interferometry

Within the kinematic approximation, the transmission function \( t(x) \) of a fluid-filled array of rectangular channels (i.e., a diffraction grating) can be conveniently written as

\[
t(x) = 1 + \left\{ e^{i(\Phi + \alpha(x))} - 1 \right\} f(x). \tag{1}
\]

Here \( \Phi = 2\pi h\Delta\delta/\lambda \) is the average phase shift of the exit wave across the grating-fluid interface, with \( \Delta\delta \) denoting the corresponding change of the refractive index (neglecting absorption [16]), \( \lambda \) the wavelength, and \( h \) the depth of the channels. The periodic window function \( f(x) \) equals unity inside the channels and vanishes elsewhere [the finite depth of the channels is implicitly included in both \( t(x) \) and \( f(x) \)]. The ensemble-averaged phase-shift modulations induced by confinement of the fluid (compared to its homogeneous counterpart) are contained in the function \( \alpha(x) \). We note that \( \alpha(x) \) is proportional to the confinement-induced fluid density modulations perpendicular to the confining channel. Throughout this study we
assume the confinement-induced phase-shift modulations to be small, justifying the approximation $e^{i\alpha(x)} \simeq 1 + i\alpha(x)$. The reader is referred to Fig. 1 for the geometric definitions.

The transmission grating diffracts into orders $m$ at the positions $2\pi m/p$ in reciprocal space. For non-zero diffraction orders [17], the Fourier coefficients of the transmission function $t(x)$ are given by

$$T_m \simeq (e^{i\phi} - 1) F_m + iA_m e^{i\phi} = T_m^0 + iA_m e^{i\phi},$$

with $F_m$ and $A_m$ denoting the Fourier coefficients of $f(x)$ and $a(x) \equiv \alpha(x)f(x)$, respectively. For convenience, $T_m$ can also be defined using the reference transmission function $t_0(x)$ (with corresponding Fourier coefficients $T_m^0$) of a known, homogeneously filled grating [obtained by setting $\alpha(x) = 0$ in Eq. (1)]. For rectangular channels, both $f(x)$ and $a(x)$ are real and symmetric; hence, their respective Fourier coefficients are also real and symmetric. The diffraction efficiencies $\eta_m = |T_m|^2$ (normalized as $\sum_m \eta_m = 1$) for the fluid-filled grating exhibiting confinement-induced density modulations can then be formulated in the particularly simple form

$$\eta_m \simeq \eta_m^0 + 2A_m F_m \sin \Phi + A_m^2.$$

As noted by Szöke [13], this set of expressions for different $m$ is formally identical to that for the intensity distribution measured over a domain in a hologram spanned by the angular coordinate $m$. Since both $F_m$ and $A_m$ are real, the image and twin image are identical; consequently, there is no twin-image problem within this approach. In the present case, the reference wave is provided by diffraction from a known, homogeneously filled grating. It consists of a complete set of diffraction orders with amplitudes $\{T_m^0\}$ and corresponding diffraction efficiencies $\{\eta_m^0\}$ [cf. the second definition of $T_m$ in Eq. (2)]. The object wave is given by the set of diffraction amplitudes $\{A_m\}$. Their interference with the reference wave gives rise to the second term in the right-hand side of Eq. (3). The third term describes the self-interference of the object.

Our starting point for determining the confinement-induced phase-shift modulations,

$$a(x) = \sum_{m=-M}^{M} A_m \cos(2\pi mx/p),$$

is the experimentally obtained diffraction efficiencies $\eta_m$ and $\eta_m^0$ [18] (up to order $M$). Moreover, since the density modulations constitute a weak phase object compared to the homogeneously filled grating [i.e., $|\alpha(x)| \ll |2\sin \Phi|$], the self-interference term in Eq. (3) can be neglected [in the present study, $|2\sin \Phi| \simeq 0.5$ and $|\alpha(x)| < 0.05$]. The set of Fourier coefficients $\{A_m\}$, and hence $a(x)$ according to Eq. (4), is then unambiguously obtained from the linear approximation to Eq. (3) (i.e., by neglecting the quadratic self-interference term $A_m^2$):

$$A_m \simeq \frac{\eta_m - \eta_m^0}{2F_m \sin \Phi}.$$

In the present study, the Fourier coefficients of the known, rectangular window function are obtained theoretically as $F_m = (w/p)\text{sinc}(\pi mw/p)\text{sinc}(q_m^z h/2)$, with $q_m^z \simeq -m^2 \lambda / p^2$ denoting the $z$ component of the momentum transfer. The effects of volume diffraction and a minor tapering of the gratings, which are restricted to high spatial frequencies (typically to diffraction orders $|m| \geq 30$ for the present microfluidic arrays, as estimated using dynamical diffraction theory), chiefly cancel out in the difference between diffraction efficiencies. Nonetheless, for high-resolution studies (i.e., when these high spatial frequencies become important), the dynamical counterpart of $F_m$ including tapering of the gratings, as obtained, e.g., using the coupled-wave theory [19], should be used. Finally, since the fluid is contained within the channels, we are effectively oversampling in reciprocal space [8] (i.e., the set of equations to be
we applied it to a confined colloidal fluid. As a model fluid, we chose a charge-stabilized and

typical diffraction pattern), leading to a real-space sampling


\[ \Delta P(x) = \sum_{m=-M}^{M} (\eta_m - \eta_m^0) \cos(2\pi mx/p) = \frac{2\sin\Phi}{p} a(x) \otimes f(-x) + \frac{1}{p} a(x) \otimes a(-x), \]

with \( \otimes \) denoting the convolution operator. Although \( \Delta P(x) \) does not yield the phase-shift modulations directly, it provides experimental access to the characteristic length scales of the system, weighted in accordance with their probability of occurrence. The second definition of \( \Delta P(x) \) in Eq. (6) has a particularly appealing interpretation with respect to the present study: The first term describes the convolution of the phase-shift modulation \( a(x) \) with the window function \( f(-x) \), whereas the second term is the self-convolution of \( a(x) \). In the present limit of a weak phase object, the latter term can be neglected. Hence our linear solution to Eq. (3) is found to be mathematically equivalent to deconvolving the difference autocorrelation function \( \Delta P(x) \) using the known window function \( f(x) \).

3. Microfluidic arrays and experimental setup

The fabrication of the microfluidic arrays follows a procedure outlined elsewhere [6]. In brief, the array, composed of several gratings with systematically varying duty cycle \( w/p \), each grating in turn consisting of approximately \( 10^3 \) identical channels (the area of one grating being \( 0.5 \times 0.5 \text{ mm}^2 \)), is written by means of electron-beam lithography on a Si(110) wafer coated by a double mask consisting of a 30 nm SiO\(_2\) and a 15 nm Cr layer. The array is transferred to the double mask using dry etching and finally into the Si wafer using anisotropic KOH etching. By aligning the confining channels parallel to the \( \langle 112 \rangle \) direction, high-aspect-ratio structures \( (h/w \approx 20) \) with nearly vertical walls (tapering angle \( \theta \approx 0.1^\circ \)) are obtained. In the present work, we fabricated microfluidic arrays with the following grating dimensions: period \( p = 400 \text{ nm}, \) height \( h \approx 2.4 \mu\text{m}, \) and channel width in the range \( w \approx 120 - 190 \text{ nm} \) [see Fig. 1 for a scanning electron microscopy (SEM) image of a typical grating]. These arrays make studies on confinement-induced ordering of fluids with particle diameters below 50 nm feasible.

The experiment was carried out at the cSAXS beamline (X12SA) of the Swiss Light Source. The experimental setup is schematically presented in Fig. 1. The scattered x rays were collected using a two-dimensional (2D), single-photon-counting pixel detector (Pilatus 2M, pixel size \( 172 \times 172 \mu\text{m}^2 \) with a total of \( 1461 \times 1560 \) pixels), which was positioned 7 m behind the sample. Hence a complete set of diffraction orders could be obtained simultaneously (the data for diffraction orders \( |m| \leq 2 \) were collected separately without using a beam stop). Moreover, the use of a 2D detector allowed in situ characterization of the fluid by small-angle x-ray scattering (SAXS). An evacuated flight tube between the sample and the detector was employed in order to minimize parasitic scattering. The (partially coherent) incident x-ray radiation (wavelength \( \lambda = 1.00 \AA \) ), impinging on the sample at normal incidence, was focused onto the detector plane in order to increase the angular resolution. The beam size at the sample was approximately \( 0.2(\text{H}) \times 0.1(\text{V}) \text{ mm}^2 \). With the present microfluidic arrays and experimental setup, the intensities of typically \( M \geq 50 \) diffraction orders could be determined reliably (see Fig. 2 for a typical diffraction pattern), leading to a real-space sampling \( \Delta r = p/(2M + 1) \leq 4.0 \text{ nm} \).

4. Results and discussion

In order to verify the diffraction-grating-based x-ray interferometry technique outlined above, we applied it to a confined colloidal fluid. As a model fluid, we chose a charge-stabilized and
Fig. 2. Typical diffraction pattern acquired from a fluid-filled grating. Due to symmetry, only the positive diffraction orders are shown. Inset: Magnified view of the 42nd to 53rd diffraction orders.

A weakly screened colloidal suspension consisting of SiO$_2$ spheres dispersed in a solution of dimethylformamide and 0.5 mM of LiCl. The particle diameter and typical nearest-neighbor distance were determined in situ from SAXS data (i.e., from the form factor and the position of the first peak in the structure factor) to be $d \simeq 48$ nm and $l \simeq 62$ nm, respectively. The volume fraction of the particles in the suspension was 11%.

The difference autocorrelation function of Eq. (6) is presented in Fig. 3 for selected channel widths. Noteworthily, already this easily obtainable quantity, i.e., a simple Fourier transform of the difference between experimental diffraction efficiencies, reveals qualitatively the confinement-induced ordering of the fluid: For the smallest channel widths, a single colloid layer is observed. However, for $w \simeq 134$ nm a second layer starts to emerge (see minima forming at $x \simeq \pm 70$ nm). The monolayers are found to segregate with increasing channel width.

The confinement-induced fluid density modulations perpendicular to the confining channel as a function of the channel width $w$, obtained using our present approach, are presented in Fig. 4. The effects observed in Fig. 3 are quantitatively verified. In particular, a pronounced condensation of two colloidal monolayers towards the channel walls is observed, irrespective of the channel width. We have verified this observation using a more elaborate iterative phase-retrieval algorithm [8]. This is exemplified in Fig. 5 as the phase-shift profile of the exit wave field across the confining channel, demonstrating the good agreement between the two different methods. However, quantitative discrepancies close to the solid-fluid interface and noise in the present approach (most strongly manifest as a dip in the centre of the channel) are observed.

The former effect can be attributed to an effective canceling of the Fresnel fringes close to the solid-fluid interface in the present approach, leading to a better description of the depletion of colloidal particles at the interface [19]. The latter effect, in turn, is due to an inadequate description of $F_m$ for high spatial frequencies (i.e., for $|m| \geq 30$). We note that the present finding, trapping of colloidal particles near the confining walls, has been observed previously and attributed to the net result of the repulsive electrostatic interactions in the system [22]. A detailed study on the trapping of colloidal particles and the role of electrostatic interactions will be presented elsewhere. Nevertheless, the results presented here clearly demonstrate the feasibility of the proposed diffraction-grating-based x-ray interferometry technique.
Fig. 3. Difference autocorrelation function $\Delta P(x)$ for selected channel widths $w$ (vertically offset for clarity).

Fig. 4. Contour plot of the confinement-induced fluid density modulations perpendicular to the confining channel as function of the channel width $w$. 
Fig. 5. Phase-shift profile across the confining channel ($w = 142$ nm). The solid line is obtained using the present interferometric approach, while the dashed line depicts the corresponding profile (including the grating) as obtained using an iterative phase-retrieval algorithm [8] (vertically offset in order to facilitate comparison). Inset: Unshifted phase profiles.

5. Outlook

It should be noted that the diffraction-grating-based x-ray interferometry technique outlined here is not wavelength-limited. With the present microfluidic arrays and experimental setup, we anticipate that studies on confinement-induced ordering of fluids with particle diameters down to $d \approx 20-30$ nm, such as micelles, are feasible. Moreover, fabrication of microfluidic arrays with channel widths $w \approx 10-50$ nm would make studies on confinement-induced ordering of proteins feasible. A unique possibility provided by coherent x rays should also be noted: the temporal counterpart of the present approach, i.e., x-ray photon correlation spectroscopy in heterodyne mixing mode [23], with diffraction from the grating acting as the static reference wave, would greatly facilitate studies on the dynamics of confined fluids. Finally, we note that a linearized interferometric approach, similar to the one demonstrated here for confined fluids, can be applied to a variety of samples partitionable into a fabricated (and hence known) structure and an unknown, weak phase object.

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