X-Ray Waveguiding Studies of Ordering Phenomena in Confined Fluids

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We have determined the structure of a colloidal fluid confined in a gap between two walls by making use of the waveguiding properties of the gap at x-ray wavelengths. The method is based on an analysis of the coupling of waveguide modes induced by the density variations in the confined fluid. Studies on suspensions confined within gaps of a few hundred nanometers showed strongly selective mode coupling effects, indicative of an ordering of the colloidal particles in layers parallel to the confining walls.

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Recent synchrotron x-ray scattering studies of liquids in contact with a single solid wall have revealed that the molecules will become layered adjacent to the wall [1,2]. An extension of such studies to liquids confined by *two* opposing walls at close distance is highly relevant, given the frequent occurrence of confined liquids in everyday life. An example is a thin lubricating film between two sliding surfaces. It has been conjectured that the ordering within the fluid is particularly pronounced, if an integer number of layers exactly fits within the gap [3]. This in turn would cause the fluid to attain solidlike properties, adversely affecting the lubrication [4].

Experimental evidence for layering effects in confined fluids has mainly come from studies performed with the surface force apparatus (SFA) [5]. Upon application of a normal force to one of the confining plates, the force was found to oscillate with decreasing gap size, with one period corresponding to the removal of a single molecular layer. A recent synchrotron x-ray diffraction study showed smectic ordering in liquid-crystal films confined within μm gaps [6,7]. The latter experiment was performed in a SFA which was modified so as to allow the beam to pass through the fluid along the direction *normal* to the confining surfaces.

In this Letter we present a novel coherent x-ray scattering method, which allows for the determination of the fluid's density profile across the gap between two parallel plates. We direct the synchrotron x-ray beam into the gap along a direction nearly *parallel* to the plates, using the system as a planar waveguide. As the guided waves have their maximum amplitude within the fluid and a rapidly decaying amplitude within the confining plates [8], the scattering contribution from the plates is minimized. This results in an unparalleled sensitivity to structural changes within the fluid. Waveguiding is possible, provided the average x-ray refractive index of the fluid is larger than that of the plate material. Most fluids of interest fulfill this requirement.

The principle of the waveguiding method is illustrated in Fig. 1. The planar waveguide supports a finite number of transverse electric (TE) modes. If the gap were empty, a given mode would propagate undisturbed through the waveguide. In the filled waveguide, however, the spatial variations in the electron density of the fluid give rise to scattering into other TE modes ("mode coupling"). The distribution of field amplitude over the modes as well as the interferences between the mode amplitudes are observed in Fraunhofer diffraction patterns of the field across the waveguide's exit plane. From these, the density profile is determined through a model-dependent analysis. We demonstrate the method by measurements of the density profile of a suspension of colloidal particles confined by flat plates of a few mm length at a distance of a few particle diameters (300–600 nm).

Specific TE modes are excited as follows. A plane electromagnetic (e.m.) wave with wave number $k = 2\pi/\lambda$ and with the electric field polarized perpendicular to the plane of incidence, is incident onto the large bottom plate of the waveguide at an angle θ_i; see Fig. 1. Interference with the reflected wave yields a standing wave pattern above the bottom plate. For θ_i values equal to a mode angle $\theta_m = (m + 1)\pi/kW$, with W the gap width and $m = 0, 1, \dots$, a single TE_m mode with mode number m passes through the entrance plane of the waveguide. At other θ_i values, in between two consecutive mode angles, the field decomposes at the entrance into a linear combination of the neighboring TE modes as described in [8].

Next we consider the propagation of modes through the planar waveguide. The e.m. field $\Psi(x, z)$ within the waveguide satisfies the scalar wave equation

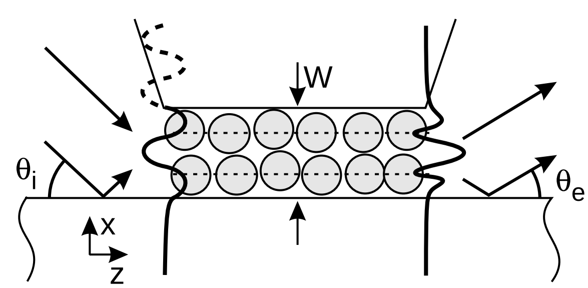

FIG. 1. Schematic of the waveguiding geometry. For illustration, the waveguide is filled with two layers of ordered fluid and a TE_2 mode is drawn at the entrance. Angles and distances are not to scale.

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$$\nabla^2\Psi(x,z) + n(x,z)^2k^2\Psi(x,z) = 0\,, \tag{1}$$

where $\nabla^2 = \partial^2/\partial x^2 + \partial^2/\partial z^2$ and $n(x,z)$ is the spatially varying refractive index. The coordinates x and z are along the directions of confinement and propagation, respectively, and their origin is taken at the bottom of the entrance plane. For x rays, $n(x,z) = 1 - a(x,z)$, with $a(x,z) \equiv \lambda^2 r_e n_e(x,z)/2\pi$ being of the order 10^{-6}. Here r_e is the classical electron radius and $n_e(x,z)$ the sought-after electron density. Seeking for a solution of Eq. (1), we make the following ansatz:

$$\Psi(x,z) = \sum_{m=0}^{M} c_m(z)\phi_m(x)e^{-i\beta_m z}, \tag{2}$$

where $\{\phi_m\}$ are the orthonormal eigenmodes of the empty waveguide, $\beta_m \simeq k\cos\theta_m$ is the corresponding propagation constant, and M is the maximum allowed mode number. The mode amplitudes have a standing-wave profile within the gap, and are evanescent within the plates [9]. Inserting Eq. (2) into Eq. (1) results in a set of coupled differential equations for the $\{c_m\}$ [10]:

$$\frac{dc_m(z)}{dz} \simeq \sum_{n=0}^{M} \Gamma_{mn}(z)c_n(z)e^{i(\beta_m-\beta_n)z}, \tag{3}$$

with the amplitude coupling coefficients given by

$$\Gamma_{mn}(z) \equiv \frac{k}{2i}\int_{-\infty}^{\infty} \phi_m(x)[n(x,z)^2 - n_0(x)^2]\phi_n(x)\,dx\,. \tag{4}$$

Here $n(x,z)$ is the refractive index of the confined medium and $n_0(x)$ the rectangular refractive index profile of the empty waveguide [$n_0(x) = 1$ for $0 < x < W$ and $n_0(x) = 1 - 2.57 \times 10^{-6}$ within the confining silica plates]. The starting values $c_m(0)$ follow from $c_m(0) = \int \phi_m(x)\Psi(x,0)\,dx$.

Given the field $\Psi(x,0)$ at the entrance and the refractive index profile $n(x,z)$, the propagating field $\Psi(x,z)$ is found by numerically solving the set of Eqs. (3). For illustration, we have calculated the field amplitude $\Psi(x,z)$ assuming a z-independent layered profile $n(x) = 1 - a_0 - a_l\cos(2\pi lx/W)$ within the gap. Here $1 - a_0$ is the spatially averaged refractive index and a_l the modulation amplitude for l layers. The incident field $\Psi(x,0)$ was chosen such that a single TE_2 mode was excited at the entrance. Figure 2a shows the field intensity $|\Psi(x,z)|^2$ within a gap of length $L = 1.2$ mm and width $W = 615$ nm, filled with five layers having refractive-index parameters $a_0 = -a_5 = 1.00 \times 10^{-6}$. The x-ray wavelength λ was chosen to have the experimental value of 0.0931 nm. Clearly, the intensity is redistributed over several modes and is concentrated in regions where both the incident field amplitude and the refractive index are highest. Note that for symmetric systems in which the plane $x = W/2$ is a mirror plane, coupling occurs only between modes of equal parity (even or odd). An ordering of the fluid medium into equidistant layers results in a further selectivity in the mode coupling. Substituting $n(x)$ into Eq. (4) and taking $\phi_m = \sqrt{2/W}\sin(k\theta_m x)$ for $0 < x < W$ and $\phi_m = 0$ elsewhere, we obtain the following selection rules for a system of l layers:

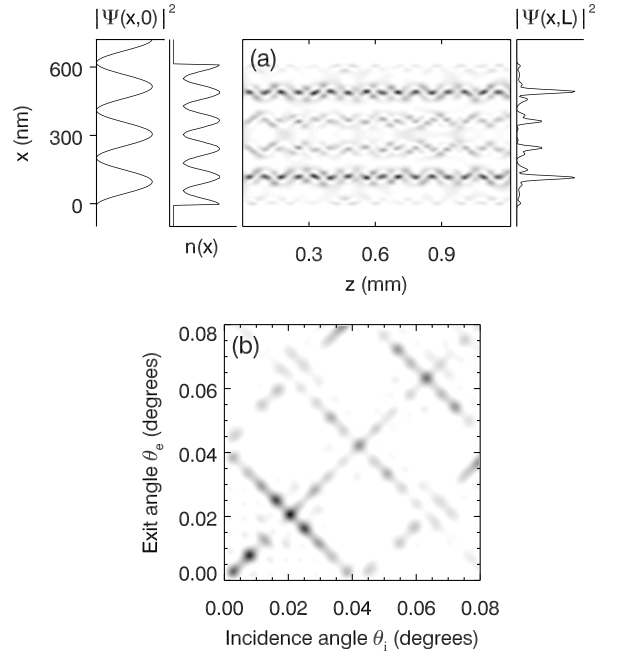

FIG. 2. (a) Intensity distribution of the field within the waveguide, calculated for a guiding medium having a refractive-index profile $n(x)$. (b) Linear contour plot of the calculated intensity $I(\theta_i, \theta_e)$, diffracted from the exit of the above waveguide.

$$\Gamma_{mn} = ika_0\delta_{m,n} + \frac{ika_l}{2}(\delta_{2l,m-n} + \delta_{2l,n-m} - \delta_{2l,m+n+2} - \delta_{2l,-m-n-2})\,, \tag{5}$$

where $\delta_{i,j}$ is the Kronecker delta. The mode coupling strengths are of magnitude $|\Gamma| \sim ka_l/2 \sim 34\ \mathrm{mm}^{-1}$.

The mode selectivity is most conveniently observed in a series of Fraunhofer diffraction patterns of the exit field $\Psi(x,L)$, each taken at a slightly increased value of θ_i starting from zero. Whenever θ_i equals θ_n, with $n = 0, 1, \ldots,$ mode n is excited at the entrance. Coupling to mode m within the waveguide then may result in a peak in the diffraction pattern at exit angle $\theta_e = \theta_m$. Figure 2b shows a contour plot of the diffracted intensity $I(\theta_i, \theta_e)$, calculated for the model system of Fig. 2a. The peaks along the codiagonals relate to the second and third terms in Eq. (5), while the cross diagonals originate from the fourth term. The fifth term is always zero for positive mode numbers. The cross diagonals intersect the main diagonal at $\theta_i = \theta_{pl-1}$, with $p = 1, 2, \ldots.$ At these angles, the nodes of the incident mode lie precisely between the layers.

Our waveguiding setup has been described elsewhere [9]. In brief, the waveguide consists of two fused-silica plates which were coated with an aluminum layer

(98% reflection) and subsequently a SiO_2 layer (650 nm). The highly reflecting aluminum layers form an optical interferometer which enables us to measure the gap width and parallelism through use of the technique of fringes of equal chromatic order (FECO) [11]. The gap size and tilt angle are controlled using a tripod of nanometer precision motors. The setup was mounted horizontally onto the diffractometer at the undulator beam line ID10A of the European Synchrotron Radiation Facility (ESRF) in Grenoble (France) [12]. A photon energy of 13.3 keV ($\lambda = 0.0931$ nm) was selected using the (111) reflection of a silicon monochromator. A mirror served to suppress higher harmonics from the undulator. The intensity of the beam of 0.1 mm diameter passing through a vertical gap of 500 nm was typically 3×10^8 photon/s. The transverse coherence length of the beam is in the vertical plane $L_v = 177$ μm and in the horizontal plane 4.5 μm. Since $L_v \gg W$, the incident field is fully coherent across the gap. In the horizontal plane, however, the beam has incoherent properties.

A colloidal suspension of $\sim$110 nm diameter SiO_2 spheres in dimethylformamide (DMF) was confined within gaps of various widths. Initially the suspension was inserted in a gap of typically a few μm width, after which the gap was reduced to the desired value. We measured Fraunhofer patterns as a function of θ_i for a gap of $W = 655$ nm, filled with 10 vol % suspension. The patterns were taken using a two-dimensional CCD camera (Sensicam, 6.7 μm pixels, 12 bit) at 2.39 m distance from the waveguide. The angular resolution, as determined by the pixel size, was 0.2 mdeg. The measurements are presented in a contour plot of $I(\theta_i, \theta_e)$; see Fig. 3a.

The intense off-diagonal peaks in the contour plot are evidence of strong mode coupling. At angles larger than 0.065°, which is the critical angle for total reflection from the DMF/SiO_2 interface, a much reduced intensity is observed. A cross diagonal intersects the diagonal at $\theta_i \approx 0.025°$. From $\theta_{l-1} = 0.025°$ we deduce $l = 6$, which indicates the presence of $\sim$6 layers. A cubic stacking of six layers of 110 nm diameter particles does not fit within a gap of 655 nm width, while a stacking of hard spheres into a closed-packed structure would result in a thickness less than the gap width (609 nm). This suggests that the particles form a closed-packed structure near the walls and are less well ordered in the center of the gap [13]. Indeed, the cross diagonal is not as sharply defined as in Fig. 2, indicating that the refractive-index profile contains more than a single Fourier component. Obviously, a 10 vol % suspension cannot result in a complete filling of the waveguide by a closed-packed structure and the structure must be discontinuous along the z direction. Evidence for this is the formation of breaks in the FECO fringes upon closure of the gap to below $\sim$1 μm. Discontinuities in the refractive-index profile along the z direction also explain the asymmetry with respect to the diagonal $\theta_i = \theta_e$ in the contour plot of Fig. 3a.

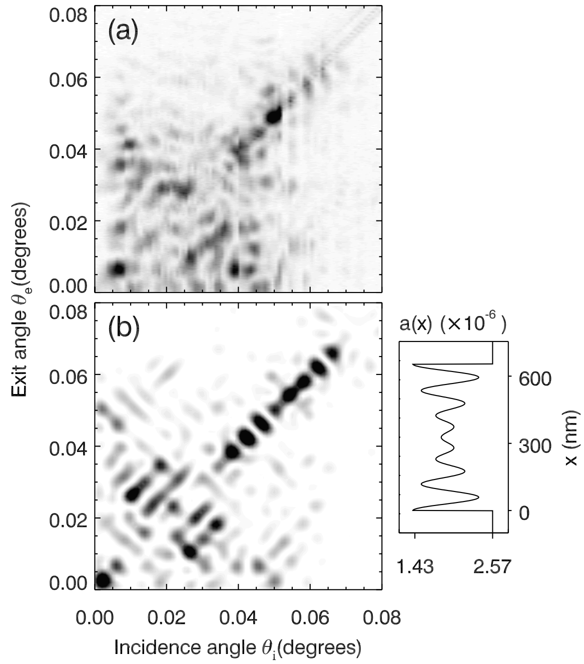

FIG. 3. Linear contour plot of the diffracted intensity $I(\theta_i, \theta_e)$, (a) measured for a waveguide having a 655 nm gap filled with a colloidal suspension (see text), and (b) calculated for the profile $n(x) = 1 - a(x)$, with parameter values as given in the text.

In a search for a fit to the data, we calculated diffraction patterns for various assumed refractive-index profiles with the use of a finite-difference beam propagation method [14]. The major features in the $I(\theta_i, \theta_e)$ plot, in particular the cross diagonal, are reproduced well for a profile of the form $n(x) = 1 - a_0 - \sum_{l=4}^{6} a_l \cos(2l\pi x/W)$, with $a_0 = 1.93 \times 10^{-6} + i3.1 \times 10^{-9}$, $a_6 = -0.25 \times 10^{-6} + i3.00 \times 10^{-9}$, $a_4/a_6 = 0.19$, and $a_5/a_6 = 0.85$ [15] (Fig. 3b). The plates are given a refractive index $n_{SiO_2} = 1 - 2.57 \times 10^{-6} - i1.25 \times 10^{-8}$, where the imaginary part here and above accounts for absorption. The waveguide, of length $L = 4.85$ mm, was assumed to have the above profile $n(x)$ only within the interval $1.81 < z < 3.85$ mm, the remainder being filled with DMF only. The striking similarity between calculations and measurements confirms the presence of six layers, with decaying order away from the confining walls. The remaining discrepancies originate from uncertainty in the density distribution along the z direction. We note here that the measurements are insensitive to the discreteness of the single particles along z, since the particle diameter is much smaller than a typical scattering length $(ka_l)^{-1}$.

We repeated the measurements in a gap of only $W = 310$ nm (Fig. 4a). In order to facilitate reduction of the gap, we diluted the suspension to 1 vol %. As expected, there are fewer guided modes, at larger angular spacing. A cross diagonal intersects the diagonal at $\theta_i \approx 0.023°$, from which we derive that two layers have formed. Figure 4b shows a plot of $I(\theta_i, \theta_e)$ which was calculated for the profile $n(x) = 1 - a_0 - \sum_{l=2}^{4} a_l \cos(2l\pi x/W)$,

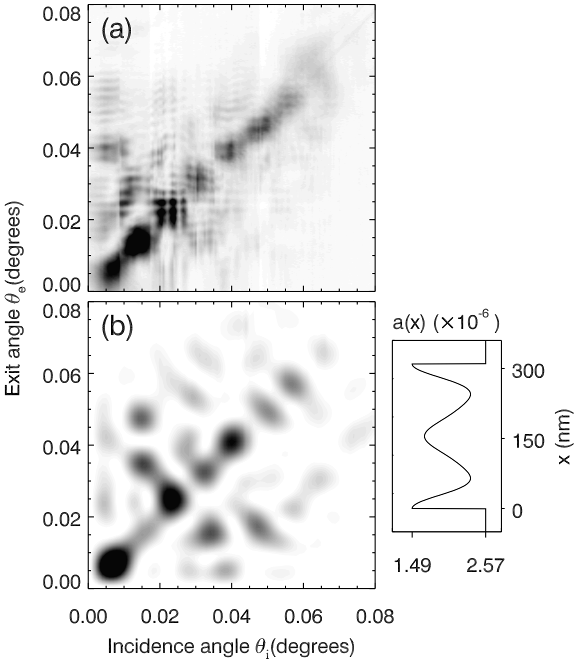

FIG. 4. Linear contour plot of the diffracted intensity $I(\theta_i, \theta_e)$, (a) measured for a waveguide having a 310 nm gap filled with a colloidal suspension (see text), and (b) calculated for the profile $n(x) = 1 - a(x)$, with parameter values as given in the text.

wherein $a_0 = 1.99 \times 10^{-6} + i1.10 \times 10^{-9}$, $a_2 = -0.36 \times 10^{-6} + i1.00 \times 10^{-9}$, $a_3/a_2 = 0.25$, and $a_4/a_2 = 0.13$ (Fig. 4b). The profile of $n(x)$ was asymmetrically positioned between $1.90 < z < 3.33$ mm so as to reproduce the asymmetry in the data with respect to the diagonal $\theta_i = \theta_e$. Again, there is reasonable agreement with the data [16].

In summary, we have determined density profiles in confined colloidal fluids using waveguiding of coherent x rays within the confined structure. In silica colloids, the proximity of the walls is found to induce a strong layering effect. The ordering of the particles in a closed-packed structure and the nonuniformity of the ordered regions in the plane of the gap strongly suggest that the confinement induces crystallization at volume densities much lower than the critical density for crystallization of colloidal hard spheres in the bulk [17].

The measured diffraction patterns are in essence phase-contrast images of the waveguide's filling. All interferences take place within the thick phase object. The detector in the far field then registers the intensity of the Fourier transform of the emerging wave field. The restriction that interferences occur only between discrete modes of the waveguide greatly simplifies the structural analysis, especially if the object's structure is translationally invariant over the length of the waveguide. Our waveguiding method can be modified to include studies of (molecular) fluids confined in much smaller gaps than reported here, provided use is made of especially tailored refractive index profiles $n_0(x)$ in the confining walls and both guided and radiative modes are detected [18].

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