Dynamics and rheology under continuous shear flow studied by x-ray photon correlation spectroscopy

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Abstract. X-ray photon correlation spectroscopy (XPCS) has emerged as a unique technique allowing the measurement of dynamics of materials on mesoscopic length scales. One of the most common problems associated with the use of bright x-ray beams is beam-induced radiation damage, and this is likely to become an even more limiting factor at future synchrotron and free-electron laser sources. Flowing the sample during data acquisition is one of the simplest methods allowing the radiation damage to be limited. In addition to distributing the dose over many different scatterers, the method also enables new functionalities such as time-resolved studies. Here, we further develop a recently proposed experimental technique that combines XPCS and continuously flowing samples. More specifically, we use a model colloidal suspension to show how the macroscopic advective response to flow and the microscopic dissipative dynamics (diffusion) can be quantified from the x-ray data. Our results show very good quantitative agreement with a Poisseuille-flow hydrodynamical model combined with Brownian mechanics. The method has many potential applications, e.g. in the study of dynamics of glasses and gels under continuous shear/flow, protein aggregation processes and the interplay between dynamics and rheology in complex fluids.

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1. Introduction

Over the past several years, x-ray photon correlation spectroscopy (XPCS) has become a well-established experimental technique that allows the direct measurement of dynamics of materials (see e.g. [1]–[4]). XPCS provides a tool complementary to dynamic light scattering (DLS) [5] by giving access to the dynamics of fluctuations on lengthscales ranging from nanometer to micron.

In an important number of systems—especially soft or biological materials—radiation damage can seriously limit the applications of XPCS. This will become an even more important issue at new (or upgraded) high-brilliance third-generation synchrotron sources and at fourth-generation light sources—free electron lasers and energy-recovery linacs—with their unprecedented brilliance several orders of magnitude stronger than available today [6].

Performing XPCS under continuous flow is a method that can limit the beam damage effects in a number of x-ray-sensitive systems. An additional benefit of such an experimental strategy is the possibility to time-resolve processes taking place in mixing flowcells [7, 8] or the possibility to study the response of a system to applied shear.

In the experiments reported here, we further develop the method presented in [9, 10] demonstrating that under specific conditions, it is possible to extract the diffusive component of the dynamics of nanoparticles suspended in a fluid undergoing shear flow. More specifically, we use the XPCS data to quantitatively measure both the diffusive and the advective, flow-induced motion of the particles. This is achieved by taking advantage of the anisotropy of the measured correlation functions. Unlike the case of a non-flowing sample where (for isotropic systems) the characteristic times depend only on the magnitude of the scattering vector $q = |\mathbf{q}|$, the correlation times measured in a flowing system depend on the relative orientation between the scattering vector and the flow direction. In a transverse flow scattering geometry (scattering wave vector $\mathbf{q} \perp$ flow direction), the correlation functions are mostly sensitive to the diffusive motion of the scatterers. On the contrary, in a longitudinal flow geometry ($\mathbf{q} \parallel$ flow) the correlation functions are strongly affected by the rheological properties of the flow (shear profile). The method has the unique advantage of enabling us to study the interplay between the advective motion of the scatterers in response to applied shear and the dissipative microscopic dynamics due to thermal diffusion.
2. Description of the XPCS-microfluidic experiment

The sample was prepared from a suspension of sterically stabilized colloidal silica spheres (purchased from Duke Scientific, radius 250 nm) by replacing the initial solvent (water) with propylene glycol (PG). The concentration of the suspension was low (<2%) in order to reduce inter-particle correlations.

The flowcell was made out of a Kapton tube with an inner radius of \( R = 0.66 \text{ mm} \) and \( \approx 100 \mu \text{m} \) thick walls. A syringe pump purchased from Harvard Apparatus Inc. pushed the solution through PEEK\textsuperscript{TM} polymer tubes from Upchurch Scientific Inc. to the Kapton flowcell. Leak-tight fittings and adapters were also purchased from Upchurch Scientific. The flow rates applied in these experiments were between \( Q = 0 \) and 80 \( \mu \text{l h}^{-1} \). Translated into an average flow velocity via \( v_0 = Q/\pi R^2 \), this gives \( v_0 \approx 0–16 \mu \text{m s}^{-1} \). The corresponding Reynolds number, defined as \( Re = v_02R\rho/\eta \), where \( \rho \) is the density and \( \eta \) the dynamic viscosity of PG, is \( Re < 10^{-6} \). In these conditions, the flow in the tube is laminar and can be well described by a parabolic Poiseuille profile for a Newtonian fluid,

\[
v(r) = 2v_0 \frac{R^2 - r^2}{R^2}.
\] (1)

The XPCS experiments were performed in a small-angle x-ray scattering (SAXS) geometry (figure 1(a)) using partially coherent x-rays at the ID10A beamline (Troïka) of the European Synchrotron Radiation Facility (ESRF). A single bounce Si(111) crystal monochromator was used to select 8 keV x-rays, having a relative bandwidth of \( \Delta \lambda/\lambda \approx 10^{-4} \). An Si mirror downstream of the monochromator was employed to suppress the radiation originating from higher order reflections. A transversely partially coherent beam was defined by using a set of high-heat-load secondary slits placed 33 m from the undulator source, a beryllium compound refractive lens (CRL) unit placed 34 m from the source, thereby focusing the beam near the sample location, at 46 m, and by a set of high-precision slits with highly polished cylindrical edges, placed just upstream of the sample, at 45.5 m. The final beam size selected by the beam-defining slits was \( 10 \times 10 \mu \text{m}^2 \). The parasitic scattering from the slits was limited by a guard slit placed a few centimeters upstream of the sample. Under these conditions, the partial coherent flux on the sample was \( \sim 10^{10} \text{ph s}^{-1} \).

The scattering was recorded with a fast two-dimensional (2D) pixelated sensor—the Maxipix detector—located 2.23 m downstream of the sample with a pixel size of 55 \( \mu \text{m} \). Under these experimental conditions, the measured speckle contrast was \( \sim 20\% \), in good agreement with calculated values\textsuperscript{6}.

The intensity autocorrelation functions,

\[
g^{(2)}(\mathbf{q}, t) = \frac{\langle I(\mathbf{q}, t_0)I(\mathbf{q}, t_0 + t) \rangle}{\langle I(\mathbf{q}, t_0) \rangle^2},
\] (2)

were calculated with a standard multi-tau correlator \textsuperscript{[12]} package developed in Python at ESRF \textsuperscript{[13]}. Here \( \langle \ldots \rangle \) denotes that the correlation functions are both ensemble averaged, and averaged over time \( t_0 \). The regions of ensemble averaging are schematically shown in figure 1(a) by dashed contour lines corresponding to the two scattering geometries considered here—longitudinal and transverse flow.

\textsuperscript{6} See for instance coherence calculator at 8-ID (APS) \textsuperscript{[11]}. 
Figure 1. (a) Schematic representation of the experimental setup. The Maxipix detector was used to record SAXS speckle patterns from the flowing colloids. Time-averaged correlation functions in transverse flow and longitudinal flow geometries are calculated by ensemble averaging single-pixel correlations over regions like the ones schematically shown by the dashed line contours. (b, c) Raw correlation functions measured in both scattering geometries for \( q = 2.5 \times 10^{-3} \text{ Å}^{-1} \), with the x-ray beam incident at the center of the flowcell \((x/R = 0)\) and at different flow rates (shown in the legend). (d, e) Single-q and single-flow correlation functions measured at different positions across the flowcell shown in the legend and schematically represented in (a).

The raw correlation functions can be seen in figures 1(b)–(e). The transverse flow correlations (figure 1(b)) measured at one location in the flowcell (at the center) are, in the low-shear limit, basically insensitive to the increasing flow rates. The longitudinal flow correlation times (figure 1(c)) become, however, increasingly faster at higher flow rates, as shown previously \([9, 10]\). Characteristic, self-beating oscillations due to the shear profile can also be clearly seen in the data.

The flow velocity profile can be probed by recording the scattering at different locations across the flow tube. This effect can be seen qualitatively in figures 1(d) and (e). As expected, the transverse flow scans (figure 1(d)) are relatively insensitive to the position across the tube. In contrast, the longitudinal flow correlations have a strong dependence on the position across the flow, measuring the local velocity profile integrated along the direction parallel to the beam (figure 1(e)). The maximum shear-induced effect on the correlation functions is obtained near the center of the tube where the flow velocity reaches its maximum value. Near the edges of the wall, the velocity approaches zero, with a flatter profile along the tube, and hence the correlation functions shift towards their nominal zero-flow values.

The theory explaining XPCS measurements is briefly presented in the following section and will be followed by a detailed quantitative analysis of the effects described above.

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3. XPCS in a laminar flow

In a homogeneous liquid, like the one used here, the temporal intensity fluctuations at a fixed $q$ are well described by a normal distribution. As a consequence, the normalized intermediate scattering function (ISF), $g^{(1)}(q, t) = S(q, t)/S(q, 0)$, with the ISF (or dynamic structure factor)

$$S(q, t) = \frac{1}{N} \sum_{i,j=1}^{N} \langle e^{-i q (r_i(t_0) - r_j(t_0 + t))} \rangle,$$

is related to the the intensity autocorrelation functions $g^{(2)}$ by the Siegert relationship,

$$g^{(2)}(q, t) = 1 + \beta \left[ g^{(1)}(q, t) \right]^2.$$

Here $\beta$ is the speckle contrast, in this setup around 20%.

Owing to a coupling between the diffusive motion of the particles and their flow-induced advective motion, the $q$-dependent ISFs describing the colloidal suspension in a cylindrical Poiseuille flow (equation (1)) have been shown [10] to be well described, in the $q$-range probed by x-rays, by

$$|g^{(1)}(q, t)|^2 = \left( g^{(2)}(q, t) - 1 \right) / \beta$$

$$= \exp(-2 D_0 q^2 t) \cdot \frac{\pi^2}{16 (q \cdot v) t} \cdot \text{erf} \left( \frac{4i (q \cdot v) t}{\pi} \right)^2 \cdot \exp \left[ -(\nu_{tr} t)^2 \right]. \quad (3)$$

The expression above depends on three different relaxation rates. The Brownian diffusion is described by $\Gamma_D = D_0 q^2$. A shear-induced (oscillatory) decay of the measured correlation function is accounted for by $\Gamma_S \propto q \cdot v$, with $v$ representing the flow velocity at the maximum of the parabolic profile probed in the direction of the beam. The third factor, given by a relaxation rate $\nu_{tr}$, measures the rate at which the correlation functions decay because particles transit through a Gaussian-shaped beam. This effect is irrelevant here. Even at the highest flow rates, the transit time is of the order of 0.6 s (size of the beam divided by the maximal velocities introduced previously), which is much larger than the other relaxation times measured here and hence this decay cannot be observed.

4. Experimental results

The free diffusion coefficient $D_0$ can be determined by fitting the transverse flow correlation functions to simple exponentials. The results are shown in figure 2. In the low-flow limit $D_0$ is, as expected, independent of both $q$ and the flow rate. At higher flow rates ($Q > 40 \mu l h^{-1}$) the correlation functions (shown in the inset) start deviating from single-exponential (straight lines in the lin–log representation) and the fitted correlation times shift towards faster values due to the increasing longitudinal components of the flow velocity. These components are present because of the finite widths of the detector regions over which $g^{(2)}(q, t)$ are ensemble averaged. The value obtained from the simple exponential fits for $D_0$ is $2.25 \times 10^6 \text{ Å}^2 \text{ s}^{-1}$. The viscosity can be estimated using the Einstein–Stokes relationship,

$$D_0 = \frac{k_B T}{6 \pi \eta R}, \quad (4)$$
Figure 2. Free diffusion coefficient obtained from single exponential fits of the transverse flow correlation functions—shown in the inset for a single value of $q = 2.5 \times 10^{-3}$ Å$^{-1}$. In the low-flow limit ($<40 \mu l/h$) the correlation times ($\tau$) are independent of the flow rate and $\tau q^2$ are $q$-independent and equal to the inverse of the free diffusion coefficient $D_0 \approx 2.2 \times 10^6$ Å$^2$ s$^{-1}$.

yielding $\eta = 0.038$ Pa s at room temperature. This is in fair agreement with tabulated values for PG, $\eta = 0.056$ Pa s (at 20$^\circ$C), the difference probably being due to a small amount of residual water present in the solvent.

The speckle contrast $\beta$ and the baseline value $g_\infty$ of the measured correlation functions were first obtained from fits with stretched exponentials following the Kohlrausch–Williams–Watts form $\beta \exp\left[\left(-2\Gamma t\right)^\gamma\right] + g_\infty$. Subsequently, the normalized correlation functions $g_{\text{norm}}^{(2)} = (g^{(2)} - g_\infty)/\beta$ were fitted using equation (3), with the value measured for $D_0$ kept constant. Examples of fits for normalized correlation functions measured in transverse flow (blue circles) and longitudinal flow (green triangles) geometries, for a single value of the scattering wave vector $q = 2.8 \times 10^{-3}$ Å$^{-1}$ and a single position in the flowcell (at the center, $x/R = 0$) at different flow rates $Q = 20–80 \mu l h^{-1}$, are shown in figure 3. The position dependence of the correlation functions for the same value of $q$, a single flow rate $Q = 40 \mu l h^{-1}$ and the same scattering geometries is displayed in figure 4.

The fits show that the very simple model used here, assuming a parabolic-shaped Poiseuille flow and hence an exact form for $g^{(2)}(q, t)$, describes the experimental data remarkably well. The most significant fitting parameter here is the shear-induced relaxation rate, $\Gamma_S = q \cdot v$, where $v$ is the maximum flow velocity along the direction of the beam ($y$). Since this is obtained at different positions across the flow tube ($x$), the fitted values also depend on $x$: $\Gamma_S(x) = q \cdot v(x)$. Here, we omit the vectorial notation and the dot product because only values measured from longitudinal flow fits are used. The $x$-dependence of the maximum flow velocity along the
Figure 3. Normalized correlation functions and fits with equation (3) for $q = 2.8 \times 10^{-3} \text{Å}^{-1}$ and $x/R = 0$ (center of the flow cell) measured at different flow rates: $Q = 0–80 \mu\text{l h}^{-1}$ (a)–(e). Blue circles: transverse flow correlation functions, $q \perp$ flow. Green triangles: longitudinal flow, $q \parallel$ flow.
Figure 4. Normalized correlation functions and fits with equation (3) for $q = 2.8 \times 10^{-3} \text{Å}^{-1}$ and $Q = 40 \mu\text{l h}^{-1}$ measured at different locations across the flowcell $x/R = 0$–0.91 (a)–(e). Blue circles: transverse flow correlation functions, $\mathbf{q} \perp$ flow. Green triangles: longitudinal flow, $\mathbf{q} \parallel$ flow.
Figure 5. (a) Fitted shear-induced relaxation $\Gamma_S$ as a function of position ($x/R$) for four different flow rates: $20 \mu l h^{-1}$ (squares), $40 \mu l h^{-1}$ (crosses), $60 \mu l h^{-1}$ (triangles) and $80 \mu l h^{-1}$ (circles)–and two values of $q$: $1.6 \times 10^{-3} \text{Å}^{-1}$ (blue) and $2.5 \times 10^{-3} \text{Å}^{-1}$ (green). The solid lines show fits with a parabolic profile equation (5); the dashed lines (extension to negative values of $x$) are guides to the eye. (b) Scaled relaxation rates ($\gamma_s$, equation (6)) for the same values of the flow rate $Q$ and wave vector $q$ collapse on a single parabolic profile across the tube.

$y$-direction in a Poiseuille-flow geometry is easily obtained from equation (1), and we obtain

$$\Gamma_S(x) \propto \frac{q Q}{\pi R^2} \left( 1 - \frac{x^2}{R^2} \right).$$

(5)

Fits with equation (5) for the shear-induced relaxation rates obtained from the fits at different locations in the flow tube are shown in figure 5(a). The data shown here were measured at four different flow rates and two different values of $q$. From equation (5) one can also see that
a scaled relaxation rate

\[ \gamma_s = \frac{\Gamma_s}{q Q/\pi R^2} \propto 1 - \left( \frac{x}{R} \right)^2 \]  

should follow a single, flow- and \( q \)-independent parabolic profile across the tube (figure 5(b)).

5. Conclusions

The results presented here show, for the first time, that XPCS can be used to measure both the advective response to applied shear and the diffusive dynamics of a colloidal suspension under continuous flow. The data show very good quantitative agreement with a simple Poiseuille-flow hydrodynamical model.

Possible future applications of this method include the study of the response to shear and the interplay between dissipative effects (diffusion) and advective motion in colloidal gels, glasses and other non-Newtonian fluids (see e.g. [14, 15]). The XPCS-flow method also provides a very useful way to avoid radiation damage. For many applications, using high-aspect-ratio flow tubes where the velocity profile is more constant (approaching a plug-flow shape [16]) is advantageous.

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