X-ray fluorescence correlation spectroscopy: a method for studying particle dynamics in condensed matter [1]

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Introduction

Photon correlation spectroscopy probing fluctuations in scattered [1] or fluorescent [2, 3] intensity to study particle dynamics in fluids is well established in the visible light regime. With the advent of high-brilliance synchrotron radiation sources, correlation spectroscopy utilizing scattered radiation has only recently been extended to the x-ray wavelength regime by using spatially coherent x-rays to study the time fluctuations of the corresponding speckle patterns [4–6]. Because x-ray fluorescence is an incoherent process, x-ray fluorescence correlation spectroscopy (XFCS) does not require coherent x-ray beams. For an assembly of noninteracting particles undergoing diffusive motion, the fractional root-mean-square fluctuation in the number of particles in a given volume will be $\langle N\rangle^{-1/2}$, where $\langle N\rangle$ is the average number of particles in the given volume. If $\langle N\rangle$ is sufficiently small, such number fluctuations can be studied in real time, by measuring the time dependence of the fluorescence intensity $I_f(t)$ and its normalized autocorrelation function $g_f(t)=\left\langle I_f(0)I_f(t)\right\rangle\Big/\left\langle I_f(0)\right\rangle^2$, thus yielding direct information about the particle dynamics. For particles involving both diffusion and sedimentation, the fluorescence autocorrelation function can be expressed in Equation (1) as:

$$g_f(t)=1+\langle N\rangle^{-1}\left(1+t/\tau_d\right)^{-1}\exp\left\{-t^2\Big/\left[\tau_s^2\left(1+t/\tau_d\right)\right]\right\}, \qquad (1)$$

where τ_d and τ_s are the translational diffusion and sedimentation time constants, respectively. The small value of $\langle N\rangle$ can be realized with either a small illuminated sample volume, or a low particle concentration. This will necessitate a high x-ray beam intensity in order to get sufficient fluorescence signal from the small number of particles. With a Fresnel zone plate and third-generation synchrotron x-ray sources, such a high-intensity microfocused x-ray beam is readily achievable [7]. A distinct advantage of the method is the element specificity by using an energy-dispersive x-ray detector.

Methods and Materials

To demonstrate the usefulness of this method for elucidating particle dynamics, two types of samples were studied. First, colloidal gold particles, which have been studied by x-ray coherent intensity correlation spectroscopy [4], represented a good choice for the initial studies. Three colloidal gold samples [8, 9] of different particle sizes of radii of approximately 100, 200, and 900 nm (denoted as samples 1 to 3, respectively) were studied to establish the relationship between particle dynamics and the particle size. The second type of sample, namely a suspension of superparamagnetic microspheres with particle diameter 0.82 mm (commonly referred to as ferrofluids, denoted as sample 4), was utilized to show the effect of the x-ray beam size to the measurements.

The samples were measured during two separate synchrotron runs on the 2-ID undulator beamline at the Advanced Photon Source (APS). The colloidal suspensions were loaded in a thin-walled quartz capillary tube of diameter 0.6 mm and placed in the focal spot of a monochromatic and microfocused beam. The estimated total beam intensity of approximately 2 x 10^8 photons/s at the focal point. The effective dimension of the illuminated volume was estimated to be approximately 1.9 mm^3. The fluorescence intensity from the sample was monitored by an energy-dispersive solid-state detector placed as close as possible to the sample to maximize the solid angle acceptance. Discriminated by a single-channel analyzer, the x-ray fluorescence signal was fed to a correlator that displays both the fluorescence intensity $I_f(t)$ in real time and its normalized autocorrelation function $g_f(t)$.

Results

Shown in Figure 1 are the averaged $g_f(t)$ measured for (A) sample 1, (B) sample 2, and (C) sample 3. The full theoretical expression given in Equation 1 fits extremely well to the data. In the fitting procedure, the gold colloids are assumed to be monodisperse. The least-square-fitted values of the hydrodynamic radii of the particles are 102, 220, and 370 nm for samples 1, 2, and 3, respectively, in good agreement with the atomic force microscopy, dynamic light scattering, and small-angle x-ray scattering measurements. It should be noted that the translational diffusion and sedimentation processes have very distinct forms for the correlation function. The translational diffusion-dominated correlation function decays approximately as t^{-1} and the sedimentation governed correlation function decays as $\exp\left(-t^2/\tau_s{}^2\right)$. To illustrate this, fits to the correlation functions using only the

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sedimentation model (dashed line in Figure 2A) or the diffusion model (dotted line in Figure 2C) are also included.

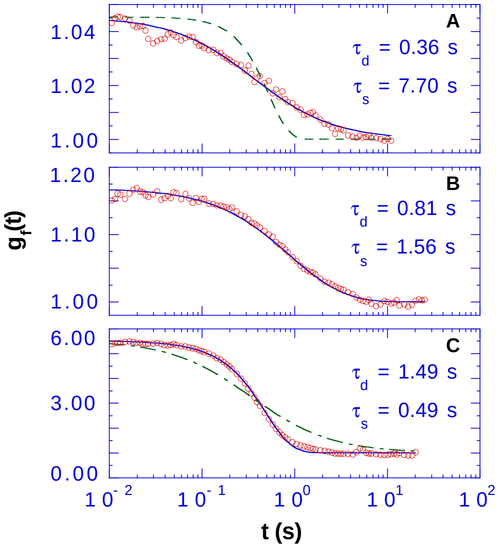

Figure 1: The experimental (circles) and theoretical (line) fluorescence autocorrelation functions for samples 1(A), 2(B), and 3(C). Two theoretical simulations are also presented using only the sedimentation model (dashed line in A) or only the diffusion model (dotted line in C).

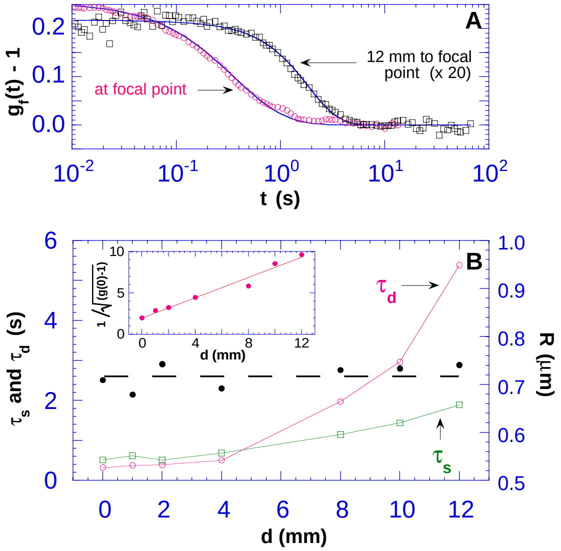

Figure 2: Experimental results for sample 4 measured at different positions, on the zone plate axis, at a distance d to the focal point. (A) the experimental (circles and rectangle) and theoretical (line) fluorescence autocorrelation functions at and 12 mm away from the focal point. The fitting parameters τ_d (circles), τ_s (rectangles) and derived values of particle radius R (dots) at each position are shown in (B). The solid lines connecting data points are for guiding the eye. The dashed line represents the mean value of R. The inset for (B) shows the relationship between $\left[g_f(0)-1\right]^{-1/2}$ and d (dots) and the linear function fit (solid line).

To demonstrate the effect of x-ray beam size on XFCS measurements, we also studied the ferrofluids (sample 4) at different locations along the zone plate axis and corresponding to different distances (d) from the focal point. As d increases to approximately 5 mm, where $\tau_d > \tau_s$, the beam size becomes so large that the parameters related to diffusion may not be accurately measured. This indicates the necessity of using microsized x-ray beams in the measurement. The reliability of the fitting parameters is further verified by the fact that hydrodynamic radius R of the microspheres, derived at each position (dots in Figure 2B), is approximately constant, with a mean value of 0.71 μm (dashed line in Figure 2B). As shown in Equation 1, the intercept of the correlation function should be proportional to $\langle N\rangle^{-1}$. Thus, $\left[g_f(0)-1\right]^{-1/2}$ should be proportional to the beam size or, in turn, to d. This has been clearly observed in the experiment (shown as the inset for Figure 2B).

Discussion

We have demonstrated a new and powerful technique to probe the dynamics of colloidal particles by real-time analysis of x-ray fluorescence intensity fluctuations. Coherent x-rays, which are required for other x-ray photon correlation spectroscopy techniques, are not needed for this method. There will be a host of novel possibilities opened up for study with this technique. These include the study of the motion of biological macromolecules containing heavy elements; the study of interdiffusion of atoms at interfaces between two species of materials; the study of the sedimentation, diffusion, or flow of colloidal particles in fluids or gels and other media; and the study of glass transitions or phase separations in liquid using tracer particles of gold or other colloids to probe the dynamics. An interesting variant would be the study of magnetic domain dynamics or domain wall motion using circularly polarized beams and the magnetic circular dichroism effect.

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