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.

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I. 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].

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.

II. BACKGROUND

Several previous articles provide a good introduction to the theoretical background of XPCS and to technical aspects of performing XPCS experiments [1, 8–10]. 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*

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4 rheological measurement.

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6 XPCS measurements usually employ an area detector so that the coherent scattering
7 intensity is determined over a range of scattering wave vectors $\mathbf{q}$ simultaneously. Analysis of
8 the scattering typically focuses on the intensity autocorrelation function $g_2(\mathbf{q}, t)$, measured
9 as a function of $\mathbf{q}$ and delay time t ,
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$$13 \quad g_2(\mathbf{q}, t) = \frac{\langle I(\mathbf{q}, \tau) I(\mathbf{q}, \tau + t) \rangle}{\langle I(\mathbf{q}) \rangle^2}, \quad (1)$$

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15 where $I(\mathbf{q}, \tau)$ is the intensity at time τ , and the averages are over detector pixels at equivalent
16 wave vector (effectively ensemble averages) and over time. In measurements on systems that
17 are rapidly evolving, the average over time is potentially invalid, and instead a “two-time”
18 analysis of the instantaneous correlations can capture the changing dynamics [15]. Detailed
19 procedures for processing coherent x-ray scattering images to determine $g_2(\mathbf{q}, t)$ that account
20 for factors such as finite exposure time, detector dark current, and other instrumental effects
21 have been developed [16]. In the case of homodyne scattering, the intensity autocorrelation
22 function is related to the field correlation function $g_1(\mathbf{q}, t)$ through the Siegert relation,
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$$32 \quad g_2(\mathbf{q}, t) = 1 + \beta |g_1(\mathbf{q}, t)|^2 \quad (2)$$

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34 where β is the instrumental optical contrast, which varies from 0 to 1 depending on the
35 coherence properties of the beam, the scattering geometry, and the solid angle subtended
36 by a detector pixel. The field correlation function, which is equivalent to the intermediate
37 scattering function, provides fundamental information about the dynamics in the sample.
38 Specifically, for a system of N scatterers,
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$$45 \quad g_1(\mathbf{q}, t) = \frac{\langle E^*(\mathbf{q}, t) E(\mathbf{q}, 0) \rangle}{\langle I(\mathbf{q}) \rangle} \sim \sum_{n=1}^N \sum_{m=1}^N \langle b_n^*(\mathbf{q}, 0) b_m(\mathbf{q}, t) \exp[-i\mathbf{q} \cdot (\mathbf{r}_n(0) - \mathbf{r}_m(t))] \rangle \quad (3)$$

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47 where $b_n(\mathbf{q}, t)$ is the scattering length of the n^{th} scatterer, $\mathbf{r}_n(t)$ is the scatterer’s position,
48 $E(\mathbf{q}, t)$ is the electric field associated with the scattered wave, which is related to the scat-
49 tering intensity by $I(\mathbf{q}, t) = E^*(\mathbf{q}, t) E(\mathbf{q}, t)$, and the brackets indicate an ensemble average.
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III. XPCS UNDER *IN SITU* SHEAR

A. 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 noninteracting and uncorrelated, the field correlation function contains only the self terms,

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

Under these conditions, three processes can contribute to the decay of the intensity autocorrelation function [12, 17]:

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 $b_n(\mathbf{q}, t)$, which otherwise can be considered constant, and causes a decay in the correlation function with a characteristic time $\tau_T = L/|\mathbf{v}_0|$, where L is the lateral extent of the incident beam through which the particles are flowing and $\mathbf{v}_0$ 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 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

$$g_1^s(\mathbf{q}, t) \sim \exp(i\mathbf{q} \cdot \mathbf{v}_0 t) \langle b^*(t) b(0) \rangle \times \left\langle \sum_{i=k}^N \exp[-i\mathbf{q} \cdot (\mathbf{r}'_k(0) - \mathbf{r}'_k(t))] \right\rangle \times \left\langle \sum_{i=k}^N \exp[-i\mathbf{q} \cdot \delta \mathbf{v}_k t] \right\rangle \quad (5)$$

where $\delta\mathbf{v}_k$ is the difference between the flow velocity of particle k and the mean flow velocity, $(\mathbf{r}'_k(0) - \mathbf{r}'_k(t))$ is the displacement of the particle due strictly to diffusion, and all particles are assumed to have identical scattering lengths. This factorization hence means the intensity autocorrelation function depends on three terms,

$$|g_1^s(\mathbf{q}, t)|^2 = |g_{1,T}(\mathbf{q}, t)|^2 |g_{1,D}(\mathbf{q}, t)|^2 |g_{1,S}(\mathbf{q}, t)|^2. \quad (6)$$

The precise form of the transit term, $|g_{1,T}(\mathbf{q}, t)|^2$, is determined by the shape of the flow velocity profile within the illuminated volume and by the intensity profile of the incident beam. However, under most conditions in which velocity gradients are present, $|g_{1,T}(\mathbf{q}, t)|^2$ decays on a longer time scale than the other terms in $|g_1^s(\mathbf{q}, t)|^2$ and can be considered approximately constant. As described by Ackerson and Clark [13], particle diffusion is anisotropically enhanced in the presence of shear flow, such that

$$|g_{1,D}(\mathbf{q}, t)|^2 \cong \exp \left[-2Dq^2t \left(1 - \frac{q_{\parallel}q_{\perp}}{q^2} \dot{\gamma}t + \frac{1}{3} \frac{q_{\parallel}^2}{q^2} (\dot{\gamma}t)^2 \right) \right] \quad (7)$$

where $q_{\parallel}$ is the magnitude of the wave vector parallel to the flow velocity, and $q_{\perp}$ is its magnitude perpendicular to the flow.

The shear term has the form,

$$|g_{1,S}(\mathbf{q}, t)|^2 = \frac{1}{N^2} \sum_{i=k}^N \sum_{i=l}^N \cos(\mathbf{q} \cdot (\delta\mathbf{v}_k - \delta\mathbf{v}_l)t) \quad (8)$$

Significantly, for velocity profiles with a single flow direction, such as homogeneous shear flow or Poiseuille flow, $|g_{1,S}(\mathbf{q}, t)|^2$ depends only on the component of the wave vector parallel to the flow and is unity for wave vectors perpendicular to the flow direction. In the first published XPCS studies of materials under shear, Fluerau and coworkers exploited this anisotropy in experiments on colloidal suspensions undergoing Poiseuille flow [17–19]. Specifically, by analyzing $g_2(\mathbf{q}, t)$ at wave vectors along the flow direction, where its decay was dominated by $|g_{1,S}(\mathbf{q}, t)|^2$, and perpendicular to the flow direction where at sufficiently small flow rates its decay was dominated by $|g_{1,D}(\mathbf{q}, t)|^2$, they simultaneously and independently mapped the shear gradient profile characterizing the flow and determined the diffusive colloidal dynamics. An example of their results is shown in Fig. 1. The capability of measuring intrinsic dynamics, such as diffusion, in a material under flow has potential application in strategies that exploit flow during data acquisition in XPCS to reduce radiation damage.

Recently, Burghardt *et al.* reported XPCS experiments on colloidal suspensions under homogeneous steady shear flow (*i. e.* flow with a time-independent and spatially uniform velocity gradient), which is a more conventional flow profile in rheological measurements [20]. In these experiments, the incident beam was parallel to the shear-gradient direction, so that in the small-angle-scattering limit of the measurements the scattering wave vectors lay in the flow-vorticity plane. In this case, Eq. (8) can be rewritten as [20]

$$|g_{1,S}(\mathbf{q}, t)|^2 = \frac{1}{H^2} \int_0^H \int_0^H \cos[q_{\parallel} \dot{\gamma} (y_2 - y_1) t] dy_1 dy_2 = \frac{\sin^2(q_{\parallel} \dot{\gamma} H t / 2)}{(q_{\parallel} \dot{\gamma} H t / 2)^2}, \quad (9)$$

where $\dot{\gamma}$ is the strain rate, and the incident beam direction is taken to be the y -direction. Again, since $|g_{1,S}(\mathbf{q}, t)|^2$ depends only on the component of the wave vector parallel to the flow, by analyzing $g_2(\mathbf{q}, t)$ along different wave-vector directions, Burghardt *et al.* were similarly able to characterize independently the velocity gradients of the shear flow and colloidal diffusion along the vorticity direction. However, a key observation that they made, which also holds true for the experiments by Fluerau and coworkers, was that the ability to resolve the colloidal diffusion was restricted to measurements at relatively low shear rates. At higher rates, the decay in the transit term $|g_{1,T}(\mathbf{q}, t)|^2$ becomes a dominant effect along $q_{\perp}$. Also, due to the need to average over pixels that subtend a finite range of scattering angles to obtain $g_2(\mathbf{q}, t)$, measurements nominally along $q_{\perp}$ must also include contributions with a small component along $q_{\parallel}$, and hence the shear term becomes also appreciable at high rates. In particular, Burghardt *et al.* concluded that measurements at sufficiently high Peclet number ($\text{Pe} = \dot{\gamma} R^2 / D$, where R is the particle radius) to observe shear-induced perturbations to the intrinsic dynamics would be unfeasible in the scattering geometry they employed, although other geometries might offer improvements [20].

B. XPCS under Large Amplitude Oscillatory Shear (LAOS)

1. Stroboscopic Rheo-XPCS: Echoes

Recently, a renewed interest in rheology incorporating large amplitude oscillatory shear (LAOS) has led to insight into the nonlinear response of soft materials. Among the innovations have been experiments combining LAOS with time-resolved small-angle neutron scattering (SANS) to uncover periodic microstructural changes in soft materials within a

shear cycle, such as the melting and recrystallization of polymer micelles [21] and oscillatory shear-induced alignment of wormlike micelles [22], as well as analytical approaches like fourier analysis and similar methods to decompose the nonlinear stress-strain response within an oscillation [23]. XPCS with LAOS could potentially overcome some of the limitations that steady shear has in accessing shear-induced structural dynamics mentioned above. Also, coherent scattering in conjunction with LAOS can uncover unique information about the particle rearrangements and other microscopic processes that underlie yielding and plastic flow in soft disordered materials. For example, studies combining LAOS with diffusing wave spectroscopy (DWS) – dynamic light scattering in the highly multiply scattering limit – have examined the shear-driven structural dynamics in foams, colloidal glasses, and other soft materials [24–29]. Very recently, Rogers and coworkers demonstrated a similar approach combining LAOS with XPCS to study the irreversible microscopic rearrangements associated with yielding of a concentrated nanocolloidal gel [30]. In contrast with DWS, where the multiple scattering makes the technique sensitive to motions over essentially a single length scale, the wave-vector dependence of $g_2(\mathbf{q}, t)$ in XPCS gives information about the shear-induced dynamics over a range of lengths. As Rogers *et al.* have shown, this capability has important advantages in studying systems where the microstructural response to shear spans multiple scales. In particular, XPCS is able to probe a wide range of length scales in concentrated systems that would multiply-scatter visible light.

The experiment by Rogers *et al.* combined XPCS with LAOS stroboscopically, wherein the acquisition of coherent scattering images was synchronized to the shear oscillation. The principle of the experiment was the following: when a nominally static soft disordered solid is subjected to shear stress, the motion of the scatterers due to the strain causes a decay of $g_2(\mathbf{q}, t)$. However, after an oscillatory strain, the scatterers will return to their original positions if the deformation is purely reversible, causing the speckle pattern to return to its original configuration and thus causing $g_2(\mathbf{q}, t)$ to return to $g_2(\mathbf{q}, 0)$. The correlation function will hence display echoes at integer multiples of the oscillation period, as illustrated in Fig. 2(a). On the other hand, if the shear induces irreversible rearrangements so that some scatterers do not return to their original positions, the amplitude of the echo peaks will be reduced, as shown schematically in Fig. 2(b), and this attenuation will provide a measure of the microscopic irreversibility.

Rogers *et al.* applied this approach to suspensions of silica nanocolloids (volume fraction

0.30) in a solution of non-absorbing polymer that introduced an entropic depletion attraction among the colloids, causing them to form a concentrated gel. A schematic representation of the oscillatory strain profile during the XPCS measurements is shown in Fig. 3. The strain followed a sinusoidal time dependence between extrema in its value. At each extremum, the strain was held constant for a short period during which a scattering image was obtained. (Periodically holding the strain fixed in this way eliminated “smearing” of $g_2(\mathbf{q}, t)$ during the x-ray exposures caused by the extreme sharpness of the echo peaks, as illustrated in Fig. 2(a).) Figure 4 displays examples of the intermediate scattering function obtained during measurements at different strain amplitudes. For the measurements under *in situ* shear, $g_2(\mathbf{q}, t)$ displays periodic peaks corresponding to the echoes in the speckle pattern. As illustrated schematically in Fig. 3, the change in strain between extrema leads to gradients in the particle displacements that alter the speckle pattern completely. Thus, $g_2(\mathbf{q}, t) \approx 1$ at $t = (n + 1/2)T$, where T is the oscillation period and n is an integer. However, at delay times separated by an integer number of repeat times, $t = nT$, the strain returns, and the speckle pattern at least partially recovers, causing $g_2(\mathbf{q}, t)$ to increase above one. At $\gamma = 4\%$, $g_2(\mathbf{q}, t = nT)$ during shear traces $g_2(\mathbf{q}, t)$ measured under quiescent conditions, indicating that the particles undergo no shear-induced irreversible rearrangements. At $\gamma = 12\%$, $g_2(\mathbf{q}, t = nT)$ decays rapidly with the number of cycles n separating two images, revealing significant irreversible rearrangement in the gel. Rogers *et al.* found that this attenuation of the echo peaks had a sharp onset as a function of strain amplitude at a threshold strain, $\gamma_c \approx 7\%$, indicating a transition to irreversible, nanoplastic deformation. The location of γ_c was near the yield point of the gel identified in macroscopic rheology. Interestingly, however, the gel rheology also displayed significant strain softening and a peak in the loss modulus at lower strain amplitudes, indicating a range of strains where the gel’s response was nonlinear but the microscopic deformations were fully reversible [30].

Rogers *et al.* also found that above the threshold for plastic deformation the echo peak height decayed exponentially with n , $g_2(q, n) = 1 + \beta \exp(-\Gamma \cdot n)$, as illustrated by the fit result in Fig. 4, and that the decay rate Γ scaled with wave vector as a weak power law, $\Gamma(q) \sim q^\alpha$ with $\alpha = 0.7 \pm 0.2$. Based on these observations, they developed a model for the shear-induced dynamics in concentrated gels based on a heterogeneous response in which regions of the gel were involved in irreversible rearrangements each cycle while the rest of the gel underwent reversible deformation. The exponential decay of $g_2(q, n)$ implies the

rearranging regions are located randomly, unbiased by the locations in previous cycles, and the scaling of Γ with q implies that the volumes V of the rearranging regions have a power-law distribution, $N(V) \sim V^{-\xi}$ with $\xi = 1.56 \pm 0.06$. Such a power-law distribution of event sizes, gleaned from the wave-vector dependence of $g_2(\mathbf{q}, t)$, indicates a nonequilibrium critical transition in the gel at yielding and illustrates the unique nanometer-scale information that XPCS combined with LAOS can uncover.

2. Echo lineshapes

A potentially promising direction for future studies combining XPCS with LAOS would involve not only comparing speckle patterns obtained stroboscopically each oscillation, as in the work of Rogers *et al.* [30], but also characterizing the full lineshape of $g_2(\mathbf{q}, t)$ at a temporal resolution that is large compared to the oscillation frequency. In particular, such lineshapes, when they deviate from the shape corresponding to an affine deformation, could give insight into nonaffine response to the shear. The expected shape of $g_2(\mathbf{q}, t)$ during LAOS on a material that does undergo affine and reversible deformation can be found by generalizing Eqs. (8) and (9) to the case of a sinusoidal strain, $\gamma(t) = \gamma_0 \cos(\omega t + \phi)$,

$$\begin{aligned}
|g_{1,S}(\mathbf{q}, t, \phi)|^2 &= \frac{1}{H^2} \int_0^H \int_0^H \cos[q_{\parallel} \gamma_0 (\cos(\phi) - \cos(\omega t + \phi))(y_2 - y_1)] dy_1 dy_2 \\
&= \frac{\sin^2(q_{\parallel} \gamma_0 H (\cos(\phi) - \cos(\omega t + \phi))/2)}{(q_{\parallel} \gamma_0 H (\cos(\phi) - \cos(\omega t + \phi))/2)^2} \\
&= \left[\frac{\sin[q_{\parallel} \gamma_0 H \sin(\frac{\omega t}{2}) \sin(\frac{\omega t}{2} + \phi)]}{q_{\parallel} \gamma_0 H \sin(\frac{\omega t}{2}) \sin(\frac{\omega t}{2} + \phi)} \right]^2
\end{aligned} \tag{10}$$

In practice, an XPCS measurement under steady-state LAOS will span multiple cycles of the shear, so that $g_2(\mathbf{q}, t)$ will be determined from an average over pairs of scattering images in which the first image is obtained at different points in the oscillation. Thus, $g_2(\mathbf{q}, t)$ will

be an average over the phase ϕ ,

$$\begin{aligned}
g_2(\mathbf{q}, t) - 1 &= \frac{1}{2\pi} \int_0^{2\pi} |g_{1,S}(\mathbf{q}, t, \phi)|^2 d\phi \\
&= \frac{\beta}{2\pi} \int_0^{2\pi} \left[\frac{\sin[q_{\parallel}\gamma_0 H \sin(\frac{\omega t}{2}) \sin(\frac{\omega t}{2} + \phi)]}{q_{\parallel}\gamma_0 H \sin(\frac{\omega t}{2}) \sin(\frac{\omega t}{2} + \phi)} \right]^2 d\phi \\
&= \frac{\beta}{\Gamma} (J_1(2\Gamma) \cdot [\pi\Gamma H_0(2\Gamma) - 1] + \Gamma J_0(2\Gamma) \cdot [2 - \pi H_1(2\Gamma)])
\end{aligned} \tag{11}$$

where $\Gamma = q_{\parallel}\gamma_0 H \sin(\frac{\omega t}{2})$, and $J_n(x)$ and $H_n(x)$ are the Bessel function of the first kind and the Struve function, respectively. Figure 2(a) displays an example of $g_2(\mathbf{q}, t)$ calculated from Eq. (11). As noted above, the extreme sharpness of the echo peaks, whose width is set by $(q_{\parallel}\gamma_0 H)^{-1}$, creates a challenge in measurements that seek to resolve the lineshape since a very high temporal resolution relative to the oscillation frequency is required.

As a test of the validity of Eq. (11) in describing the XPCS intensity autocorrelation function from a material undergoing affine oscillatory deformation, Fig. 5 displays $g_2(\mathbf{q}, t)$ from measurements on a dilute colloidal suspension in the highly viscous liquid polyglycerol subjected to an oscillatory shear at two strain amplitudes. The plot focuses on the initial decay in $g_2(\mathbf{q}, t)$ (rather than the echo peaks) to avoid complications from slow diffusion of the colloids that affects the correlations at larger delay times. The correlation function is shown for a single wave-vector magnitude, $q = 0.024 \text{ nm}^{-1}$, over varying ranges of angle θ between $\mathbf{q}$ and the flow direction ($q_{\parallel} = q \cos \theta$). The solid lines in the figure are the results of calculations using Eq. (11) and are compared with the data using no free parameters. The calculated lineshapes correspond closely to the data except at wave vectors close to the vorticity direction ($\theta \approx 90^\circ$). These discrepancies are not surprising since near the vorticity direction the transit and shear terms have comparable decay rates, making the validity of their factorization questionable. Also, near the vorticity direction the comparison between calculated and measured lineshapes is particularly sensitive to any misalignments that introduce uncertainty in θ . These issues aside, the otherwise good agreement between the calculated and measured lineshapes in Fig. 5 indicates that the XPCS correlation functions can accurately assess the deformation of materials during LAOS when the strain is affine.

A scientifically more interesting measurement would be one in which this agreement breaks down, thereby providing a microscopic perspective on nonaffine shear response. As an illustration of such a break down, Fig. 6 displays $g_2(\mathbf{q}, t)$ from a measurement on the

same concentrated nanocolloidal gel as in the experiment by Rogers *et al.* [30] during *in situ* oscillatory shear strain. In the measurement the detector frame rate, 60 fps, was much higher than the oscillation frequency, $f \approx 0.136$ Hz, to assure good temporal resolution. The strain amplitude, $\gamma_0 = 0.01$, was in the regime below the yield point where the echo peaks showed negligible attenuation but where the macroscopic rheology showed strain softening and enhanced dissipation [30]. The wave-vector magnitude, $q \approx 0.2 \text{ nm}^{-1}$, was near the gel's structure factor peak, and hence the scale of the motions being probed was on the order of the interparticle spacing. Unlike with affine deformations, where echo peaks broaden as the angle θ between the wave vector and the flow direction increases (and hence $q_{\parallel}$ decreases), in Fig. 6 the echo peak is broadest at an oblique angle, $\theta \approx 70^\circ$, indicating a nonaffine distortion. Such behavior in the concentrated gel is perhaps not surprising since particle interactions likely prevent perfectly affine strain at these length scales. However, as Fig. 6 illustrates, XPCS with LAOS can provide detailed information about these distortions in nanostructured soft materials at the particle scale, which with appropriate modeling could lead to quantitative insight into the microscopic origins of their nonlinear rheology.

IV. XPCS USING HETERODYNE DETECTION

As mentioned above, XPCS measurements performed using a heterodyne method on systems undergoing deformation and flow can provide information distinct from those using a homodyne method. In a heterodyne method, the total measured intensity is the coherent sum of the scattering from the sample and a static reference signal, $I_t(\mathbf{q}, t) = (E_s^*(t) + E_r^*)(E_s(t) + E_r)$. The heterodyne intensity autocorrelation function then is

$$g_2^{het}(\mathbf{q}, t) = \frac{\langle (E_s^*(t) + E_r^*)(E_s(t) + E_r)(E_s^*(0) + E_r^*)(E_s(0) + E_r) \rangle}{\langle I_t(\mathbf{q}) \rangle^2} \quad (12)$$

Expanding this expression leads to sixteen terms, of which ten are zero and the other six can be combined to give

$$g_2^{het}(\mathbf{q}, t) = 1 + \beta(1 - X)^2 + X^2\beta g_1^2(\mathbf{q}, t) + 2X(1 - X)\beta Re[g_1(\mathbf{q}, t)] \quad (13)$$

where $X(q) = \langle I_s \rangle / \langle I_t \rangle$. Thus, from a heterodyne measurement, one obtains phase information regarding $g_1(\mathbf{q}, t)$ and not only its modulus as in a homodyne measurement. For systems under *in situ* deformation and flow, this information enables determination of mean

velocities in a heterodyne measurement, as opposed to only velocity gradients obtained from a homodyne measurement. For instance, in the case of a dilute suspension of noninteracting colloids, where the mean particle velocity leads to a phase factor in $g_1(\mathbf{q}, t)$ like in Eq. (5), one obtains

$$g_2^{het}(\mathbf{q}, t) = g_0 + X^2 \beta g_1^2(\mathbf{q}, t) + 2X(1 - X)\beta [\cos(\omega t) \text{Re}[g_1'(\mathbf{q}, t)] + \sin(\omega t) \text{Im}[g_1'(\mathbf{q}, t)]] \quad (14)$$

where $g_0(q) = 1 + \beta(1 - X)^2$, $g_1'(\mathbf{q}, t) = \exp(-i\mathbf{q} \cdot \mathbf{v}_0 t)g_1(\mathbf{q}, t)$, and $\omega = \mathbf{q} \cdot \mathbf{v}_0$. (We note that for a dilute suspension of noninteracting colloids, $g_1'(\mathbf{q}, t) = g_{1,D}(\mathbf{q}, t)g_{1,S}(\mathbf{q}, t)g_{1,T}(\mathbf{q})$.)

In heterodyne DLS measurements, the incident beam is often used as the reference signal that is mixed with the scattering, but such configurations are difficult to achieve with x-rays, although fortuitous scattering geometries have enabled heterodyne XPCS measurements where diffuse and specular scattering are mixed [31, 32], and other XPCS experiments have shown a heterodyne signal when the sample was dynamically heterogeneous such that scattering from mobile portions mixed with that from static portions [33]. Livet *et al.* developed heterodyne methods for XPCS in which the scattering from a static pack of dry silica nanoparticles immediately upstream of the sample produced a scattering pattern that served as the reference, and they demonstrated this approach in experiments on dilute suspensions of diffusing colloids and on filled elastomers [34, 35]. Recently, such a heterodyne configuration has also been used to measure the velocities of tracer nanoparticles in pressure-driven microfluidic flow [36]. Typically, flow measurement depends on the ability to visualize passive tracer particles in the visible spectrum, whereas in this case the ability of heterodyne XPCS to measure velocities in opaque suspensions of gold nanoparticles was demonstrated.

In another recent application of XPCS using a heterodyne method with a static reference sample, Ehrburger-Dolle *et al.* studied the nanometer-scale structural dynamics of filled elastomers under *in situ* tensile strain [37]. Employing an apparatus that enabled simultaneous force measurements and x-ray scattering on the strained elastomers, they characterized the stress relaxation and accompanying particle dynamics that followed a step strain on elastomers containing two types of fillers: silica nanoparticles and carbon black. The elastomers displayed a slow stress relaxation that followed either a weak power law or a logarithmic time dependence depending on the filler. By positioning the static reference sample relative to the elastomer appropriately, Ehrburger-Dolle *et al.* were able to alternate *in situ* between heterodyne and homodyne measurements, which allowed them to track several dy-

namical processes that occurred in parallel with this stress relaxation. Specifically, from the heterodyne measurements they detected a mean velocity (averaged over illuminated volume) indicating local strain accompanying the stress relaxation, while in the homodyne measurements, they characterized the velocity gradient. Figure 7 shows an example of the heterodyne correlation functions from this work. Both the heterodyne and homodyne correlation functions were also damped by a contribution due to random convective motion of the particles like that seen with XPCS in a wide range of glassy materials and often ascribed to heterogeneous stress relaxation [1, 15]. The measured rate of each of the microscopic processes displayed a power-law decay with increasing age since the step strain but with power-law exponents that varied depending on the type of filler, illustrating the importance of particle-particle and particle-matrix interaction in dictating the microscopic nature of stress relaxation in filled elastomers. Although technically challenging, these experiments demonstrated the capability of XPCS using heterodyne detection to untangle a complicated set of dynamical processes in materials under stress.

V. XPCS MICRORHEOLOGY

As described previously [1], another approach to rheology in which XPCS shows considerable promise is in microrheology. In microrheology, the rheological properties of complex fluids are characterized by monitoring the motion of colloidal probes suspended in the material. This method has several advantages over conventional rheometry including feasibility of studying systems that are intrinsically small, access to high-frequency dynamics, and sensitivity to spatial heterogeneity [38]. A common method in microrheology involves passively tracking the Brownian motion of the particles to extract their mean-squared displacement, $\langle \Delta r^2(t) \rangle$, which under appropriate conditions can be related to the macroscopic creep compliance $J(t)$ of the surrounding fluid through a generalized Stokes-Einstein relation [38],

$$J(t) = \frac{\pi R}{k_B T} \langle \Delta r^2(t) \rangle \quad (15)$$

where T is the temperature and R is the tracer particle radius. Even in instances where the material is heterogeneous, $\langle \Delta r^2(t) \rangle$ can be thought of as a probe of *local* creep compliance. This relation between probe dynamics and viscoelasticity can be recast in terms of the more familiar complex shear modulus $G^*(\omega)$ by using the relation between $G^*(\omega)$ and the com-

plex creep compliance $J^*(\omega) \equiv i\omega\mathcal{F}_u\{J(t)\}$, where $\mathcal{F}_u$ is the unilateral Fourier transform: $G^*(\omega)J^*(\omega) = 1$, which gives

$$G^*(\omega) = \frac{k_B T}{\pi i \omega R \mathcal{F}_u\{\langle \Delta r^2(t) \rangle\}}. \quad (16)$$

A criterion for XPCS microrheology, then, is to disperse within the medium a highly dilute suspension of noninteracting particles whose x-ray scattering intensity nevertheless overwhelms that of the medium so that their mean squared displacement can be determined. This can be achieved for example by using particles composed of high-Z elements such as gold, where nanoparticle suspensions at volume fractions as low as 0.01% in soft materials have been shown to dominate the scattering in the SAXS regime. For such conditions, $g_1(q, t)$ is related to the particles' mean-squared displacement through [11],

$$g_1(q, t) = \exp(-\langle \Delta r^2(t) \rangle q^2 / 6). \quad (17)$$

In a recent example of such a microrheological approach, Ruta *et al.* have employed silica nanoparticles as tracers in an XPCS experiment tracking the viscoelastic transition in a biopolymer solution undergoing gelation [39].

A key advantage of performing microrheology with XPCS is the unusually large viscoelastic parameters that can potentially be accessed. For example, for probes of radius R in an elastic solid, $\langle \Delta r^2(t) \rangle$ asymptotes at long times to a constant value (determined by equipartition of thermal energy), $\langle \Delta r^2(t) \rangle \rightarrow \Delta r_\infty^2 \approx k_B T / \pi G_0 R$, where G_0 is the shear modulus. Concomitantly, $g_1(q, t)$ decays to a finite constant. We conservatively estimate that measurements using nanoparticle tracers can distinguish quantitatively a 10% decay in $g_1(q, t)$ at $q = 0.5 \text{ nm}^{-1}$, corresponding to G_0 exceeding 10^7 dynes/cm^2 . In a viscous medium with viscosity η , on the other hand, the particles undergo simple diffusion with a mean-squared displacement that increases linearly with time, $\langle \Delta r^2(t) \rangle = 6Dt$ with diffusion constant, $D = kT/6\pi\eta R$, and hence $g_1(q, t)$ decays fully as a simple exponential. Assuming for instance that in XPCS measurements using probes with radius $R = 3 \text{ nm}$ one can resolve decays in $g_1(q, t)$ at $q = 0.5 \text{ nm}^{-1}$ with correlation times exceeding 500 s, the accessible range of viscosities should exceed 10^7 poise, a value outside the range of conventional rheometry.

Indeed, several studies have tracked the diffusive motion of colloidal tracers in deeply supercooled molecular liquids and polymer melts approaching the glass transition temperature T_g , demonstrating this capability [40–43]. However, a common feature of these

measurements is an observed crossover in the dynamics from simple diffusion to hyperdiffusive motion characterized by compressed exponential correlation functions, typically in the temperature range $1.1T_g - 1.2T_g$. The origin of these dynamics remains controversial. One interpretation has invoked a continuous-time random walk model, while another has adopted a picture of strain motion in response to heterogeneous stress relaxation originally developed for colloidal gels [15]. Two recent XPCS studies of these hyperdiffusive dynamics have provided interesting insights that, in our view, support the picture of heterogeneous strain in response stress relaxation. In the first, Shinohara *et al.* combined XPCS with diffracted x-ray tracking to monitor separately the translational and rotational motion of carbon black nanocrystals in unvulcanized styrene-butadiene rubber [44]. The rotational correlation times were extremely large in comparison to the rate of translational motion, as one might expect for particles being advected in strain fields whose characteristic scale is large compared to the particle size. In the second, Conrad *et al.* measured silica tracer motion in polypropylene glycol with XPCS and extended the analysis beyond $g_2(q, t)$ to examine higher-order correlations in the scattering intensity from which they extracted the variance in the instantaneous intensity correlations [42]. With the onset of the hyperdiffusive motion, they observed an increase in the variance, which is a signature of increasingly correlated motion as one would again expect with particles being advected in strain fields whose characteristic scale is large compared to the interparticle spacing.

In the first demonstrated application of XPCS to microrheology, Papagiannopoulos *et al.* characterized the mobility of silica colloids in viscoelastic polymer solutions and compared the results to the solutions' frequency-dependent shear rheology [45]. However, to date most examples of XPCS microrheology studies, such as those on glass forming liquids and polymers mentioned above, have been restricted primarily to characterizing the viscosities of viscous materials. In a notable example, Koga *et al.* conducted a series of experiments to investigate the effects of nanoconfinement on the viscosity and glass transition temperature in polymer films by taking advantage of the spatial resolution possible with x-ray reflectivity [46, 47]. Incorporating into the films a highly dilute concentration of gold nanoparticles, they employed grazing-incidence XPCS to characterize the mobility of the nanoparticles, and hence the viscosity of their local environment, at varying depths from the film surface. To determine the depth dependence, they compared results obtained when the angle of incidence was below the critical angle for total external reflection, so

that the near-surface region was probed, with results obtained with the angle just above the critical angle where the first-resonance enhancement of the electric field intensity takes place, thereby maximizing the x-ray intensity near the center of the films. In thicker films (thicknesses exceeding 100 nm), they observed that the diffusion coefficient was modestly larger – as much as about 50% larger – near the film surface compared with near the film center, with the difference being greatest for polymers well above the entanglement molecular weight. The authors concluded that the polymer viscosity decreases modestly near the surface due to a reduction in entanglement density, rather than a shift in the glass transition temperature, near the surface. For thinner films, they observed a more dramatic contrast in nanoparticle diffusivity between the free-surface region and the film center. In this case, they were able to identify a pronounced enhancement of the viscosity due to effects of an irreversibly absorbed layer on the supporting substrate whose influence on the dynamics propagated tens of nanometers into the film. Examples of some of these results are shown in Fig. 8. Another very recent XPCS study by Begam *et al.* on nanoparticle motion in thin polymer films observed greatly enhanced particle mobility, which the authors attributed to strong hydrodynamic interactions and slip at the particle-polymer interface [48].

The studies by Koga *et al.* followed the traditional strategy of microrheology wherein the Brownian motion of the colloidal probes reflects the material’s viscoelastic properties through Eqs. (15) and (16). However, if the probe size is comparable to or smaller than the length scales characterizing the microstructure underlying the viscoelasticity, the correspondence between the probe mobility and rheology breaks down [49–52], and these deviations can provide alternative information about the microstructure and micromechanics that might otherwise be inaccessible. Since XPCS can track the motion of nanometer-sized particles over nanometer-scale distances, it can provide unique access to the structural dynamics of nanostructured soft material through this mode of microrheology. This capability was demonstrated recently by Guo *et al.* [53] in an XPCS study tracking nanoparticle motion in high-molecular-weight polymers, where the relevant entities are chain entanglements. The characteristic lengths of this microstructure that emerge from models of entanglements are typically on the nanometer scale, and the time scales characterizing their dynamics can extend to many seconds. While such models account successfully for various macroscopic properties of polymer melts and solutions [54], such as scaling behavior of the rheology, this challenging combination of length and time scales has permitted few direct microscopic

1 investigations of entanglement behavior. By tuning the particle size in their XPCS study to
 2 the length scales relevant to entanglements in solutions of high-molecular-weight polystyrene,
 3 Guo *et al.* obtained a local microrheological viewpoint. As illustrated in Fig. 9, they found
 4 that the nanoparticles underwent subdiffusion with a mean-squared displacement that grows
 5 as $\langle \Delta r^2(t) \rangle \sim t^\alpha$ with $\alpha = 0.27$ to 0.53 depending on solution parameters. This anomalous
 6 diffusion persisted over the full extent of the nanoparticle displacements accessed in the
 7 experiments, $6 \text{ nm} \lesssim \langle \Delta r^2(t) \rangle^{1/2} \lesssim 50 \text{ nm}$, which spanned from a fraction of an entanglement
 8 spacing to several entanglement spacings. Further, the nanoparticle mobility did not scale
 9 with the macroscopic viscosity as the polymer molecular weight was varied, as one would
 10 expect for the diffusivity of a larger colloid, but rather was enhanced above expectations
 11 based on macroscopic rheology. Nevertheless, the mobility was sensitive to the molecular
 12 weight in a manner demonstrating an important role for entanglements in dictating the
 13 nanoparticle motion. The authors concluded that the enhanced mobility was caused by
 14 fluctuations of the entanglement mesh within the local environment of the nanoparticles
 15 and further that the subdiffusive nature of the motion provided a measure of the temporal
 16 behavior of these fluctuations.
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39 VI. SUMMARY AND PROSPECTS FOR THE FUTURE

40 The past decade has seen a number of advances in the application of SAXS and SANS to
 41 characterize *in situ* the microstructural response of complex fluids and disordered soft solids
 42 during shear rheology and other modes of deformation and flow [55–57], and such tech-
 43 niques are becoming an increasingly mainstream tool in soft matter research. However, a
 44 full understanding of the interdependence of macroscopic rheology and microscopic response
 45 requires information not only about changes in structure caused by flow but also about the
 46 structural dynamics induced or influenced by applied stress. The example discussed in Sec-
 47 tion IIIB1 above of the microstructural origins of yielding in concentrated nanocolloidal
 48 gels illustrates this point. In such concentrated amorphous materials, the effects of yield-
 49 ing on the structure factor probed with SAXS can be negligible [30]; however, the dynamic
 50 structure factor characterized by XPCS reveals the salient microstructural response. Indeed,
 51 beyond accessing structural dynamics at nanometer scales, other demonstrated advantages
 52 of XPCS, such as the abilities to measure opaque samples and to interrogate heterogeneous
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dynamics with micrometer-sized beams, make the technique attractive for characterizing structural dynamics associated with rheological behavior. As mentioned above, opportunities to employ XPCS in this manner are likely to expand since beamlines optimized for the technique are becoming equipped with instrumentation for *in situ* rheology.

However, challenges remain to be overcome if the promise of rheo-XPCS is to be fully realized. For example, the limitation noted by Burghardt *et al.* [20] and discussed in Section III A, wherein access to intrinsic dynamics in materials under steady shear is restricted to shear rates below those causing significant shear-induced effects, is a major constraint of the scattering geometries employed to date. Geometries in which the scattering plane coincides with the shear gradient-vorticity plane or with the flow-shear gradient plane [57], rather than with the flow-vorticity plane as in previous studies, would potentially both mitigate this limitation and open other opportunities for new kinds of measurements. Indeed, as rheo-SANS studies have demonstrated [55], these alternative geometries can provide particularly insightful perspectives on systems exhibiting flow-driven instabilities, such as shear banding and shear-induced phase transitions. In this regard, the next-generation synchrotrons employing multi-band achromat (MBA) technology currently under development could have profound impact, since they promise significantly higher brightness beams at high x-ray energy (20 keV and above) that should facilitate coherent scattering experiments using sample environments requiring a large x-ray penetration depth. Specifically, while current synchrotrons provide insufficient coherent flux at 20 keV for XPCS, those employing MBA technology are expected to have coherent fluxes at 20 keV that far exceeds that at 8 keV today.

Another potential benefit of the high-brightness, high-energy sources promised by the MBA technology is the reduction of radiation damage, which is an ever-present concern in synchrotron studies of soft materials. For example, the photoelectric absorption cross section of carbon varies with x-ray energy E approximately as E^{-2} for energies up to around 20 keV. Above 20 keV, Compton scattering from carbon contributes significantly, negating the advantages of further increasing energy to reduce damage. For materials composed of higher-Z elements, the potential gains extend to even higher energies, and the impact of leveraging the high-energy coherent flux from an MBA lattice to reduce radiation damage should be even more pronounced.

Another challenge for rheo-XPCS concerns measurements incorporating LAOS. As the work described in Section III B above illustrates, XPCS with *in situ* LAOS can uncover the

microscopic features of nonaffine deformations associated with nonlinear rheology. However, quantitative understanding of such results, like those illustrated in Fig. 6, will require the development of approaches for modeling the echo lineshapes. A potentially fruitful strategy that could deepen the interpretation of LAOS and other rheo-XPCS measurements would be to incorporate cross-correlation analysis of speckle patterns that quantify not only time correlations of the intensity at fixed $\mathbf{q}$ but also time correlations between intensities at different wave vectors [58, 59]. In the case of materials under *in situ* deformation and flow, the structural distortions associated with strain can be expressed as a continuous transformation of points in reciprocal space [12] that should have signatures in the time-dependent speckle pattern that such cross-correlation methods could capture. Finally, we note that another potentially fruitful direction for future study is one combining the XPCS microrheology approaches discussed in Section V with *in situ* mechanical deformation and flow to obtain local rheological information about materials that are driven into stress-induced non-equilibrium states. Indeed, the heterodyne studies of filled elastomers during stress relaxation described in Section IV can be considered a step in this direction. While the technical challenges of such measurements would in general likely be formidable, the resulting scientific insight could be substantial.

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FIG. 1: Normalized XPCS intensity correlation functions measured on a nanocolloidal suspension undergoing Poiseuille flow at flow rates that increase from panel (a) to panel (c). Each panel shows correlation functions at a fixed wave-vector magnitude ($q = 2.1 \times 10^{-2} \text{ nm}^{-1}$) and wave-vector directions parallel (red triangles) and perpendicular (blue squares) to the flow direction. The solid lines are the results of fits using a form equivalent to Eq. (6) with $|g_{1,S}(\mathbf{q}, t)|^2$ calculated for the shear-gradient profile of the Poiseuille flow. (See Reference [17] for details.) The dashed line shows the correlation function of the quiescent suspension, whose decay is due to diffusion. At low flow rates, the correlation function at wave vectors perpendicular to the flow provides a good measure of the intrinsic diffusive dynamics, but at higher flow rates factors due to the flow become dominant. Figure reproduced from Reference [17] with kind permission of The European Physical Journal (EPJ).

FIG. 2: (a) Calculated XPCS intensity autocorrelation function from a material undergoing affine deformation due to an *in situ* oscillatory shear strain with period T . The lineshape is based on Eq. (11) with $q_{||} = 0.025 \text{ nm}^{-1}$, $\gamma_0 = 0.01$, and $H = 500 \text{ }\mu\text{m}$. (b) Schematic of the correlation function depicting the attenuation of the echo peaks resulting from strain-induced irreversible microscopic rearrangements.

FIG. 3: Schematic of the strain profile and microstructural response during XPCS measurements with LAOS reported in Ref. [30]. The strain followed a sinusoidal form between extrema (green). At each extremum the strain was held constant (red) for a short period during which a coherent x-ray exposure was obtained. The cartoons of the amorphous solid illustrate the change in strain each half-period and the recovery of the microstructure each full period. The circled particles highlight a region that undergoes irreversible rearrangement during the cycle. The bottom panels display details of representative speckle patterns.

FIG. 4: Shear echoes in the XPCS intensity autocorrelation function measured on a concentrated nanocolloidal gel during application of oscillatory strain with amplitudes $\gamma = 4$ % (blue squares) and 12 % (red circles) at $q = 0.18 \text{ nm}^{-1}$. The applied strain rate between extrema corresponded to a sine wave with frequency 0.318 Hz and the hold time at each extremum was 0.5 s, leading to an effective oscillation period of 4.14 s. The dashed red and blue lines are guides to the eye. The echoes peaks at $\gamma = 4$ % track the intensity autocorrelation of the quiescent gel (dash-dotted black line), indicating that shear plays no role in decorrelation for this strain amplitude. The solid red line is the result of a fit of an exponential decay to the echo peaks at $\gamma = 12$ %.

FIG. 5: XPCS intensity autocorrelation function measured on a dilute colloidal suspension in viscous polyglycerol undergoing *in situ* oscillatory shear strain with $\omega = 2 \text{ s}^{-1}$ at (a) $\gamma_0 = 0.02$ and (b) $\gamma_0 = 0.05$. Results are shown at wave-vector magnitude $q = 0.024 \text{ nm}^{-1}$ at varying ranges of angle θ between $\mathbf{q}$ and the flow direction, $q_{\parallel} = q \cos \theta$. The solid lines are the results of calculations based on Eq. (11) and are compared with the data using no free parameters. (The sample thickness was $H = 500 \text{ }\mu\text{m}$.)

FIG. 6: XPCS intensity autocorrelation function measured on a concentrated nanocolloidal gel undergoing *in situ* oscillatory shear strain with $\gamma_0 = 0.01$ and $\omega = 0.85 \text{ s}^{-1}$. Results are shown at $q = 0.2 \text{ nm}^{-1}$, a wave-vector near interparticle structure factor peak, over three different ranges of angle θ between $\mathbf{q}$ and the flow direction as indicated in the legend.

FIG. 7: Examples of heterodyne XPCS correlation functions measured on silica-nanoparticle and carbon-black filled elastomers undergoing stress relaxation following a step strain. The frequency of oscillations in the correlation function provides a measure of the local strain velocity associated with the relaxation, while the damping of the oscillations informs about microscopic motions. Figure reproduced from Reference [37], copyright 2012 by the American Chemical Society.

FIG. 8: Correlation times extracted from $g_2(\mathbf{q}, t)$ from XPCS microrheology measurements on gold nanoparticles embedded in films of entangled polystyrene on solid substrates. By tuning the angle of incidence of the x-ray beam with respect to the film surface, the nanoparticle mobility at varying depths in the film is probed, and from the wave-vector dependence of the correlation times, $\tau = 1/2Dq_{||}^2$ where $q_{||}$ is the wave vector parallel to the film surface, local polymer viscosities are obtained. The films show a surface mobile layer at the air-polymer interface, which is attributed to a reduction in entanglement density, and a significant increase in the local viscosity approaching the solid substrate due to effects from an irreversibly adsorbed layer. Figure reproduced from Reference [47], copyright 2011 by the American Physical Society.

FIG. 9: XPCS intensity autocorrelation function for a polystyrene solution (molecular weight of 10^6 g/mol and volume fraction of 0.30) containing a dilute concentration of Au nanoparticles at $T = -20$ C and $q = 0.09$ nm $^{-1}$. The line is the result of a fit using a stretched-exponential form, $g_2(q, t) = 1 + \beta[\exp[-2(t/\tau_{SE})^\alpha]]$ with $\alpha = 0.45 \pm 0.05$. The correlation time τ_{SE} varies with wave vector as a power law, $\tau_{SE} \sim q^{-p}$ with $p \approx 4$, as illustrated in the inset. Such a stretched-exponential lineshape and wave-vector dependence imply the nanoparticles undergo subdiffusive motion with mean squared displacement $\langle \Delta r^2(t) \rangle \sim t^\alpha$. Plot adapted from Reference [53].

FIG. 10: This is the graphical abstract. (There is no Figure 10).