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Rheo-XPCS

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ABSTRACT

We review recent efforts and discuss future prospects in research employing X-ray photon correlation spectroscopy (XPCS) to interrogate the nanometer-scale structural dynamics of soft materials undergoing in situ mechanical deformation and flow. Examples of such rheo-XPCS experiments include those incorporating conventional homogeneous shear deformation, including notably large amplitude oscillatory shear (LAOS), as well as other modes of flow and deformation, such as tensile strain and flow within microfluidic environments. Particular attention is given to opportunities in such studies to reveal the structural dynamics associated with nonlinear rheological behavior such as yielding. We also review recent related work employing XPCS as a microrheological tool by tracking nanoparticle mobility within complex fluids.

1. Introduction

Complex fluids and disordered soft solids – such as polymer solutions, dense colloidal suspensions, gels, and many biologically relevant materials – differ from simple liquids or solids due to internal structure on the nanometer or micrometer scale. The presence of these structures, and importantly their tendency to interact and to organize in a hierarchical manner, instills these materials with elaborate properties, particularly in how they deform and flow. Such materials are viscoelastic; they exhibit a combination of viscous and elastic behavior. Often their mechanical response can display a time dependence that spans from sub-milliseconds to minutes or even hours. Another key aspect of the rheology of many complex fluids and disordered soft solids is their strongly nonlinear response, such as shear thinning, shear thickening, and thixotropic behavior. Underlying the nonlinear macroscopic deformation and flow properties are shear-induced changes to the internal microstructure. Identifying and understanding the connections between these microscopic structural dynamics and the macroscopic rheological properties remain a central challenge for the field of soft matter. These special attributes of viscoelastic materials also enable them to play central roles in key technologies affecting a broad range of sectors from energy and transportation to health, agriculture, and national defense.

In recent years, X-ray photon correlation spectroscopy (XPCS) has emerged as a powerful probe for gaining direct insight into the microstructural dynamics that are relevant to soft materials' rheology. Conceptually similar to dynamic light scattering (DLS), XPCS exploits partially coherent X-ray sources available at third-generation synchrotrons to produce X-ray scattering speckle patterns from a material that depend on the instantaneous electron density distribution within the material. The time correlations of these speckle patterns provide information about the microscopic structural dynamics. When employed in a small-angle X-ray scattering (SAXS) geometry, XPCS accesses the structural dynamics over a range of length scales from nanometers to hundreds of nanometers and over a range of time scales from milliseconds to hundreds of seconds that figure prominently in the rheological behavior of many soft materials. This capability has led to efforts to connect the microscopic information about structural dynamics obtained from XPCS to the macroscopic mechanical response in a host of materials with interesting and complicated rheology. A review of this field covering research up to 2011 has described such studies of colloidal gels, block copolymer mesophases, polymer thin films, and other soft materials [1]. More recent examples where XPCS has made connections between rheology and nanoscale dynamics include studies of glassy clay suspensions [2], azopolymer films [3], interfacial nanoparticle gels and glasses [4,5], films of densely branched comb polymers [6], and peptide-based gels [7].

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Recently, research has begun to expand the repertoire of XPCS by using it as an in situ probe of structural dynamics during mechanical deformation and flow. These studies have included subjecting samples to conventional homogeneous shear deformation as well as to other modes of flow and deformation, including in situ XPCS studies on materials under tensile strain and under flow within microfluidic environments. This strategy shows strong promise for gaining new insights, and the field appears poised for growth with at least two synchrotron beamlines optimized for XPCS now having in situ rheometry capabilities (8-ID of the Advanced Photon Source and P10 of Petra III). In this article, we briefly review some of the early efforts in this research area and discuss some of its challenges and future prospects. We also describe recent related work that has employed XPCS as a microrheological tool to obtain complementary rheological information by tracking nanoparticle mobility within complex fluids.

2. Background

Several previous articles provide a good introduction to the theoretical background of XPCS and to technical aspects of performing XPCS experiments [1,8,9,10]. Here, we focus on the theory relevant to XPCS measurements under in situ flow, which follows closely that developed for DLS under flow [11–14]. In both cases, the coherence of the incident beam causes interference effects in the scattering that result in highly irregular, speckled scattering patterns, and the temporal evolution of this speckle contains information about the sample dynamics. To interrogate deformation and flow in materials, DLS and XPCS studies have applied both homodyne methods, where the signal is comprised solely of scattering from the sample, and heterodyne methods, where scattering from the sample is mixed with that from a reference sample. (Heterodyning can also occur in coherent scattering from samples with heterogeneous dynamics when the scattering from a fluid portion mixes with that from a nonergodic portion.) As described below, homodyne and heterodyne methods provide different information when the scatterers have a net velocity, such as during an in situ rheological measurement.

XPCS measurements usually employ an area detector so that the coherent scattering intensity is determined over a range of scattering wave vectors $\boldsymbol{q}$ simultaneously. Analysis of the scattering typically focuses on the intensity autocorrelation function $g_2(\boldsymbol{q}, t)$, measured as a function of $\boldsymbol{q}$ and delay time t,

$$g_2(\boldsymbol{q},t) = \frac{\langle I(\boldsymbol{q},\tau) I(\boldsymbol{q},\tau+t)\rangle}{\langle I(\boldsymbol{q})\rangle^2}, \tag{1}$$

where $I(\boldsymbol{q}, \tau)$ is the intensity at time τ, and the averages are over detector pixels at equivalent wave vector (effectively ensemble averages) and over time. In measurements on systems that are rapidly evolving, the average over time is potentially invalid, and instead a “two-time” analysis of the instantaneous correlations can capture the changing dynamics [15]. Detailed procedures for processing coherent X-ray scattering images to determine $g_2(\boldsymbol{q}, t)$ that account for factors such as finite exposure time, detector dark current, and other instrumental effects have been developed [16]. In the case of homodyne scattering, the intensity autocorrelation function is related to the field correlation function $g_1(\boldsymbol{q}, t)$ through the Siegert relation,

$$g_2(\boldsymbol{q},t) = 1 + \beta |g_1(\boldsymbol{q},t)|^2 \tag{2}$$

where β is the instrumental optical contrast, which varies from 0 to 1 depending on the coherence properties of the beam, the scattering geometry, and the solid angle subtended by a detector pixel. The field correlation function, which is equivalent to the intermediate scattering function, provides fundamental information about the dynamics in the sample. Specifically, for a system of N scatterers,

$$\begin{aligned} g_1(\boldsymbol{q},t) &= \frac{\langle E^*(\boldsymbol{q},t) E(\boldsymbol{q},0)\rangle}{\langle I(\boldsymbol{q})\rangle} \\ &\sim \sum_{n=1}^{N}\sum_{m=1}^{N} \left\langle b_n^*(\boldsymbol{q},0) b_m(\boldsymbol{q},t) \exp[-i\boldsymbol{q}\cdot(\boldsymbol{r}_n(0)-\boldsymbol{r}_m(t))]\right\rangle \end{aligned} \tag{3}$$

where $b_n(\boldsymbol{q}, t)$ is the scattering length of the nth scatterer, $\boldsymbol{r}_n(t)$ is the scatterer's position, $E(\boldsymbol{q}, t)$ is the electric field associated with the scattered wave, which is related to the scattering intensity by $I(\boldsymbol{q}, t) = E^*(\boldsymbol{q}, t)E(\boldsymbol{q}, t)$, and the brackets indicate an ensemble average.

3. XPCS under in situ shear

3.1. Homodyne studies under steady shear

To date, most XPCS investigations of materials during in situ shear flow have focused on homodyne SAXS measurements on dilute colloidal suspensions. In this case, where the particles can be assumed to be non-interacting and uncorrelated, the field correlation function contains only the self terms,

$$g_1(\boldsymbol{q},t) = g_1^s(\boldsymbol{q},t) \sim \sum_{n=1}^{N} \left\langle b_n^*(\boldsymbol{q},0) b_n(\boldsymbol{q},t) \exp[-i\boldsymbol{q}\cdot(\boldsymbol{r}_n(0)-\boldsymbol{r}_n(t))]\right\rangle. \tag{4}$$

Under these conditions, three processes can contribute to the decay of the intensity autocorrelation function [7,12]:

i) Particle diffusion, which causes a decay in the correlation function with a characteristic time $\tau_D = 1/Dq^2$, where D is the diffusion coefficient.
ii) Shear deformation, wherein X-rays scattered from particles moving in the shear flow are Doppler shifted, and hence the scattering from pairs of particles moving at different velocities becomes phase shifted. As described below, when the incident beam is parallel to the shear gradient direction, the resulting correlation function becomes modulated on a time scale $\tau_S = (q\,\dot{\gamma}\,H\cos\theta)^{-1}$, where $\dot{\gamma}$ is the local velocity gradient, H is the sample thickness along the shear-gradient direction, and θ is the angle between the local mean velocity and the scattering wave vector.
iii) Transit through the illuminated volume. Due to the net flow, particles exit and new particles enter the illuminated volume. This effect is captured by a time dependence of $b_n(\boldsymbol{q}, t)$, which otherwise can be considered constant, and causes a decay in the correlation function with a characteristic time $\tau_T = L/|\boldsymbol{v}_0|$, where L is the lateral extent of the incident beam through which the particles are flowing and $\boldsymbol{v}_0$ is the mean particle velocity.

As shown by Fuller et al., these three contributions to the decay of the intensity autocorrelation function can be factorized provided that their characteristic times are well separated [12]. In this case, as described by Busch et al. [17], this factorization is conveniently performed by rewriting the intermediate scattering function as

$$\begin{aligned} g_1^s(\boldsymbol{q},t) \sim\ & \exp(i\boldsymbol{q}\cdot\boldsymbol{v_0}t)\langle b^*(t)b(0)\rangle \\ & \times \left\langle \sum_{k=1}^{N} \exp\left[-i\boldsymbol{q}\cdot\left(\boldsymbol{r}'_k(0)-\boldsymbol{r}'_k(t)\right)\right] \right\rangle \\ & \times \left\langle \sum_{k=1}^{N} \exp[-i\boldsymbol{q}\cdot\delta\boldsymbol{v}_k t] \right\rangle \end{aligned} \tag{5}$$

where $\delta\boldsymbol{v}_k$ is the difference between the flow velocity of particle k and the mean flow velocity, $(\boldsymbol{r}'_k(0)-\boldsymbol{r}'_k(t))$ is the displacement of the particle