Grating-based holographic X-ray diffraction: theory and application to confined fluids

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A grating-based holographic X-ray diffraction technique has been developed for reconstructing density profiles of nano-scale fluids confined in channel arrays. Within this approach, the reference wave is due to diffraction from the fabricated channel array, whereas the object wave is generated by the confinement-induced ordering of the fluid. The ensemble-averaged density profile of the fluid across the confining channel, which constitutes a weak phase object, is then determined in a model-independent manner from the interference between the reference and object waves by direct Fourier inversion. The validity of the linear holographic approach and its connection to the autocorrelation function, the inclusion of channel tapering, and volume-diffraction effects are discussed in detail.

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1. Introduction

Confined fluids are abundant in nature and technology, with water or oil in porous rocks, blood cells in narrow vessels, and various micro- or nanofluidic devices being just a few examples. It is well known that the presence of a solid surface induces ordering of fluids perpendicular to the surface (Huisman *et al.*, 1997; van der Veen & Reichert, 2004). In the case of fluids confined between two solid surfaces, this effect is expected to be even more pronounced. However, direct observation of the ordering is hampered by restrictions imposed on the probe. A solution to this problem is provided by highly penetrating hard X-rays, as has been demonstrated using waveguiding (Zwanenburg *et al.*, 2000) and reflectivity (Seeck *et al.*, 2002) techniques. A further improvement was the recent introduction of microfluidic channel arrays (Diaz *et al.*, 2005), which act both as fluid containers and as transmission diffraction gratings. The advantage of such channel arrays is twofold: (i) a greatly enhanced scattering volume and (ii) the possibility of using well known crystallographic techniques. Using an iterative phase-retrieval algorithm (Bunk, Diaz, Pfeiffer, David, Schmitt *et al.*, 2007), the ensemble-averaged electron density profile perpendicular to the confining channel can then be obtained in a model-independent manner (Bunk, Diaz, Pfeiffer, David, Padeste *et al.*, 2007). This has allowed detailed studies on, for example, electrostatic trapping of colloidal monolayers near charged walls (Satapathy *et al.*, 2008) as well as buckling and layering transitions in confined colloids (Satapathy *et al.*, 2009).

The reconstruction of an object from X-ray diffraction data relies on determining the diffracted amplitudes. However, the experiment provides the intensities instead, *i.e.* the well known phase problem, with the information on the scattering phases being lost (at least without *a priori* knowledge about either the object or the probe). An elegant approach for phase retrieval is given by the holographic interpretation of diffraction patterns (Szöke, 1993) (henceforth termed holographic X-ray diffraction), in which the information on the scattering phases is contained in the interference between the X-rays scattered from known and unknown parts of a crystal. This technique has previously proven useful, for example, for completing the crystal structures of biomolecules (Maalouf *et al.*, 1993) and obtaining surface electron densities (Saldin *et al.*, 2001).

In this research paper, we provide a rigorous derivation of the novel grating-based holographic X-ray diffraction technique (Nygård, Satapathy, Bunk, Diaz *et al.*, 2008) and apply it for reconstructing density profiles of nano-scale fluids confined in channel arrays. The novelty of the approach, in comparison with the aforementioned crystallographic studies, lies in the partitioning of the sample into a fabricated, periodic structure, *i.e.* the homogeneously filled channel array, and the unknown object to be studied, *i.e.* the ensemble-averaged fluid density profile (averaged both laterally within each channel and over a set of identical channels). Hence, the method provides structural information on nano-scale objects instead of atomic or molecular systems. The reference wave in the present approach is due to diffraction from the fabricated periodic structure, whereas the confinement-induced fluid ordering gives rise to the object wave. In the limit of a weak phase object, the fluid density profile can then be determined

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in a model-independent manner from the interference between the reference and object waves by direct Fourier inversion.

Our experimental approach differs from holographic X-ray microscopy techniques, such as Fourier transform holography (McNulty *et al.*, 1992), in a fundamental manner. We take advantage of the full incident flux by using a macroscopic beam. Hence, we have only partially coherent illumination, similar to the crystallographic work by Szöke (1993). As a consequence, we obtain the ensemble-averaged density, in contrast to the single realizations probed by microscopy.

The rest of the paper is organized as follows: The theoretical framework of the present method is outlined in §2 (and Appendix A). In particular, the validity of the linear holographic approach and its connection to the autocorrelation (Patterson) function, an approach to include channel tapering, and volume-diffraction effects, *i.e.* effects due to a nonplanar wavefield inside the channel, are discussed in detail. The experimental aspects are briefly presented in §3. The technique is demonstrated on a confined colloidal suspension and compared with an iterative phase-retrieval algorithm (Bunk, Diaz, Pfeiffer, David, Schmitt *et al.*, 2007) in §4, while the work is summarized in §5.

2. Theory

In the present approach, the fluid is confined within a linear array of rectangular channels, *i.e.* a diffraction grating. The reader is referred to Fig. 1 for a schematic of the experimental setup and the geometric definitions. Scattering of an incident plane wave from the fluid-filled grating results in both discrete diffraction peaks, due to the periodicity of the sample, and a diffuse contribution, which originates from short-range spatial variations in the fluid density (Diaz & van der Veen, 2007). Here we only discuss the former contribution, which gives the ensemble-averaged fluid density profile perpendicular to the confining channel. The latter contribution, yielding the local structure of the confined fluid, has been discussed elsewhere (Nygård *et al.*, 2009).

2.1. Grating-based holographic X-ray diffraction

Within the kinematic (first Born) approximation, the transmission function $t(x)$ of a fluid-filled grating, consisting of identical, rectangular channels, is conveniently expressed as

$$t(x) = 1 + (\exp[i\{\Phi + \alpha(x)\}] - 1)f(x). \quad (1)$$

Here $\Phi = kh\Delta\delta$ denotes the average phase shift of the exit wave across the grating–fluid interface (see Fig. 2), $k = 2\pi/\lambda$ the magnitude of the wavevector with λ the wavelength, and h the depth of the channels. The average change in the real part of the refractive index across the grating–fluid interface is denoted by $\Delta\delta$. For photon energies far away from absorption resonances, it is given by $\Delta\delta = 2\pi r_e \Delta n_e / k^2$, r_e and Δn_e being the classical electron radius and the average change in the electron density across the grating–fluid interface, respectively. The term $f(x)$ is a periodic window function, which is

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 profile across the confining channel, which is due to the confinement-induced fluid ordering and is defined with respect to the average phase shift Φ , is contained in the function $\alpha(x)$ (see Fig. 2). Since the phase-shift profile is proportional to the projected electron line density over a grating period, finding $\alpha(x)$ is equivalent to determining the electron density profile of the confined fluid. We note that the factorization of the transmission function in equation (1) into a complex function and a real, periodic window function greatly facilitates the calculation of the diffraction properties, as will be made evident below.

Absorption could be included in the present approach by adding an imaginary part to the refractive index, $\Delta\delta \rightarrow \Delta\delta + i\Delta\beta$, with $\Delta\beta$ denoting the average change in the imaginary part of the refractive index across the grating–fluid interface. This change in the imaginary part relates to the absorption contrast $\Delta\mu$ through $\Delta\mu = 2k\Delta\beta$, with μ denoting the linear attenuation coefficient. Since $\Delta\beta/\Delta\delta \simeq 10^{-2}$ in the present study (see Table 1 for the relevant optical parameters), we can neglect absorption, *i.e.* we assume the channel arrays to act as pure phase gratings.

In the following, we make use of the approximation $\exp[i\alpha(x)] \simeq 1 + i\alpha(x)$. Hence, the transmission function of equation (1) can be reformulated as

Figure 1
Schematic of the experimental setup (left) and geometric definitions (right, shown in the xz plane).

Figure 2
Schematic phase-shift profile of the exit wave across a fluid-filled channel (solid line). The dashed line depicts the average phase shift Φ across the grating–fluid interface.

Table 1

Optical parameters for the used materials at a wavelength of $\lambda = 0.100$ nm (Henke *et al.*, 1993).

DMF denotes dimethylformamide (C_3H_7NO).

Material	δ	β
Si	3.17×10^{-6}	3.16×10^{-8}
SiO ₂	2.72×10^{-6}	1.52×10^{-8}
DMF	1.40×10^{-6}	1.20×10^{-9}

$$t(x) \simeq 1 + [\exp(i\Phi) - 1]f(x) + ia(x)\exp(i\Phi) = t_0(x) + ia(x)\exp(i\Phi), \quad (2)$$

where we have set $a(x) \equiv \alpha(x)f(x)$. For convenience, we have also defined the corresponding transmission function $t_0(x)$ of a fictitious, homogeneously filled grating [obtained by setting $\alpha(x) = 0$ in equation (1)], which we will use as a reference throughout this study.

The grating diffracts into orders m at the positions $2\pi m/p$ in reciprocal space, with p denoting the grating period. The corresponding diffraction amplitudes, *i.e.* the Fourier coefficients of the transmission function of equation (2), are given by

$$T_m \simeq \delta_{m0} + [\exp(i\Phi) - 1]F_m + iA_m \exp(i\Phi) = T_m^0 + iA_m \exp(i\Phi), \quad (3)$$

with T_m , F_m , A_m and T_m^0 denoting the Fourier coefficients of $t(x)$, $f(x)$, $a(x)$ and $t_0(x)$, respectively, and δ_{m0} the Kronecker delta. Since both $f(x)$ and $a(x)$ are real and symmetric for rectangular channels, their Fourier coefficients are also real and symmetric, a property that greatly facilitates the reconstruction. Moreover, it follows from the definition of $\alpha(x)$ that $A_0 = 0$. Consequently, the diffraction efficiency $\eta_m = |T_m|^2$ (normalized as $\sum_m \eta_m = 1$) for the zeroth diffraction order is given by $\eta_0 = |T_0|^2 \simeq |T_0^0|^2$, *i.e.* the confinement-induced ordering of the fluid has a negligible effect on η_0 to within first order of $\alpha(x)$. This, in turn, implies $\sum_{m \neq 0} \eta_m \simeq \sum_{m \neq 0} \eta_m^0$, with $\eta_m^0 = |T_m^0|^2$ denoting the reference diffraction efficiencies of the homogeneously filled grating.

Within the above approximations, the diffraction efficiencies of the nonzero diffraction orders for the fluid-filled grating exhibiting confinement-induced ordering can be written as

$$\eta_m \simeq \eta_m^0 + 2A_m F_m \sin \Phi + A_m^2. \quad (4)$$

As pointed out by Szöke (1993), this set of equations for different diffraction orders m is formally equal to the intensity pattern recorded in holography (see *e.g.* Goodman, 2005). It should be noted that in the present approach there is no holographic twin-image problem. The complicated reference wave is given by diffraction from the fabricated (and hence known), homogeneously filled grating, and it consists of a complete set of diffraction orders with amplitudes $\{T_m^0\}$ (and corresponding diffraction efficiencies $\{\eta_m^0\}$). The set of diffraction amplitudes $\{A_m\}$ composes the object wave. The interference between reference and object waves results in the

second term on the right-hand side of equation (4), while the self-interference of the object wave gives rise to the third term.

The confinement-induced phase-shift profile,

$$a(x) = \sum_{m \neq 0} A_m \cos(2\pi m x/p), \quad (5)$$

and hence the corresponding density profile of the fluid, is determined using the experimentally obtained diffraction efficiencies η_m (up to order M). Since the confinement necessarily leads to ordering of the fluid, the reference diffraction efficiencies η_m^0 are obtained from the experimental diffraction efficiencies η_m^e of the empty grating by scaling, $\eta_m^0 \simeq (\sum_{m \neq 0} \eta_m / \sum_{m \neq 0} \eta_m^e) \eta_m^e$ (see Appendix A for a justification of this procedure). Importantly, the fluid ordering constitutes a weak phase object compared with the homogeneously filled grating, *i.e.* $|\alpha(x)| \ll |2 \sin \Phi|$ [in the present study, $|2 \sin \Phi| \simeq 0.5$ and $|\alpha(x)| < 0.05$]. Consequently, the set of diffraction amplitudes $\{A_m\}$, and hence the phase-shift profile according to equation (5), can be determined from the linear holographic approximation [*i.e.* neglecting the quadratic self-interference term A_m^2 in equation (4)]:

$$A_m \simeq \frac{\eta_m - \eta_m^0}{2F_m \sin \Phi}. \quad (6)$$

The validity of this approximation will be discussed in §4 in terms of model calculations. Within kinematic diffraction theory, the Fourier coefficients of the rectangular window function are given by

$$F_m = \frac{w}{p} \text{sinc}\left(\frac{\pi m w}{p}\right) \text{sinc}\left(\frac{q_z^m h}{2}\right), \quad (7)$$

with w denoting the average channel width. The curvature of the Ewald sphere can be approximated as $q_z \simeq -q_x^2/(2k)$, which at the diffraction condition $q_x = 2\pi m/p$ leads to the z component of the momentum transfer being $q_z^m \simeq -\pi m^2 \lambda/p^2$. We note that the effects of channel tapering (typically the tapering angle $\theta \simeq 0.1^\circ$ for the present gratings) and volume diffraction have been neglected hitherto. These effects, which are manifest at high spatial frequencies (typically at $|m| \geq 30$ in the present study), effectively cancel in the subtraction of the reference diffraction efficiencies. A more thorough discussion of these effects will be given in §2.4.

2.2. Density refinement

The fluid is contained within the channels. Consequently, the set of equations to be solved is overdetermined by a factor p/w , *i.e.* we are oversampling in reciprocal space (Bunk, Diaz, Pfeiffer, David, Schmitt *et al.*, 2007). Such *a priori* knowledge has been utilized extensively in combination with iterative algorithms for phase retrieval in the field of coherent diffractive imaging [see, *e.g.*, Miao *et al.* (1999)]. In the present holographic approach, the object can be reconstructed irrespective of the oversampling in reciprocal space. However, the oversampling can be used for density refinement in a straightforward manner as follows: We write the function $a(x)$ as a discrete set of values $\{a_n\}$, sampled in intervals $\Delta x = p/(2M + 1)$ centered at equidistant points $\{x_n\}$ over the

period $-p/2 \leq x \leq p/2$. Since a_n vanishes for $|n| > P$, with the integer $P \equiv [wM/p]$, we can express the Fourier coefficients of $a(x)$ as the sum

$$A_m = (\Delta x/p) \sum_{n=-P}^P a_n \cos(2\pi m x_n/p). \quad (8)$$

There are in total M independent values of $\{A_m\}$, *i.e.* there are M independent linear equations, from which P independent values $\{a_n\}$ are to be determined (here we recall that $A_{-m} = A_m$, $a_{-n} = a_n$, $A_0 = 0$ and $\sum_n a_n = 0$). Since $P < M$, there are more equations than unknowns, and we can find a solution to the overdetermined set of equations by minimizing a least-squares deviation:

$$\chi^2 = \sum_{m=-M}^M \left[A_m - (\Delta x/p) \sum_{n=-P}^P a_n \cos(2\pi m x_n/p) \right]^2. \quad (9)$$

We note that the optimization of the fluid density profile using such an approach is analogous to the method of solvent flattening used for structure refinement in crystallography (Terwilliger, 1999).

2.3. Difference autocorrelation function

Next we make a connection between the approach outlined above and the autocorrelation function of the grating's transmission function (normalized to dimensionless units):

$$P(x) \equiv (1/p) t(x) \otimes t^*(-x) = \sum_{m=-\infty}^{\infty} \eta_m \cos(2\pi m x/p), \quad (10)$$

with $\otimes$ denoting the convolution operator and $*$ the complex conjugate. In the present study, $P(x)$ is particularly useful for two reasons: (i) The autocorrelation function $P_0(x)$ of the reference transmission function $t_0(x)$ provides a means to assess the experimentally determined diffraction efficiencies, the autocorrelation function of a rectangular window function being triangular. (ii) The difference autocorrelation function (Terwilliger *et al.*, 1987),

$$\Delta P(x) \equiv P(x) - P_0(x) = \sum_{m=-\infty}^{\infty} (\eta_m - \eta_m^0) \cos(2\pi m x/p), \quad (11)$$

which is straightforwardly determined from the experimental diffraction efficiencies, provides indirect information on the fluid density profile in terms of the characteristic length scales of the system, weighted with their probability of occurrence. The application of this property will be demonstrated in §4.

The difference autocorrelation function can also be conveniently formulated as a sum of convolutions:

$$\Delta P(x) \simeq (2 \sin \Phi/p) a(x) \otimes f(x) + (1/p) a(x) \otimes a(x), \quad (12)$$

where we have used the symmetry $f(x) = f(-x)$ and $a(x) = a(-x)$. This definition of $\Delta P(x)$ has a simple interpretation in real space, which greatly facilitates its analysis: The first term on the right-hand side describes the convolution of the object [the phase-shift profile $a(x)$] with a known reference function [the window function $f(x)$], whereas the second term is the self-convolution of the object. In the

present case of a weak phase object, the self-convolution term can be neglected,

$$\Delta P(x) \simeq (2 \sin \Phi/p) a(x) \otimes f(x), \quad (13)$$

an approximation that will be discussed in more detail in §4. By combining equations (11) and (13), the linear holographic approximation of equation (6) is found to be mathematically equivalent to deconvolving the difference autocorrelation function $\Delta P(x)$ using the known window function $f(x)$. We also note a formal similarity between the present approach and the convolution square-root technique used for determining the electron density from small-angle X-ray scattering (SAXS) data (Glatter, 1981).

2.4. Effects of channel tapering and volume diffraction

So far, we have worked within kinematic diffraction theory and assumed the confining channels to be rectangular. However, these approximations do not strictly hold for the high spatial frequencies. In particular, by including the tapering of the channels and volume-diffraction effects, the window function $f(x)$ is no longer symmetric in the z direction. Consequently, its Fourier coefficients are complex. Since the confinement-induced fluid ordering constitutes a weak phase object compared with the homogeneously filled grating, the effects of volume diffraction on A_m are negligible (Nygård, Satapathy, Bunk, Pfeiffer *et al.*, 2008). Moreover, within the accuracy of the present approach (see the last paragraph of this subsection), the effects of channel tapering on A_m can be neglected. The counterpart of equation (6) can then be written as

$$A_m \simeq \frac{\eta_m - \eta_m^0}{2\Phi \Re[\tilde{F}_m]}, \quad (14)$$

where $\Re$ denotes the real part of a complex quantity and we have used the approximation $\exp(\pm i\Phi) \simeq 1 \pm i\Phi$. The term $\tilde{F}_m$ denotes the Fourier coefficients of the window function including tapering. Within kinematic diffraction theory it is given by¹

$$\tilde{F}_m = \frac{1}{i2\pi m} \sum_{n=0}^1 \exp\left(\frac{i^{2n+1}\pi m w}{p}\right) \text{sinc}\left[\frac{h}{2}\left(q_z^m - \frac{i^{2n}2\pi m \theta}{p}\right)\right]. \quad (15)$$

The volume-diffraction effects are accounted for within dynamic diffraction theory. In practice, these effects are straightforwardly studied using the coupled-wave theory, which has previously been used for analyzing the focusing properties of diffractive X-ray optics (Schneider, 1997). In Fig. 3 we present the diffraction efficiencies of a typical empty channel array, with parameters $p = 400$ nm, $w = 142$ nm, $h = 2.4$ μ m and $\theta = 0$, as obtained using three levels of diffraction theory: kinematic theory either neglecting or including the z component of the momentum transfer q_z , and dynamic theory (Nygård, Satapathy, Bunk, Pfeiffer *et al.*, 2008). The kinematic theory is found to be in good (reason-

¹ In the limit of no tapering, equation (15) reduces to equation (7).

able) agreement with dynamic diffraction theory up to diffraction order $m \simeq 30$ ($m \geq 50$), provided the z component of the momentum transfer is included.

In Fig. 3 we also compare the diffraction efficiencies of an empty channel array ($p = 400$ nm, $w = 142$ nm and $h = 2.4$ μ m) as obtained within kinematic diffraction theory by either neglecting [equation (7)] or including [equation (15)] the tapering angle $\theta = 0.1^\circ \simeq 1.7$ mrad. The diffraction efficiencies are found to deviate strongly for $|m| \geq 30$, indicating the importance of including channel tapering in high-resolution studies. The importance of including the channel tapering is also verified by comparison with the experimental diffraction efficiencies.

Throughout this study, the phase-shift profile $\alpha(x)$ is averaged both laterally within each channel, *i.e.* in the y and z directions, and over a set of identical channels. Formally, this corresponds to assuming that $\alpha(x)$ exhibits no z dependence. Hence, the tapering of the channel arrays provides a fundamental limit on the resolution of the technique. In particular, the variation of the channel width in the z direction due to the tapering limits the real-space resolution to $\Delta x_\theta \simeq \theta h$, the corresponding diffraction order being $m_\theta \simeq [p/(\theta h) - 1]/2$. Inserting typical values $p = 400$ nm, $h = 2.4$ μ m and $\theta = 0.1^\circ \simeq 1.7$ mrad, we obtain $\Delta x_\theta \simeq 4.2$ nm and $m_\theta \simeq 47$. We note that this fundamental limit on the resolution also

applies to previous work using an iterative phase-retrieval algorithm (Bunk, Diaz, Pfeiffer, David, Schmitt *et al.*, 2007).

3. Experimental

Details on the microfluidic channel arrays, the model fluid and the experimental setup have been reported elsewhere (Nygård, Satapathy, Bunk, Diaz *et al.*, 2008; Nygård *et al.*, 2009). Nevertheless, we also briefly describe them here for completeness.

3.1. Samples

3.1.1. Microfluidic channel arrays. For confinement we use a microfluidic chip, consisting of a set of channel arrays with the following parameters: a period of $p = 400$ nm, a height of $h = 2.4$ μ m, a systematically varied channel width in the range $w \simeq 120$ –190 nm and a total area of 0.5×0.5 mm each. Moreover, we include holes of the same area as the arrays, allowing us to characterize the bulk fluid *in situ* using SAXS. The microfluidic chip was glued on a glass slide, which (i) prevents evaporation of the fluid and (ii) allows a free exchange of particles and ions because of the resulting fluid reservoir between the glass slide and the microfluidic chip.

The fabrication of the channel arrays follows closely a procedure developed for fabricating diffraction gratings of larger dimensions, the details of which have been reported elsewhere (Diaz *et al.*, 2005; David *et al.*, 2007). In brief, a $\langle 110 \rangle$ -oriented silicon wafer is coated with a double mask consisting of 30 nm-thick SiO_2 and 15 nm-thick Cr layers by means of thermal oxidation and evaporation, respectively. Next, the channel arrays, consisting of approximately 1000 identical channels, are patterned parallel to the silicon $\langle 112 \rangle$ crystallographic direction using electron-beam lithography. The pattern is then transferred into the double mask using dry-etching techniques. Finally, the structures are etched into silicon using a 20% solution of KOH at 333 K. This procedure leads to nearly vertical etching into silicon (the tapering angle being approximately $\theta \simeq 0.1^\circ$) and high aspect ratios (in the present study $h/w \simeq 13$ –19). We anticipate that the present channel arrays allow studies on confinement-induced ordering of fluids with particle diameters down to 20–30 nm. The reader is referred to Fig. 4 for a cross-sectional scanning electron microscopy (SEM) image of a typical channel array.

3.1.2. Colloids. In §4, the present grating-based holographic X-ray diffraction technique is demonstrated on a confined fluid. As a model system, we use a colloidal suspension consisting of negatively charged spherical SiO_2 particles dispersed in a solution of dimethylformamide and 0.5 mM LiCl. The synthesis of the particles has been performed according to the procedure described by Osseo-Asare and Arriagada (Osseo-Asare & Arriagada, 1990; Arriagada & Osseo-Asare, 1999).

The *in situ* SAXS characterization of the bulk colloid has been described elsewhere (Nygård *et al.*, 2009) (see Fig. 5 for the SAXS data). In brief, the modeling is carried out within the decoupling approximation (Kotlarchyk & Chen, 1983).

Figure 3

Diffraction efficiencies η_m^e of an empty channel array ($p = 400$ nm, $w = 142$ nm and $h = 2.4$ μ m). Top: Tapering angle $\theta = 0$. The dashed-dotted and solid lines are determined using kinematic diffraction theory [equations (7) and (17)] neglecting (*i.e.* $q_z^m = 0$) and including the z component of the momentum transfer, respectively. The dashed line is obtained using dynamic diffraction theory (Nygård, Satapathy, Bunk, Pfeiffer *et al.*, 2008). Bottom: Tapering angle $\theta = 0.1^\circ \simeq 1.7$ mrad. The solid and dashed lines are determined using kinematic diffraction theory neglecting [equation (7)] and including [equation (15)] the tapering angle, respectively. The dashed-dotted line denotes the experimental data.

First, the square modulus of the spherical particle form factor, with the polydispersity of the particles being included using the Schulz–Flory distribution (Borchert *et al.*, 2005), is fitted in the momentum-transfer range $0.3 \leq q \leq 1.0 \text{ nm}^{-1}$. This gives the average particle radius $R = 24.1$ (1) nm and the polydispersity $\Delta R/R = 0.038$ (2), in agreement with results obtained using transmission electron microscopy. Second, the particle–particle interactions are modeled as screened Coulomb repulsions within the rescaled mean spherical approximation (Hayter & Penfold, 1981; Hansen & Hayter, 1982). The fit, in the momentum-transfer range $q \geq 0.03 \text{ nm}^{-1}$, yields the Debye screening length $\kappa^{-1} = 8.4 \text{ nm}$ and the particle volume fraction $\varphi = 0.167$.

3.2. Experimental details

The experiment was performed at the cSAXS beamline (X12SA) of the Swiss Light Source, Paul Scherrer Institut, Villigen, Switzerland (see Fig. 1 for a schematic of the experimental setup). The X-rays impinged at normal incidence on the channel array and the scattered X-rays were detected in transmission mode 7 m behind the sample. For detection we used the two-dimensional single-photon-counting pixel detector Pilatus 2M (Kraft *et al.*, 2009), which has a pixel size of $172 \times 172 \mu\text{m}$ and a total of 1461×1560 pixels. The incident X-ray beam, with a wavelength of $\lambda = 0.100 \text{ nm}$ and a beam size of $0.2 \times 0.1 \text{ mm}$ (horizontal $\times$ vertical) at the sample position, was focused onto the detector plane in order to maximize the angular resolution. The resulting angular resolution was $24 \mu\text{rad}$, corresponding to a momentum-transfer resolution of $\Delta q = 1.5 \times 10^{-3} \text{ nm}^{-1}$. Finally, an evacuated flight tube was inserted between the sample and the detector in order to minimize parasitic scattering.

The complete diffraction pattern was obtained from both the empty and the fluid-filled channel array. In practice, it was

Figure 4

Cross-sectional SEM image of a typical channel array used for confinement in the present study. The white marker denotes a horizontal distance of 400 nm.

determined by combining two separate diffraction patterns for diffraction orders $|m| \geq 3$ and $|m| \leq 2$, obtained with and without a central beam stop, respectively (and using attenuators in the latter case). The total exposure time for each complete diffraction pattern was 220 s. Fig. 6 shows a representative diffraction pattern obtained using the present channel arrays and experimental setup: typically we can reliably determine the diffraction efficiencies up to $M \simeq 50$ diffraction orders, which allows a reconstruction of the fluid density with a real-space sampling interval $\Delta x = p/(2M + 1) \simeq 4.0 \text{ nm}$.

The transverse coherence length of the incident X-ray beam in the vertical direction was estimated to be approximately $20 \mu\text{m}$ at the sample position (assuming the theoretical coherence length and taking into account focusing). Hence, approximately 50 periods of 400 nm length are illuminated by a coherent X-ray beam. Moreover, the grating period is fabricated with a sub-nanometre precision, when averaged over the transverse coherence lengths of the X-ray beam. Consequently, we observe distinct diffraction peaks with a low

Figure 5

In situ SAXS characterization of the bulk colloid. The solid (dashed) line denotes a model of polydisperse spherical particles with (without) particle interactions (see text for details).

Figure 6

Typical diffraction pattern acquired from a fluid-filled channel array. Only positive diffraction orders are shown, because of the symmetry. The inset shows a magnification of the 42nd to 53rd diffraction orders.

background in between (see Fig. 6), making these experiments feasible.

4. Results and discussion

In this section we provide computational and experimental results demonstrating the feasibility of the present grating-based holographic X-ray diffraction technique. The physics of confined fluids, however, is beyond the scope of this research paper and will be discussed elsewhere.

4.1. Volume fraction

In Appendix A, we derive a connection between the average phase shift Φ across the grating–fluid interface and the diffraction efficiencies η_m and η_m^e of the fluid-filled and empty gratings,

$$\frac{\sin^2(\Phi/2)}{\sin^2(\Phi_e/2)} \simeq \frac{\sum_{m \neq 0} \eta_m}{\sum_{m \neq 0} \eta_m^e}, \quad (16)$$

with Φ_e denoting the average phase shift across the grating–air interface. Since $\{\eta_m\}$ and $\{\eta_m^e\}$ are obtained experimentally and Φ_e is known from the grating properties, equation (16) yields Φ and hence the average refractive index of the confined fluid. This allows us to determine the volume fraction of the confined fluid (Bunk, Diaz, Pfeiffer, David, Schmitt *et al.*, 2007). Fig. 7 shows the volume fraction of the confined fluid, as determined from the diffraction efficiencies of a set of gratings with different channel widths. We note that the average volume fraction as determined from Fig. 7, $\varphi = 0.172$ (4), is in excellent agreement with the value $\varphi = 0.167$ independently determined from the *in situ* SAXS characterization. This demonstrates the feasibility of determining the volume fraction from the diffraction efficiencies.

4.2. Difference autocorrelation function

In order to gain more insight on the difference autocorrelation function $\Delta P(x)$, we have studied it by means of model calculations. The results are presented in Fig. 8, which

Figure 7
Volume fraction φ of the confined colloid, as determined from the diffraction efficiencies of a set of channel arrays with different channel widths.

shows $\Delta P(x)$ for two typical phase-shift profiles (*i.e.* monolayered and bilayered fluids), both including [equation (12)] and neglecting [equation (13)] the self-convolution term. Two particular effects should be noted: (i) The influence of the self-convolution term is minor, which greatly facilitates the interpretation of $\Delta P(x)$. (ii) Clear signatures of fluid layers are observed as minima (note that $\sin \Phi < 0$) in $\Delta P(x)$ at $x \simeq \pm 30$ nm as well as $x_1 \simeq \pm 25$ nm and $x_2 \simeq \pm 115$ nm for the monolayered and bilayered fluids, respectively. The latter observation demonstrates the feasibility of studying ordering phenomena in confined fluids using the difference autocorrelation function.

Next we turn to the experimental $\Delta P(x)$ obtained from the confined colloid, which is shown in Fig. 9 for selected channel widths (using diffraction orders $|m| \leq 50$). For clarity we also draw dashed lines highlighting the signatures of colloidal layers. Notably, a transition from a monolayer to a bilayer is clearly observed with increasing channel width. This experimental finding corroborates that $\Delta P(x)$ is indeed sensitive to subtle structural effects in confined fluids.

4.3. Reconstruction

In order to demonstrate the effect of the linearization on the reconstruction, we resort to model calculations. The dashed lines in Fig. 10 show two model phase-shift profiles $a(x)$ across the confining channel, as determined from the difference autocorrelation functions $\Delta P(x)$ (*i.e.* the dashed lines in

Figure 8
Top: Model phase-shift profiles across the confining channel using typical parameters $p = 400$ nm, $\Phi = -0.25$ and $|\alpha(x)| \leq 0.03$ (vertically offset by 0.08 for clarity). Bottom: Difference autocorrelation function $\Delta P(x)$ including [dashed line, equation (12)] and neglecting [solid line, equation (13)] the self-convolution term, shown for the phase-shift profiles of the top panel (vertically offset by 1.2×10^{-3} for clarity).

the bottom panel of Fig. 8) by deconvolution using the window function $f(x)$. These correspond to the phase-shift profiles as obtained using the present linear holographic approximation. For comparison, the solid lines present the exact phase-shift profiles from the top panel of Fig. 8. Although the result obtained using the linear holographic approximation is in general found to be in good agreement with the exact result, quantitative disagreement remains: (i) The amplitude of the phase-shift profile, and to a lesser extent the positions of the maxima and minima, are affected by the linearization procedure. The effect of the duty cycle w/p should be noted: Within kinematic diffraction theory and assuming rectangular channels, F_m vanishes when the factor mw/p is an integer [see equation (7)]. Consequently, the linear approximation is not valid for these diffraction orders. In practice, however, the non-integer (inverse) duty cycle p/w of the fabricated channel arrays, the channel tapering and the volume-diffraction effects render this less of a problem. (ii) The linearization of equation (4) induces a nonvanishing phase-shift profile outside the

Figure 9

Experimental difference autocorrelation function $\Delta P(x)$ for selected channel widths w (each vertically offset by 10^{-3} for clarity). The dashed lines highlight the signatures of colloidal layers.

Figure 10

Model phase-shift profiles $a(x)$ across the confining channel (vertically offset by 0.08 for clarity). The dashed lines are determined from the difference autocorrelation functions $\Delta P(x)$ of Fig. 8 (*i.e.* from the dashed lines of the bottom panel) by deconvolution using the window function $f(x)$. The solid lines denote the exact profiles from the top panel of Fig. 8.

channel. However, this is removed in the reconstruction using the density-refinement procedure as described in §2.2.

Next we turn to the experimental phase-shift profile as obtained using the grating-based holographic X-ray diffraction technique. This is shown in Fig. 11 for selected channel widths both neglecting [equation (7)] and including [equation (15)] the tapering angle $\theta \simeq 0.1^\circ$ (using diffraction orders $|m| \leq 50$). Two effects should be noted: (i) A transition from a monolayer to a bilayer is observed with increasing channel width, as expected from the analysis of $\Delta P(x)$ in Fig. 9. (ii) The high-frequency noise observed assuming rectangular channels is suppressed when including channel tapering. Again, this indicates the importance of including the channel tapering in high-resolution studies, as already inferred from the theoretical diffraction efficiencies of Fig. 3.

Finally, we compare the present holographic phase-retrieval approach with a previously developed algorithm, in which the phase-shift profile across the grating period (including both the fluid and the grating) is obtained iteratively utilizing both real-space and reciprocal-space constraints (Bunk, Diaz, Pfeiffer, David, Schmitt *et al.*, 2007). The fundamental differences between these two approaches can be summarized as follows: (i) The present approach is more transparent in terms of the approximations made and how the reconstruction is carried out. (ii) The iterative algorithm does not rely on the linear approximation. (iii) The accuracy of the present approach is fundamentally limited by how accurately the channel array is described, *i.e.* the accuracy of F_m (or $\tilde{F}_m$). No such restriction applies to the iterative algorithm. In Fig. 12 we present the phase-shift profiles of the exit wavefield across the confining channel for a representative fluid-filled grating as determined using both the present approach and the iterative phase-retrieval algorithm. The agreement between the two methods is good, although quantitative disagreement remains: (i) We observe differences close to the solid–fluid interface. These can be attributed to an effective canceling in the present approach of the Fresnel fringes close to the solid–fluid interface (Nygård, Satapathy, Bunk, Pfeiffer *et al.*, 2008), leading to a more accurate description of the density profile in this

Figure 11

Experimental phase-shift profiles $a(x)$ across the confining channel for selected channel widths w (each vertically offset by 0.05 for clarity). The solid and dashed lines are obtained by neglecting [equation (7)] and including [equation (15)] the tapering angle $\theta \simeq 0.1^\circ$, respectively.

region. (ii) We also observe differences in the centre of the channel. These, in turn, can partly be attributed to an inaccurate description of $\tilde{F}_m$ for high spatial frequencies, *i.e.* for $|m| \geq 30$.

5. Summary and outlook

In summary, we have developed a grating-based holographic X-ray diffraction technique for reconstructing density profiles of nano-scale fluids confined in channel arrays. Within this approach, the reference and object waves are generated by the fabricated channel array and the confinement-induced ordering of the fluid, respectively. The ensemble-averaged density profile of the fluid across the confining channel is then obtained from the interference between the reference and object waves by direct Fourier inversion. In particular, we have focused on the validity of the linear holographic approach and its connection to the autocorrelation function, the inclusion of channel tapering, and volume-diffraction effects.

Finally, it should be noted that the present grating-based holographic X-ray diffraction technique is not limited to studies on confined fluids. For example, a linear holographic approach, similar to the present one, could be applied for studies on ordering phenomena in thin polymer films. We also mention the possibility provided by coherent X-rays: although a challenging experiment, the time-dependent counterpart of the present approach using diffraction from the channel array as a static reference wave, *i.e.* X-ray photon correlation spectroscopy in heterodyne mixing mode (Gutt *et al.*, 2003; Livet *et al.*, 2006), could be used to study the dynamics of soft matter in confinement.

APPENDIX A

Reference diffraction efficiencies

Throughout this study, the density of the confined fluid is compared to that of a fictitious reference fluid, which is composed of the same fluid constituents and homogeneously fills the same channel array. By setting $\alpha(x) = 0$ in equation (1), the reference diffraction efficiencies $\{\eta_m^0\}$, introduced in §2.1, are readily obtained for nonzero diffraction orders as

$$\eta_m^0 = 4F_m^2 \sin^2(\Phi/2), \quad (17)$$

with F_m as defined in equation (7) [or, equivalently, using $\tilde{F}_m$ as defined in equation (15)]. The sum of the diffraction efficiencies is

$$\sum_{m \neq 0} \eta_m^0 \propto \sin^2(\Phi/2). \quad (18)$$

However, since a fluid-filled channel array will always exhibit confinement-induced fluid ordering, the reference diffraction efficiencies $\{\eta_m^0\}$ cannot be directly determined experimentally.

A solution to this problem is provided by the diffraction efficiencies $\{\eta_m^e\}$ of the empty diffraction grating (for nonzero diffraction orders), which are experimentally obtainable and

Figure 12

Experimental phase-shift profiles $a(x)$ across the confining channel for $w = 142$ nm. The solid line is reconstructed using the linear holographic approach including the tapering angle $\theta \simeq 0.1^\circ$. For comparison, the dashed line depicts the profile (including the channel) determined using an iterative phase-retrieval algorithm (Bunk, Diaz, Pfeiffer, David, Schmitt *et al.*, 2007). The latter profile is vertically offset by 0.23 in order to facilitate comparison. The inset shows a magnification of the profiles.

differ, within kinematic diffraction theory, from the reference diffraction efficiencies $\{\eta_m^0\}$ only by a constant factor:

$$\eta_m^0 = S \eta_m^e, \quad (19)$$

with

$$S = \frac{\sin^2(\Phi/2)}{\sin^2(\Phi_e/2)}. \quad (20)$$

The factor $S < 1$ accounts for the reduced average phase shift across the grating–fluid interface, as compared with the grating–air interface. By using equation (18) and the corresponding relation for the empty diffraction grating, combined with $\sum_{m \neq 0} \eta_m \simeq \sum_{m \neq 0} \eta_m^0$ (see §2.1), S can be reformulated as

$$S \simeq \frac{\sum_{m \neq 0} \eta_m}{\sum_{m \neq 0} \eta_m^e}. \quad (21)$$

Since both sums in equation (21) run over experimentally obtainable values, the factor S is readily determined.

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References

- Arriagada, F. J. & Osseo-Asare, K. (1999). *J. Colloid Interface Sci.* **211**, 210–220.
- Borchert, H., Shevchenko, E. V., Robert, A., Mekis, I., Kornowski, A., Grübel, G. & Weller, H. (2005). *Langmuir*, **21**, 1931–1936.
- Bunk, O., Diaz, A., Pfeiffer, F., David, C., Padeste, C., Keymeulen, H., Willmott, P. R., Patterson, B. D., Schmitt, B., Satapathy, D. K., van der Veen, J. F., Guo, H. & Wegdam, G. H. (2007). *Phys. Rev. E*, **75**, 021501.
- Bunk, O., Diaz, A., Pfeiffer, F., David, C., Schmitt, B., Satapathy, D. K. & van der Veen, J. F. (2007). *Acta Cryst. A*, **63**, 306–314.
- David, C., Bruder, J., Rohbeck, T., Grünzweig, C., Kottler, C., Diaz, A., Bunk, O. & Pfeiffer, F. (2007). *Microelectron. Eng.* **84**, 1172–1177.
- Diaz, A., David, C., Guo, H., Keymeulen, H., Pfeiffer, F., Wegdam, G., Weitkamp, T. & van der Veen, J. F. (2005). *Physica B*, **357**, 199–203.

- Diaz, A. & van der Veen, J. F. (2007). *Thin Solid Films*, **515**, 5645–5653.
- Glatter, O. (1981). *J. Appl. Cryst.* **14**, 101–108.
- Goodman, J. W. (2005). *Introduction to Fourier Optics*, 3rd ed. Englewood: Roberts and Company Publishers.
- Gutt, C., Ghaderi, T., Chamard, V., Madsen, A., Seydel, T., Tolan, M., Sprung, M., Grübel, G. & Sinha, S. K. (2003). *Phys. Rev. Lett.* **91**, 076104.
- Hansen, J.-P. & Hayter, J.-B. (1982). *Mol. Phys.* **46**, 651–656.
- Hayter, J. B. & Penfold, J. (1981). *Mol. Phys.* **42**, 109–118.
- Henke, B. L., Gullikson, E. M. & Davis, J. C. (1993). *Atom. Data Nucl. Data Tables*, **54**, 181–342.
- Huisman, W. J., Peters, J. F., Zwanenburg, M. J., de Vries, S. A., Derry, T. E., Abernathy, D. & van der Veen, J. F. (1997). *Nature (London)*, **390**, 379–381.
- Kotlarchyk, M. & Chen, S.-H. (1983). *J. Chem. Phys.* **79**, 2461–2469.
- Kraft, P., Bergamaschi, A., Broennimann, Ch., Dinapoli, R., Eikenberry, E. F., Henrich, B., Johnson, I., Mozzanica, A., Schlepütz, C. M., Willmott, P. R. & Schmitt, B. (2009). *J. Synchrotron Rad.* **16**, 368–375.
- Livet, F., Bley, F., Ehrburger-Dolle, F., Morfin, I., Geissler, E. & Sutton, M. (2006). *J. Synchrotron Rad.* **13**, 453–458.
- Maalouf, G. J., Hoch, J. C., Stern, A. S., Szöke, H. & Szöke, A. (1993). *Acta Cryst. A* **49**, 866–871.
- McNulty, I., Kirz, J., Jacobsen, C., Anderson, E. H., Howells, M. R. & Kern, D. P. (1992). *Science*, **256**, 1009–1012.
- Miao, J., Charalambous, P., Kirz, J. & Sayre, D. (1999). *Nature (London)*, **400**, 342–344.
- Nygård, K., Satapathy, D. K., Buitenhuis, J., Perret, E., Bunk, O., David, C. & van der Veen, J. F. (2009). *Europhys. Lett.* **86**, 66001.
- Nygård, K., Satapathy, D. K., Bunk, O., Diaz, A., Perret, E., Buitenhuis, J., Pfeiffer, F., David, C. & van der Veen, J. F. (2008). *Opt. Express*, **16**, 20522–20529.
- Nygård, K., Satapathy, D. K., Bunk, O., Pfeiffer, F., David, C. & van der Veen, J. F. (2008). *Appl. Phys. Lett.* **92**, 214105.
- Osseo-Asare, K. & Arriagada, F. J. (1990). *Colloids Surf.* **50**, 321–339.
- Saldin, D. K., Harder, R., Vogler, H., Moritz, W. & Robinson, I. K. (2001). *Comput. Phys. Commun.* **137**, 12–24.
- Satapathy, D. K., Bunk, O., Jefimovs, K., Nygård, K., Guo, H., Diaz, A., Perret, E., Pfeiffer, F., David, C., Wegdam, G. H. & van der Veen, J. F. (2008). *Phys. Rev. Lett.* **101**, 136103.
- Satapathy, D. K., Nygård, K., Bunk, O., Jefimovs, K., Perret, E., Diaz, A., Pfeiffer, F., David, C. & van der Veen, J. F. (2009). *Europhys. Lett.* **87**, 34001.
- Schneider, G. (1997). *Appl. Phys. Lett.* **71**, 2242–2244.
- Seeck, O. H., Kim, H., Lee, D. R., Shu, D., Kaendler, I. D., Basu, J. K. & Sinha, S. K. (2002). *Europhys. Lett.* **60**, 376–382.
- Szöke, A. (1993). *Acta Cryst. A* **49**, 853–866.
- Terwilliger, T. C. (1999). *Acta Cryst. D* **55**, 1863–1871.
- Terwilliger, T. C., Kim, S.-H. & Eisenberg, D. (1987). *Acta Cryst. A* **43**, 1–5.
- Veen, J. F. van der & Reichert, H. (2004). *MRS Bulletin*, **29**, 958–962.
- Zwanenburg, M. J., Bongaerts, J. H. H., Peters, J. F., Riese, D. O. & van der Veen, J. F. (2000). *Phys. Rev. Lett.* **85**, 5154–5157.