Photon Correlation Spectroscopy of Colloidal Palladium Using a Coherent X-Ray Beam

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We have used an intense coherent x-ray beam and a real time digital autocorrelator to study the low frequency dynamics of colloidal palladium in glycerol by x-ray photon correlation spectroscopy (XPCS). The translational diffusion was studied in the q range from 1.5×10^{-3} to 6×10^{-3} Å^{-1} and in the temperature range from 279 to 293 K. The measured relaxation rates were proportional to q^2 and inversely proportional to viscosity as expected for a translational diffusion process. This experiment shows that XPCS can be performed in a wide time range (10^{-4} to 100 s) and opens up a new opportunity for the study of the dynamics of nontransparent media. [S0031-9007(96)01912-6]

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Complex relaxations in disordered systems have been studied successfully by scattering of both visible light and neutrons. Neutron based techniques (inelastic and quasielastic neutron scattering, neutron spin echo) can probe the dynamic properties of matter at high frequencies from ω typically equal to 10^{14} s^{-1} down to about 10^7 s^{-1} and achieve atomic resolution. Scattering vectors between 0.02 and 10 Å^{-1} are usually accessible in these experiments. Photon correlation spectroscopy, on the other hand, can cover the low frequency dynamics ($\omega < 10^6$ s^{-1}) with visible light, but probes only the long wavelength $q < 4 \times 10^{-3}$ Å^{-1} region in materials not absorbing visible light [1]. Only recently have intense coherent hard x-ray beams from third generation synchrotron radiation sources become available, opening up the possibility for correlation spectroscopy experiments with x rays capable of probing the low frequency dynamics (10^6 to 10^{-3} s^{-1}) in a q range from 1×10^{-3} Å^{-1} up to several Å^{-1}, thus providing atomic resolution.

The feasibility of XPCS for measuring low frequency dynamics has been shown recently for a limited time range (correlation functions ranging from 1 to 10^3 s) by studying equilibrium critical fluctuations in Fe_3Al [2] and Brownian motion of gold colloids [3,4]. The latter study by Dierker *et al.* [4] is particularly interesting because the dynamics of metal colloidal suspensions in the concentration range which was studied in this experiment ($c \approx 1$ vol. %) is inaccessible to conventional light scattering due to high absorption and/or multiple scattering. Dierker *et al.* report relaxation rates for spherical, nonaggregated gold colloids with screened Coulomb interactions that do not obey q^2 scaling indicating an unexplained deviation from simple translational diffusion. Deviations from q^2 scaling have been observed before in dynamic light scattering studies of charged colloidal suspensions [5] and in aggregated gold colloids where rotational diffusion of the aggregates can modify the q dependence of the relaxation rate [6].

We have studied the diffusive dynamics in an optically opaque sample of colloidal palladium aggregates in glycerol using the intense coherent x-ray beam at the TROIKA undulator beam line of the ESRF combined with a fast digital autocorrelator. This enabled us to measure correlation functions covering a time range of 6 decades (10^{-4} to 10^2 s). We have measured the q dependence of the relaxation rates beyond the range reachable by conventional light scattering, as well as the temperature dependence of the diffusion coefficient. The data show that the dynamics in the covered q range (1.5×10^{-3} to 6.5×10^{-3} Å^{-1}) is dominated by aggregates of colloidal palladium characterized by a hydrodynamic radius $R_h = 1220$ Å and a fractal dimension of 2.81. The measured relaxation rates were proportional to q^2 and inversely proportional to viscosity as expected for a translational diffusion process. There is no indication for contributions from rotational diffusion in the covered q range. The experiment also demonstrates that XPCS will definitely be capable of covering relaxation times between 10^{-6} and 10^3 s underlining the potential of XPCS as a unique microscopic tool for the study of low frequency dynamics.

XPCS probes the dynamic properties of matter by analyzing the temporal correlations among photons scattered by the material. Correlations can be quantified via the normalized time correlation function $g(t)$,

$$g(t) = \frac{\langle n(t')n(t' + t)\rangle}{\langle n\rangle^2}, \tag{1}$$

where $n(t)$ is the number of scattered photons at time t and the brackets denote the time average. In the absence of dynamics $g(t) = 1$ and the diffraction pattern of a disordered system consists of a static speckle pattern [7,8]. Correlation spectroscopy requires the sample to be illuminated coherently, implying the need for an intense x-ray beam with sufficient transverse and longitudinal coherence length [7]. More specifically, the maximum path length difference (PLD) in the sample has to be smaller than the longitudinal coherence length ξ_l of the beam. This requires in a transmission geometry $2h \sin\theta \tan\theta < \xi_l$ and $L \sin 2\theta < \xi_l$ where h and L are thickness and transverse size of the scattering volume, respectively, and 2θ is the scattering angle. In addition, L must be smaller than or comparable to the transverse coherence length ξ_t. Whereas these conditions are relatively easy to fulfill with laser light, the last condition requires a highly collimated beam in the case of x rays which can be produced by using very small (μm sized) pinholes in the beam. Only high brilliance undulator sources can provide sufficient flux under these experimental conditions.

The experiment was performed on beam line 9 (TROIKA) [9] at the European Synchrotron Radiation Facility (ESRF). The beam line was configured to provide maximum coherent flux by restricting the longitudinal coherence length to about 100 Å. Figure 1 shows a schematic layout of the beam line setup. The gap of the high β undulator was tuned to provide photons with an energy of 8.2 keV (1.51 Å) at the peak of the third undulator harmonic. The nominal transverse coherence length $\xi_t = \lambda R_s / 2d_s$ of the x-ray beam was 52 μm in the vertical direction at the position of the sample at a distance $R_s = 46$ m from the source. The vertical size d_s of the source is 67 μm. Primary slits at the 27 m point of the beam line were closed to 100 μm in order to provide a coherence length of 14 μm in the horizontal direction at the sample position. A flat water-cooled Si mirror located 44.2 m from the source was set to a critical energy just above 8.2 keV for rejection of higher harmonics and was used to deflect the beam horizontally out of the white undulator cone. Low energy x rays (harmonics 1 and 2) were eliminated in upstream beryllium windows and carbon absorbers. A second Si mirror mounted on a piezoelectric bender was installed in vertical reflection geometry 0.76 m downstream of the first mirror in order to reduce the harmonic content of the incident beam to less than 5×10^{-3}. A laterally coherent x-ray beam was then selected by a 12 μm diameter pinhole aperture. The coherent flux was increased by focusing the beam vertically through the collimating pinhole until the vertical beam divergence matched the horizontal divergence, giving a transverse coherence length of roughly 14 μm in both directions. The integrated flux through the 12 μm pinhole was 10^9 photons/sec at 100 mA storage ring current. A set of guard slits of 100 μm size just before the sample was used to remove scattering from the pinhole.

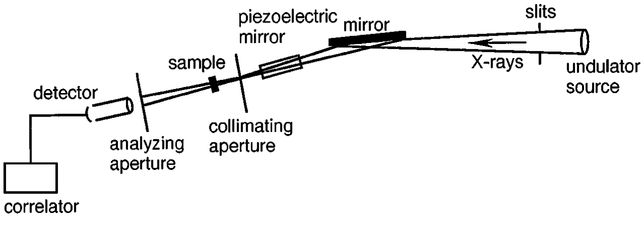

FIG. 1. Schematic setup of the Troika beam line for the experiment.

The longitudinal coherence length $\xi_l = \lambda(\lambda/\Delta\lambda)$ was determined by the bandwidth $\Delta\lambda/\lambda = 1/nN$ of the third ($n = 3$) harmonic of the undulator with period $N = 35$. The measured bandwidth using a Si(111) analyzer crystal was 1.3%. This corresponds to a longitudinal coherence length of $\xi_l = 116$ Å. The coherence requirement that the maximum path length difference PLD $< \xi_l$ is satisfied up to scattering angles 2θ of 4.8 mrad corresponding to $q = 2 \times 10^{-2}$ Å^{-1}. This value extends considerably beyond the q range ($q_{\max} \approx 4 \times 10^{-3}$ Å^{-1}) accessible with visible light. The low q limit in XPCS is determined by the tails of the Fraunhofer diffraction of the main beam which in the present case is given by $q_{\min} = 10^{-3}$ Å^{-1}.

To detect the intensity fluctuations the area of the detector has to be comparable to the size of the speckles, whose angular width is λ/L, with L being the size of the pinhole aperture. For this purpose an analyzing aperture of 20 μm size in front of a standard scintillation counter at a distance of 1.3 m from the sample was used. Correlation functions were measured by a digital ALV5000/E (ALV Langen, Germany) correlator.

The sample used was a solution of colloidal palladium in glycerol. The colloid was produced by electrochemical reduction of palladium cations in the presence of the zwitterionic surfactant dimethyldodecylammoniopropansulfonate [10,11]. In that way the particles are stabilized and the colloid is soluble in glycerol. Glycerol was chosen as a solvent because it provides high viscosity in an easily accessible temperature range (6 Pa s at 279 K to 0.9 Pa s at 293 K). Transmission electron microscopy (TEM) gave a radius of 20 to 30 Å for the metallic core of the colloid. If the shell of the stabilizer around the metallic core is taken into account, the diameter is estimated to be 70 Å. The volume concentration of the metallic part in the solution was 0.3% and the sample was a completely opaque, black suspension. A thin glass capillary with a diameter of 1 mm (transmission 82%) served as the sample container. The transmission of the sample including the container was 21%.

A measurement of the static structure factor is shown in Fig. 2. An extension of the data taken at the Troika beam line to higher scattering vectors was made by a measurement with a conventional SAXS setup using a commercial Kratky camera and noncoherent x rays from a sealed tube. In the double logarithmic representation the asymptotic Porod limit $I(q) \propto q^{-4}$ can clearly be recognized at high q [12]. For $q \geq 0.08$ Å^{-1} the scattering from the individual palladium particles dominates $I(q)$, as can be seen in the inset, which shows $I(q)\, q^4$ and a model function describing the scattering intensity by a distribution of spherical particles with different radii. In this model the form factor $F(qR)$ for a sphere of size R is convolved with a Gaussian distribution of radii R, where $F(qR)$ is given

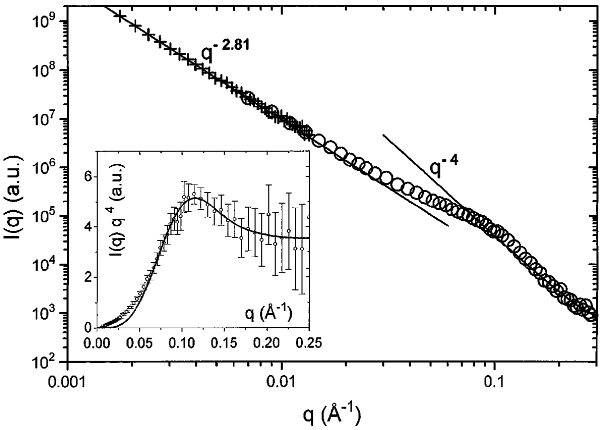

FIG. 2. Static structure factor $I(q)$ of colloidal palladium solution. The data marked by crosses were measured at the ESRF Troika beam line; the data marked by open circles were measured with a Kratky camera and a sealed x-ray tube. The solid lines display the power law behavior at low and high q. In the inset $I(q)q^4$ versus q is shown in comparison to a model function describing the scattering by an ensemble of spherical paricles with a distribution of sphere sizes.

by

$$F(qR) = 9\left[\frac{\sin qR - qR\cos qR}{(qR)^3}\right]^2. \tag{2}$$

The corresponding average radius is $R = 13$ Å with a standard deviation $\sigma_R = 9$ Å. These values are consistent with the TEM data for the size of the metallic core. The further increase of $I(q)$ at small q, which would not show up for isolated spheres and which cannot be described by the model introduced above, indicates the existence of aggregates, whose internal structure is reflected in this q range. In this regime $I(q)$ can approximately be described by power law scattering, $I(q) \propto q^{-\alpha}$, a behavior which is often found in aggregates and is usually interpreted in terms of a fractal structure of the aggregates [13,14]. The data are best fitted by an exponent $\alpha = 2.81$, corresponding to a fractal dimension with the same value. The exact size of the aggregates cannot be determined from the measurements of the static structure factor $I(q)$, since the Guinier limit $qR_{\mathrm{agg}} \ll 1$ with $I(q) \propto e^{-q^2R_{\mathrm{agg}}^2/3}$ is not reached in the accessible q range of the experiment [12].

Time correlation functions were acquired at 279 K in transmission geometry for scattering vectors ranging from $q = 1.58 \times 10^{-3}$ Å^{-1} to $q = 6.31 \times 10^{-3}$ Å^{-1}. Figure 3 shows a correlation function covering almost 6 decades in time taken at $q = 1.58 \times 10^{-3}$ Å^{-1}. The acquisition time was 30 min at a count rate of 3.4 kHz. Also shown is a correlation function of the incident beam proving the absence of any correlated noise introduced by the detector or the incident beam.

For a diffusion process the expected functional form of the correlation function is [1]

$$g(q,t) = A(q)\,e^{-2\Gamma t} + 1, \qquad \text{with } \Gamma = q^2 D\,. \tag{3}$$

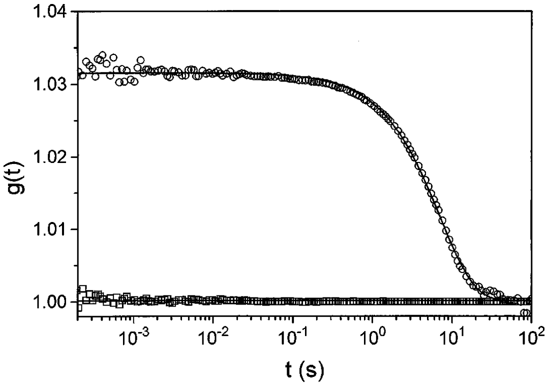

FIG. 3. Correlation function $g(t)$ measured for palladium colloid in glycerol at $q = 1.58 \times 10^{-3}$ Å^{-1} and $T = 279$ K. The solid line corresponds to a fit with an exponential decay. For comparison a correlation function measured for the incident beam is shown.

D is the diffusion constant. For translational diffusion one expects

$$D \approx \frac{kT}{6\pi\eta R_h^{\mathrm{app}}}\,, \tag{4}$$

where k is the Boltzmann constant, T the temperature, η the viscosity of the solvent, and R_h^{app} the apparent hydrodynamic radius of the diffusing particles. Only in the limiting case of concentration $c \rightarrow 0$ the value of R_h^{app} gives exactly the hydrodynamic radius R_h of the diffusing particles [15]. The prefactor $A(q)$ reflects the coherence of the primary beam, and values between 0.01 and 0.10 are typically achieved with this wide bandpass configuration. We attribute these small values to imperfections of optical elements that can compromise the coherence. In the present experiment $A(q)$ ranges from 0.03 at low q to 0.01 at the highest q values. These values for $A(q)$ are consistent with the amplitude of static speckle patterns measured with the same experimental setup. As the solid line in Fig. 3 shows, the correlation function can be well described by an exponential decay.

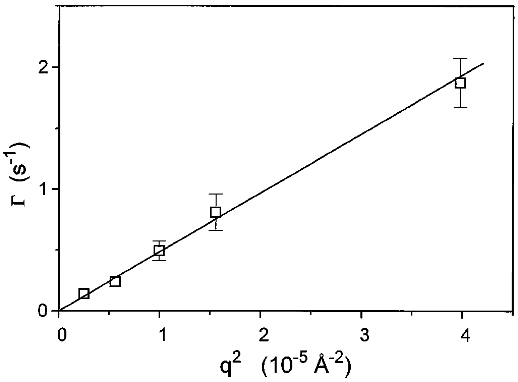

FIG. 4. Relaxation rates Γ determined from the correlation functions plotted vs q^2. The linear relationship confirms the diffusive nature of the process observed [Eq. (3)].

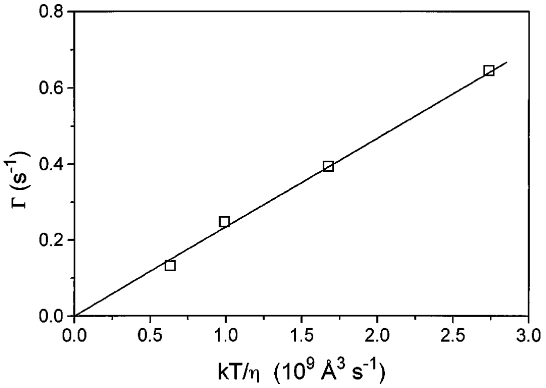

FIG. 5. Relaxation rates Γ determined from the correlation functions plotted vs kT/η. The linear dependence found in this representation is the expected behavior for a diffusion process [Eq. (4)].

The scattering vector dependence of the relaxation rates is displayed in Fig. 4 and shows a q^2 dependence over the q range covered. This is the behavior expected for diffusion of aggregates, if the contribution from rotational diffusion is negligible. The diffusion coefficient determined from the data is $D = 5.1 \times 10^{-12}$ cm$^2/s$.

The temperature dependence of the relaxation rate Γ has been measured for a fixed $q = 1.58 \times 10^{-3}$ Å^{-1}. The data are plotted as a function of kT/η in Fig. 5 using the temperature dependence of the glycerol viscosity [16]. The linear relationship displayed in Fig. 5 agrees well with Eq. (4) demonstrating that the temperature dependence of D is indeed given by the temperature dependence of the viscosity of glycerol; i.e., the colloids in the sample do not influence the dynamics of the surrounding medium. This confirms the validity of the picture of simple Brownian motion, observed in the relaxation process. The value for the hydrodynamic radius calculated from the data shown in Figs. 4 and 5 is $R_h = 1220 \pm 100$ Å. This value is about a factor of 15 higher than the radius of the individual colloids, if the shell of the stabilizer around the metallic core is taken into account. This finding agrees well with the conclusion drawn from the analysis of the measured static scattered intensity. The colloidal particles form aggregates whose diffusion is observed in the XPCS experiment. It is important to note that the fact that the measured correlation functions can be well described by a single exponential decay does not necessarily imply a uniform size of the aggregates, since the scattering power of particles of different sizes is proportional to the sixth power of the particle radius. The correlation function is therefore dominated by the largest particles, implying that the extracted diffusion coefficient applies to these aggregates. For comparison a dynamic light scattering experiment was performed with a very diluted sample. The hydrodynamic radius determined from the first cumulant is $R_h = 900$ Å, a value which is slightly smaller than the result of the XPCS experiment, suggesting that the colloidal aggregates break up somewhat on dilution.

In conclusion, we have shown that the dynamics of colloidal systems and disordered systems in general can be studied quantitatively by x-ray photon correlation spectroscopy in a wide time range ($10^{-4} \leq t \leq 100$ s). Our results, obtained on a palladium colloid, demonstrate that metal colloidal aggregates can be investigated by studying their dynamics with XPCS in a q range and concentration range exceeding that accessible with visible light techniques. Further progress can be expected from fast 2D detectors that will give access to important phenomena in disordered systems, such as critical fluctuations at an order-disorder transition, density fluctuations in liquids undergoing a glass transition, or the short wavelength dynamics of colloids.

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