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LETTER TO THE EDITOR

Microrheology of polymeric solutions using x-ray photon correlation spectroscopy

A Papagiannopoulos¹, T A Waigh¹, A Fluerasu², C Fernyhough³ and A Madsen²

¹ Department of Physics and Astronomy, University of Leeds, Leeds LS2 9JT, UK

² European Synchrotron Radiation Facility, F-38043 Grenoble, France

³ Department of Chemistry, University of Sheffield, Brook Hill, Sheffield S3 7HF, UK

E-mail: t.a.waigh@leeds.ac.uk

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Abstract

We demonstrate the technique of XPCS microrheology on opaque polymeric solutions (1–20% w/w) using colloidal silica probes. The short time decay of the intensity correlation function provides the mean square displacement (MSD) of the colloidal probes. The MSDs of the probes are subsequently transformed using the generalized Stokes–Einstein equation, allowing the linear viscoelastic spectra of a biopolymer (gellan) and a synthetic polyelectrolyte (polystyrene sulfonate, PSS) to be calculated over two decades of frequency. MSDs can be measured that are two orders of magnitude smaller than those possible with video particle tracking microrheology, with a sensitivity of $\sim 10 \text{ nm s}^{-1}$ for displacements of $\sim \text{nm}$ s. The XPCS data for water, glycerol and PSS combs are in agreement with video particle tracking microrheology experiments performed at lower polymer concentrations.

1. Introduction

X-ray photon correlation spectroscopy (XPCS) is a relatively new method for measuring the dynamics of condensed matter, extending the standard physical technique of dynamic light scattering (DLS) into the x-ray regime [1]. The method depends on the availability of high brilliance synchrotron radiation sources where the x-ray beam can be made partially coherent by fine collimation and well defined monochromatization. The detector size also needs to be matched to the size of the coherent speckles scattered by the sample [2]. Fluctuations in the intensity of the speckles then provide information on the sample dynamics, and the length scale probed is defined by the angle through which the scattered beam is deflected (the momentum transfer). The XPCS technique has now been demonstrated with a series of soft condensed matter systems including smectic membranes [3, 4], clay suspensions [5], magnetic colloids [6, 7] and block copolymer micelles and vesicles [8, 9].

Recently microrheology has been a growth field in soft condensed matter physics [10]. The aim of microrheology is to study the viscoelasticity of materials as a function of length scale. A series of new microrheological methods have been developed including diffusing wave spectroscopy (DWS) [11], optical tweezers [12], video particle tracking [13] and magnetic microrheology [14]. These techniques have a number of advantages over bulk rheology methods; a wide range of frequencies can be probed (10^{-2} – 10^6 Hz), and small sample volumes can be explored (μl) [10]. In the following article we introduce a new technique, XPCS microrheology, and apply it to opaque polymeric solutions. We thus extend the method of single-scattering DLS microrheology [15] into the x-ray regime.

2. Method

Colloidal silica spheres were purchased from Polysciences (diameter, $0.45\ \mu\text{m}$) and used as probes in XPCS microrheology experiments at concentrations of 1% and 2% w/w. Polystyrene spheres (diameter, $0.55\ \mu\text{m}$) were also purchased from Polysciences and used as probes in video particle tracking microrheology. Anionically polymerized polystyrene sulfonate combs were prepared at the University of Sheffield (M_w $2027\ \text{kg mol}^{-1}$; the average number of main chain monomers is 1876, the number of side-chain monomers is 324 and the average number of branches per chain is 14), and gellan (a charged gelling bacterial polysaccharide) was purchased from Fluka. The apparatus for video particle tracking experiments was described previously and allows the calculation of MSDs in two dimensions in the range 0.02–10 s [16].

The XPCS measurements were performed at the Troika beamline ID10A of the ESRF where three undulators operating in series were set to have coinciding harmonics at 8 keV ($\lambda = 1.55\ \text{\AA}$). The emerging synchrotron beam was diffracted horizontally from a single-bounce Si(111) Bragg monochromator crystal ($\Delta\lambda/\lambda \approx 1.4 \times 10^{-4}$) and vertically from a silicon mirror to obtain monochromatic radiation without contributions from higher order harmonics. The source size (FWHM) was approximately $30 \times 900\ \mu\text{m}^2$ ($v \times h$) and the source–sample distance was 46 m. In the vertical direction the synchrotron beam was focused by a cylindrical compound refractive beryllium lens in order to enhance the flux. In the horizontal direction the beam was collimated to achieve a smaller source size and symmetrize the transverse coherence lengths. A $10\ \mu\text{m}$ pinhole before the sample was used to select the ‘coherent’ part of the beam. The intensity was $2 \times 10^9\ \text{photons s}^{-1}$ through the pinhole. Immediately before the sample, a guard slit was carefully placed to block the fringes appearing from the pinhole scattering.

3. Results and discussion

Small angle x-ray scattering (SAXS) profiles were measured from the same samples as were examined with XPCS. The profiles show the relative intensity of scattered x-rays as a function of momentum transfer ($q = (4\pi/\lambda) \sin \theta/2$; θ is the scattering angle). A representative SAXS profile for silica spheres inside a 4% w/w comb PSS solution is shown in figure 1. The oscillations in a clear, well defined form factor can be seen. Fits of a polydisperse form factor for non-interacting hard spheres to this SAXS profile and similar profiles for the range of complex fluids examined with XPCS microrheology establish that the silica probes are the dominant scatterers, provide a probe size for use with the general Stokes–Einstein inversion (radius (a) is calculated to be 222 nm) and indicate a small polydispersity (the standard deviation (σ) of a Gaussian distribution is 0.0468) that facilitates the data analysis. The small deviations of the data from the model at low q are due to the finite size of the slits defining the width of the x-ray beam. The invariance of the scattering at a series of polymer concentrations indicated

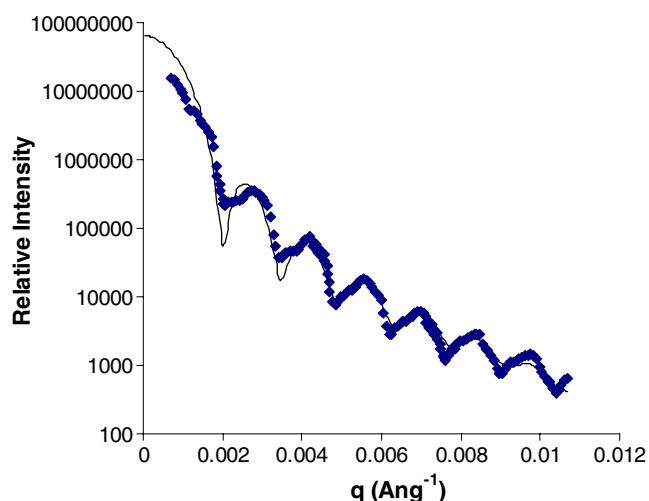


Figure 1. Small angle x-ray scattering (intensity versus momentum transfer) is shown from silica probe spheres embedded in aqueous solutions of polystyrene sulfonate combs (4% w/w, filled diamonds). A fit of a form factor for non-interacting polydisperse hard spheres is indicated (continuous line, radius 222 nm, and the Gaussian polydispersity σ is 0.0468).

(This figure is in colour only in the electronic version)

that negligible aggregation of the probe colloids took place, validating the subsequent data analysis.

XPCS correlation functions were then taken at the maxima of the form factor. Representative correlation functions measured at momentum transfers of $0.001424 \text{ \AA}^{-1}$ are shown in figure 2. Single-exponential decays occur with the simple Newtonian liquids (water and glycerol) indicating normal Brownian diffusion, but the viscoelastic fluids, gellan and PSS combs show more complex non-exponential behaviours. The inset to figure 2 indicates the variations of the correlation function with momentum transfer for silica probes in water at two different q values.

For dilute solutions of colloidal spheres the following equation is known to hold for the field correlation function [17]:

$$g^{(1)}(t) = \exp\left(\frac{-q^2 \langle r^2(t) \rangle}{6}\right) \quad (1)$$

where $\langle r^2(t) \rangle$ is the mean square displacement. The Siegert equation [18] relating the field correlation function ($g^{(1)}(t)$) to the measured intensity correlation function ($g^{(2)}(t)$) is

$$g^{(2)}(t) = 1 + |g^{(1)}(t)|^2.$$

In combination with the Siegert relationship, equation (1) allows the mean square fluctuations of the probe particles (proportional to the compliance of the viscoelastic specimen) to be calculated [15], figure 3. There is good agreement between the MSDs from glycerol, water and 1% w/w PSS combs measured with XPCS microrheology and those found using video particle tracking microrheology (remembering that a factor of 3/2 is required to move from MSDs measured in two dimensions (VPT) to ones measured in three dimensions (XPCS)). The Newtonian liquids (glycerol and water) provide, using the conventional Stokes–Einstein relationship, the viscosity of the standards as 37 and 0.81 cP with XPCS data in fair agreement with accepted values (45.3 and 0.89 cP). We conclude that any localized heating from x-ray irradiation does not induce substantial convective motion of the samples. Errors in the

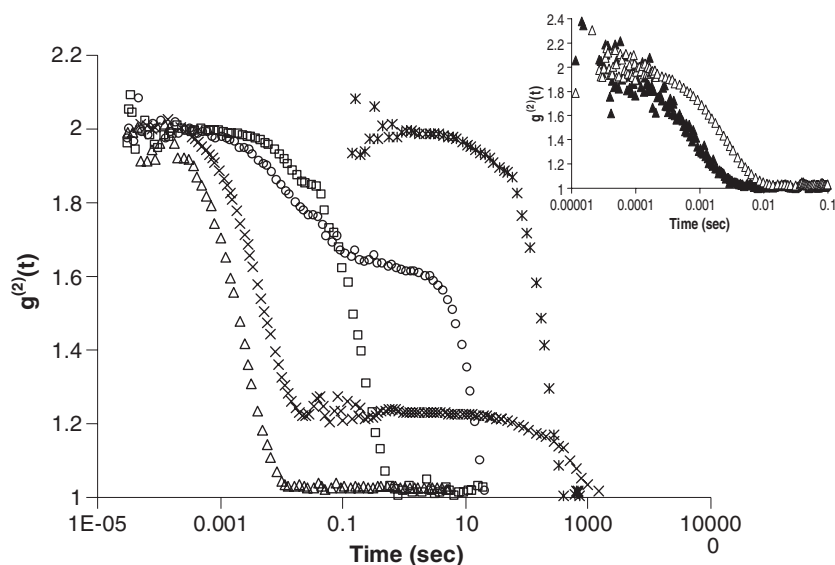


Figure 2. Correlation functions measured from colloidal probes embedded in solutions of gellan (5% w/w crosses), polystyrene sulfonate combs (1% w/w, open circles; 20% w/w, stars), water (open triangles) and glycerol (80% w/w, open squares). All the correlation functions were measured at the same value of the momentum transfer (q is $0.001424 \text{ \AA}^{-1}$) and thus identical points on the form factor of the spherical silica probes. Inset: correlation functions for silica in water calculated at q values of 0.001424 (open triangles) and 0.00256 \AA^{-1} (filled triangles).

calculation of the contrast for normalizing the correlation functions have a small effect on the resultant MSDs when correlation functions with well defined short time behaviour are chosen. Accurate VPT data were not available from 5% gellan or 4% or 20% combs, since the fluctuations are too small to measure accurately with the technique [10, 19] and introduce erroneous subdiffusive motions in the calculated MSDs.

From a practical point of view, equation (1) provides a self-consistency check for the data analysis (not available with DWS [20]). The diffusive q^2 dependence of the data for each viscoelastic sample can be checked at a series of momentum transfers. This superposition of data sets taken at different momentum transfers validates the compliances calculated with equation (1) (figure 3 inset). Reduction of the concentration of the colloidal probes below 1% w/w is expected to provide a wider range of timescales [17] over which equation (1) is valid and consequently a larger range of frequencies for the linear viscoelasticity. The current experiment yields a range of two decades for the compliance (figure 3). From the gradient of the MSDs on figure 3 we can empirically calculate the sensitivity of the XPCS microrheology technique as 10 nm s^{-1} .

The x-ray capillaries used in the XPCS experiments hold $10 \mu\text{l}$ s of sample, which compares favourably with bulk rheological methods (mls). Video particle tracking microrheology is limited to a lower range of shear moduli (viscosities less than 90% glycerol/water [10]) than XPCS microrheology, since XPCS microrheology is a much more sensitive technique for measuring the amplitude of probe particle fluctuations. The MSDs measurable with XPCS are two orders of magnitude lower than those possible with video particle tracking microrheology (figure 3). Furthermore XPCS microrheology has a much wider range of timescales than the video techniques (10^{-4} – 100 s compared with 0.02 – 100 s). The timescales and MSDs measurable with the XPCS techniques are comparable with those measured using optical

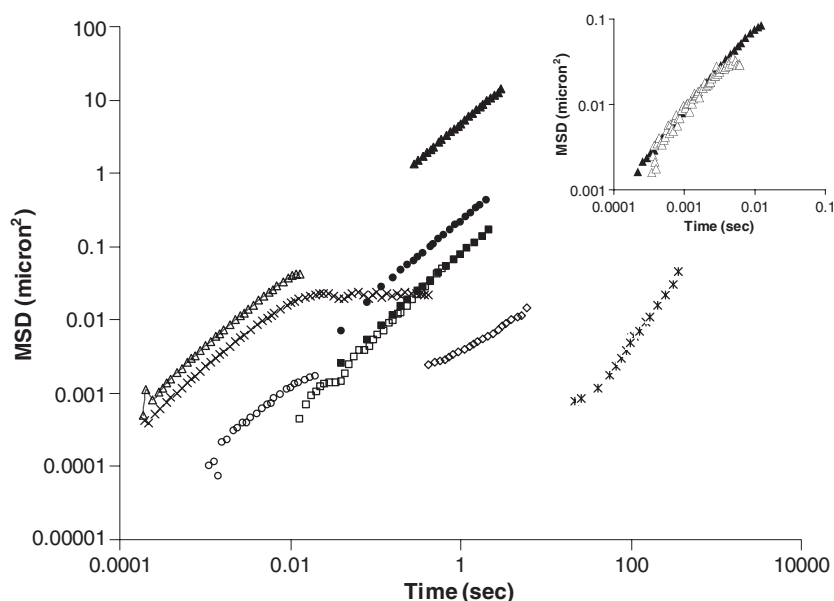


Figure 3. Mean square displacements from XPCS microrheology and video particle tracking microrheology of colloidal spheres in water (XPCS, open triangles; VPT, closed triangles), glycerol (80% w/w, XPCS, open squares; VPT, closed squares), gellan (5% w/w, XPCS, crosses), polystyrene sulfonate combs (1% w/w, XPCS, open circles; VPT, closed circles; 4% w/w, XPCS, open diamonds; and 20% w/w, XPCS, stars), shown as a function of time. The inset shows the superposition of the XPCS MSDs for silica in water at two different q values (0.001424, closed triangles; 0.00256 \AA^{-1} , open triangles).

tweezers methods for transparent materials [10], although access to oversubscribed synchrotron facilities is a continual problem with the x-ray method. Fluorescent correlation spectroscopy (FCS) also offers a method for examining the viscoelasticity of concentrated semi-transparent polymeric materials in the range 10^{-4} –100 s [25–27]. Here the MSDs are a sensitive function of the scattering volume (corresponding to a single q value) and research into the application of the GSE equation is required, using a series of scattering volumes to verify equation (1) and properly establish the validity of FCS microrheology [28, 29].

The generalized Stokes–Einstein (GSE) equation [11] allows the real shear modulus ($\tilde{G}(s)$) as a function of the Laplace frequency (s) to be constructed from the Laplace transformed mean square displacement ($\langle r^2(s) \rangle$)

$$\tilde{G}(s) = s\tilde{\eta}(s) = \frac{s}{6\pi a} \left[\frac{6kT}{s^2 \langle \Delta r^2(s) \rangle} - ms \right] \quad (2)$$

where m is the mass of the probe, $\tilde{\eta}$ is the Laplace transformed viscosity, a is the radius of the probe and kT is the thermal energy. $\langle r^2(s) \rangle$ was evaluated numerically following the methods of Mason and Weitz [11]. Subsequently the complex shear modulus ($G^*(\omega) = G'(\omega) + iG''(\omega)$) as a function of the real frequency (ω) is constructed by analytic continuation of $\tilde{G}(s)$ [11]. The complex shear moduli calculated using the GSE equation for gellan are shown in figure 4. The long elastic plateau in G' at low frequencies is expected from gellan due to its behaviour as a physical gel [21]. Helical cross-links provide the strong elastic component of the shear modulus observed at lower frequencies [22]. We highlight that the lack of superposition of data sets at different momentum transfers below 0.01 Hz implies a relative error of a factor of 2 in the absolute value of the shear modulus for this range of data. However the superposition of data

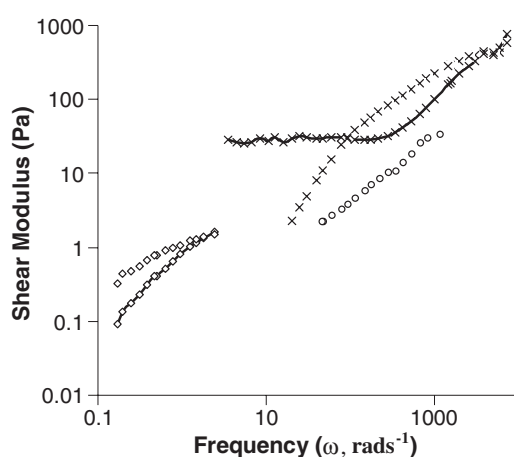


Figure 4. Complex shear modulus of aqueous solutions of gellan (5% w/w, G' , crosses with line; G'' , crosses) and polystyrene sulfonate combs (1% w/w, G'' , open circles; and 4% w/w, G' , open diamonds with line; G'' , open diamonds) calculated from XPCS MSDs (figure 3).

obtained at different q values below <0.01 Hz lends confidence to the accurate quantification of the gellan viscosity at high frequencies. Improvement of the contrast of the correlation functions is another long term goal with XPCS experiments.

At low concentrations comb polyelectrolytes are principally viscous [23] in agreement with the almost linear dependence of the MSD on time measured with the 1% PSS comb shown in figure 3. This is also observed in the dominant viscous contribution to the shear moduli shown in figure 4. The elastic modulus (G') was immeasurably small with the 1% w/w PSS comb and is not included in figure 4. The molecular mechanism for this viscosity will be approached in detail in subsequent articles. In particular a novel rheological feature for the comb polyelectrolytes occurs at the brush overlap concentration [23], where the dynamics of the side-chains transforms from Zimm (unscreened) to Rouse (screened) behaviour. Passive microrheology techniques [10] such as XPCS microrheology offer an ideal method for measuring the viscosity of polyelectrolytes, since these techniques probe the zero-shear limit, which is often difficult to measure in bulk rheology experiments with strongly shear thinning polyelectrolyte solutions.

Crucially we note that the technique of XPCS microrheology allows one of the previous conditions for a successful XPCS experiment to be circumvented. High x-ray contrast is no longer required for the sample, since the silicon probes provide this, and only beam stability and resistance to beam damage are needed. Therefore we have been able to study a biological system, a bacterial polysaccharide (gellan) in water, for the first time with an XPCS technique.

A similar technique of quasi-elastic neutron microrheology (e.g. studying hydrogenated polystyrene probe spheres in a deuterated complex fluid) could extend the timescales available for single-scattering microrheology to hundreds of picoseconds. These timescales are beyond those accessible with DWS or PCS, although the neutron technique offers a much more limited range of times than the XPCS method. Again quasi-elastic neutron microrheology would not be dependent on a strong contrast mechanism for the viscoelastic sample.

Many more XPCS microrheology experiments are planned and we hope this new technique will allow access to the high frequency viscoelasticity of a large range of opaque complex fluids including melt polymers, pastes and jammed colloids [24]. The sole requirements for the viscoelastic fluids to be measured using the XPCS method are that they can stabilize the

colloidal probes and withstand the irradiation by the x-ray beam. The technique could also be extended down to the timescales of 50 ns previously demonstrated with XPCS. This would require careful choice of sample contrast and synchrotron filling mode [4], but would allow the measurement of the viscoelasticity of opaque materials at frequencies comparable with those of diffusing wave spectroscopy measurements [11].

4. Conclusions

We have demonstrated the novel technique of XPCS microrheology with respect to two aqueous polymeric systems: gellan and polystyrene sulfonate combs. XPCS microrheology is one of the first microrheology techniques to tackle the measurement of the viscoelasticity of optically opaque complex fluids. The frequency range studied in the experiments spans two decades, and may be extended in future studies by increased dilution of the probe spheres. The measurable mean square displacements of the probe spheres (sensitivity of ~ 10 nm s^{-1} down to displacements of \sim nms) are two orders of magnitude smaller than that possible in video particle tracking experiments and over a much wider range of timescales ($\sim 10^{-4}$ –100 s).

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References

- [1] Grubel G and Zontone F 2004 *J. Alloys Compounds* **362** 3
- [2] Sutton M, Mochrie S G J, Greytak T, Nagler S E, Berman L E, Held G A and Stephenson G B 1991 *Nature* **352** 608
- [3] de Jeu W H, Madsen A, Sikharulidze I and Sprunt S 2005 *Physica B* **357** 39
- [4] Sikharulidze I, Dolbnya I P, Fera A, Madsen A, Ostrovskii B I and de Jeu W H 2002 *Phys. Rev. Lett.* **88** 1155031
- [5] Bandyopadhyay R, Liang D, Yardimci H, Sessoms D A, Borthwick M A, Mochrie S G J, Harden J L and Leheny R L 2004 *Phys. Rev. Lett.* **93** 2283021
- [6] Lal J, Abernathy D L, Auvray L, Diat O and Grubel G 2001 *Eur. Phys. J. E* **4** 263
- [7] Robert A, Wagner J, Autenrieth T, Hartl W and Grubel G 2005 *J. Chem. Phys.* **122** 0847011
- [8] Mochrie S G J, Mayes A M, Sandy A R, Sutton M, Brauer S, Stephenson G B, Abernathy D L and Grubel G 1997 *Phys. Rev. Lett.* **78** 1275
- [9] Falus P, Borthwick M A and Mochrie S G J 2005 *Phys. Rev. Lett.* **94** 016105
- [10] Waigh T A 2005 *Rep. Prog. Phys.* **68** 685
- [11] Mason T G and Weitz D A 1995 *Phys. Rev. Lett.* **74** 1250
- [12] Starrs L and Bartlett P 2003 *Faraday Discuss.* **123** 323
- [13] Xu J, Palmer A and Wirtz D 1998 *Macromolecules* **31** 6486
- [14] Bausch A R, Moller W and Sackmann E 1999 *Biophys. J.* **76** 573
- [15] Dasgupta B R, Tee S Y, Crocker J C, Frisken B J and Weitz D A 2003 *Phys. Rev. E* **65** 515051
- [16] Di Cola E, Waigh T A, Trinick J, Tskhovrebova L, Houmeida A, Pyckhout-Hintzen W and Dewhurst C 2005 *Biophys. J.* **88** 4095
- [17] Pusey P N 1991 *Les Houches—Liquids, Freezing and Glass Transition* (Amsterdam: Elsevier) p 764
- [18] Siegert A J F 1943 *MIT Radiation Lab. Report* No. 465
- [19] Savin T and Doyle P S 2005 *Biophys. J.* **88** 623
- [20] Pine D J, Weitz D A, Chaikin P M and Herbolzheimer E 1988 *Phys. Rev. Lett.* **60** 1134
- [21] Miyoshi E and Nishinari K 1999 *Colloid Polym. Sci.* **277** 727
- [22] Izumi Y, Kikuta S, Sakai K and Takezawa H 1996 *Carbohydrate Polym.* **30** 121
- [23] Waigh T A, Papagiannopoulos A, Voice A, Bansil R, Unwin A P, Dewhurst C, Turner B and Afdhal N 2002 *Langmuir* **18** 7188
- [24] Larson R G 1999 *The Structure and Dynamics of Complex Fluids* (Oxford: Oxford University Press)
- [25] Michelman-Ribeiro A 2004 *Macromolecules* **37** 10212
- [26] Best A, Pakula T and Fytas G 2005 *Macromolecules* **38** 4539
- [27] Fatin-Rouge N, Starchev K and Buffle J 2004 *Biophys. J.* **86** 2710
- [28] Berne B J and Pecora R 2000 *Dynamic Light Scattering* (New York: Dover)
- [29] Masuda A, Ushida K and Riken T O 2005 *Biophys. J.* **88** 3583