

Synchrotron x-rays and condensed matter/Rayonnement X synchrotron et matière condensée

## A review of X-ray intensity fluctuation spectroscopy

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### Abstract

This article reviews the literature on X-ray fluctuation intensity spectroscopy or, as it is often called, X-ray photon correlation spectroscopy. It highlights measurements using different types of diffuse scattering. **To cite this article:** *M. Sutton, C. R. Physique 9 (2008)*.

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### Résumé

**Une revue de la spectroscopie de fluctuation d'intensité des rayons X.** Cet article passe en revue la littérature sur la spectroscopie de fluctuation d'intensité en rayons X, souvent appelée aussi spectroscopie de corrélation de photons X. Il met l'accent sur les divers types de mesures de diffraction diffuse. **Pour citer cet article :** *M. Sutton, C. R. Physique 9 (2008)*.

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### 1. Introduction

I would like to start this review with an historical introduction into the ideas of coherence of light. Understanding the properties of light, in particular its coherence, has played an important role in the history of physics. Deeply interconnected with the properties of light are the processes which create it. The interplay between light and its sources has played an essential role in the development of our understanding of the atomic behaviour of the world and its underlying quantum nature. For example, simply measuring the spectrum of the light emitted by a gas of atoms gives detailed information on the energy levels and their lifetimes. The intensity spectrum  $I(\omega)$  which is the square of the electric field  $E(\omega)$  is

$$\begin{aligned} I(\omega) &= |E(\omega)|^2 = \frac{1}{4\pi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} E^*(t) E(t') e^{i\omega(t-t')} dt dt' \\ &= \frac{1}{4\pi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} E^*(t) E(t + \tau) e^{i\omega\tau} dt d\tau. \end{aligned} \quad (1)$$

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Evaluating this integral can be tricky. Using stationarity, the average of  $E^*(t)E(t + \tau)$  is independent of  $t$  and since measurements occur over a finite time interval the electric-field correlation function is defined as

$$\langle E^*(t)E(t + \tau) \rangle = \frac{1}{T} \int_{-T/2}^{T/2} E^*(t)E(t + \tau) d\tau \quad (2)$$

where  $T$  is large finite time. Substituting Eq. (2) into Eq. (1) gives us the Wiener–Khinchin theorem relating the frequency spectrum to the correlation function.

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle E^*(t)E(t + \tau) \rangle e^{i\omega\tau} d\tau \quad (3)$$

One conventionally uses the normalized frequency spectrum

$$\begin{aligned} F(\omega) &= \frac{|E(\omega)|^2}{\int_{-\infty}^{\infty} |E(\omega)|^2 d\omega} \\ &= \frac{1}{2\pi} \int_{-\infty}^{\infty} g^{(1)}(\tau) e^{i\omega\tau} d\tau \end{aligned} \quad (4)$$

which also defines the normalized first-order correlation function

$$g^{(1)}(\tau) = \frac{\langle E^*(t)E(t + \tau) \rangle}{\langle E^*(t)E(t) \rangle} \quad (5)$$

This is called the degree of first-order temporal coherence of the light.

Applying these formulae to a gas emitting light, one can imagine an atom travelling through space emitting light at its resonant frequency  $\omega_0$ . This emission will have its phase randomly interrupted by collisions. Thus, collisions change the coherence of the light and correspondingly increase its frequency spread. Simple kinetic theory gives that the first order coherence for this case is

$$g^{(1)}(\tau) = e^{-i\omega_0\tau - \gamma_{\text{coll}}|\tau|} \quad (6)$$

where  $\gamma_{\text{coll}}$  is the average collision rate. Its Fourier transform gives the Lorentzian spectrum associated with collisional broadening.

The above has focused on the temporal coherence, similar arguments apply to spatial coherence, i.e. how are two points correlated in space?

$$g^{(1)}(\vec{\delta r}, \tau) = \frac{\langle E^*(\vec{r} + \vec{\delta r}, t + \tau)E(\vec{r}, t) \rangle}{\langle E^*(\vec{r}, t)E(\vec{r}, t) \rangle} \quad (7)$$

Just as temporal coherence is related to frequency spread, spatial coherence is related to how parallel the light is. Thus, spatial coherence is related to diffraction and is affected by diffuse or random scattering.

First-order coherence does not fully explain all the coherence effects of light. Hanbury Brown and Twiss [1] demonstrated that correlations of intensity data could be measured. They demonstrated that two coherent light beams could be made to interfere with each other. Although easy to explain by classical fields, the conventional wisdom of the time suggested that quantum mechanics would imply that separate photons are independent and thus uncorrelated [2]. Quickly, Purcell [3] showed how correlations in photon statistics leads to the Hanbury Brown and Twiss result and Glauber [4–6] put the arguments on firm theoretical grounds. Hanbury Brown and Twiss [7] used their intensity–intensity interferometer to measure the spatial correlation between photons emitted by a star (Sirius A) and thus were able to infer the diameter of the star. This should be compared to the measurement of the diameter of Betelgeuse ( $\alpha$  Orionis) using a Michelson stellar interferometer [8].

These new correlations depend on the second-order degree of coherence defined as

$$\begin{aligned} g^{(2)}(\tau) &= \frac{\langle I(t)I(t + \tau) \rangle}{\langle I(t) \rangle^2} \\ &= \frac{\langle E^*(t)E(t)E^*(t + \tau)E(t + \tau) \rangle}{\langle E^*(t)E(t) \rangle^2} \end{aligned} \quad (8)$$

and thus involve fourth order correlations of the electric fields, whereas  $g^{(1)}(\tau)$  involves only second-order correlations. Mathematically, it can be shown that  $0 \leq |g^{(1)}(\tau)| \leq 1$  and  $g^{(1)}(0) = 1$ . When  $|g^{(1)}(\tau)| = 1$ , light is first-order coherent but it may not be fully second-order coherent. Also, mathematically, it can be shown that  $0 \leq g^{(2)}(\tau) \leq \infty$  but only when quantum mechanics is invoked. Classically, the electric fields are such that  $1 \leq g^{(2)}(\tau) \leq \infty$ . Thus having  $0 \leq g^{(2)}(\tau) < 1$  can be considered solely a quantum effect. The correlations in the light describe the probability distribution of the electric fields (or the photons). A constant monochromatic light source, a perfect laser, has  $|g^{(1)}| = 1$  and  $g^{(2)} = 1$ . The thermal fluctuations of the emitting atoms of a typical thermal light source will have electric field amplitudes with Gaussian probabilities. For this case it is easy to show

$$g^{(2)}(\tau) = 1 + |g^{(1)}(\tau)|^2 \quad (9)$$

This implies that the probability of measuring a second photon just after measuring the first one, is increased and aptly named photon bunching. The case with  $g^{(2)} < 1$ , called photon anti-bunching, implies that the first photon measured reduces the probability of measuring a second. It is easy to visualize that for something like a *two level atom*, the emission of a first photon reduces the chance of an atom emitting a second photon since the atom is now in its ground state. Such a system will generate light that is anti-bunched. Studying light statistics says much about light-atom interactions [9].

First-order coherence refers to interference effects in electric fields and in optics is usually associated with interferometric measurements. Such measurements are quite sensitive to phase fluctuations and movements on length scales smaller than a wavelength. Intensity correlations, on the other hand, are much less sensitive to phase fluctuations and allow otherwise difficult or impossible measurements to be performed. For instance, measurement of stellar diameters by a Michelson stellar interferometer requires precision to within wavelengths of the light, whereas intensity interferometers need only be aligned to the longitudinal coherence lengths (often many centimeters). The Narrabri intensity–intensity interferometer could measure with arm lengths of 188 m [10]. Michelson stellar interferometers are more sensitive than the equivalent intensity–intensity interferometers when the measurements are possible.

Intensity fluctuation spectroscopy depends on the second-order coherence of scattered light. By the Born approximation, the electric fields hitting the detector are linearly related to the product of the electric fields incident on the sample and the density fluctuations of the sample. Using the known coherence properties of the incident light, one can infer how the properties of the sample have modified this coherence. In turn, this will give information on the temporal fluctuations of the sample under study. This is the basis of dynamical light scattering (DLS) developed in the mid-sixties just as lasers were being developed. DLS was often promoted as a high resolution spectroscopy (sub-megahertz) because at that time, laser line widths were much larger than that.

Second-order coherence is related to the fluctuations of the intensity and so DLS is called intensity fluctuation spectroscopy (IFS). Another name given is photon correlation spectroscopy (PCS). The extension of the technique to X-rays [11] resulting in XIFS or XPCS. Since dynamical X-ray diffraction has a different meaning DXS is not used.

The conventional explanation of XIFS [12,13] is based on how the diffraction from disordered material under coherent illumination leads to a speckle pattern. The speckles have a typical size and arise because of the constructive interference of the random scatterers. The speckles are the fluctuations in intensity that  $g^{(2)}(\tau)$  measures. As the random scatterers move about, say because of Brownian motion, the speckle intensities fluctuate in time and the dynamics of the particles can be inferred. By measuring the time constants as a function of wave-vector one obtains detailed information on the equation of motion of the system under study.

XIFS have several advantages or differences from DLS. The shorter wavelengths of X-rays allow one to study smaller length scales as small as nanometers. Since structure affects the kinetics, it is particularly useful to measure time constants where the material is most structured. One of the main difficulties with interpreting DLS is correcting for multiple scattering, but this is not an issue with X-rays as essentially everything is transparent to them. Two big advantages of using light, are the availability of flexible optics and the existence of highly coherent sources (lasers).

There are several good introductions into coherence as relevant for IFS. Refs. [14,15] are primarily about coherence of light and Ref. [16] is on X-rays. An article by Pusey [17] is a very good introduction into IFS itself, while Refs. [13, 12,18] are more directly related to XIFS. The first of these is a chapter in the HERCULES series of texts.

In this review, the next section will first summarize some of the technical details relevant for XIFS and then it will review the current literature, highlighting measurements using different types of diffuse scattering.

## 2. Intensity fluctuation spectroscopy

Typical XIFS measurements are performed in the limit where X-ray sources can be treated as Gaussian. One complication, not so far discussed, is partial coherence, see Refs. [17,12]. The main effect of partial coherence, with Gaussian beams, is to modify the relationship between  $g^{(1)}$  and  $g^{(2)}$  to be

$$g^{(2)}(\tau) = 1 + \beta |g^{(1)}(\tau)|^2 \quad (10)$$

where the coherence factor  $\beta$  varies between 0 and 1. It accounts for the smearing induced by scattering from a diffraction region which is larger than one coherence volume. Roughly, one can think of  $\beta$  as one over the number of coherence volumes in the diffraction volume. The coherence factor is related to *visibility* or the size of intensity fluctuations. Explicitly the visibility is defined as  $(I_{\max} - I_{\min}) / (I_{\max} + I_{\min})$  and is proportional to  $\sqrt{\beta}$ .

Since XIFS experiments are often starved of photons, it is useful to first discuss the signal to noise for measuring  $g^{(2)}(\tau)$ . From Jakeman [19]  $s/n = \beta \bar{n} \sqrt{N}$ , where  $\bar{n}$  is the average number of photons per speckle and  $N$  is the number of speckles measured. It worth rewriting this in two ways. First, in terms of the average count rate  $I_0$  and speckle coherence time  $\tau_c$ ,  $\bar{n} = I_0 \tau_c$ . Since there are  $T/\tau_c$  coherence times in a total measurement time  $T$ ,  $N$  can be factored as the product of the number of coherence times and the number of speckles simultaneously measured  $N_{\text{sp}}$ . So

$$\begin{aligned} \frac{s}{n} &= \beta I_0 \tau_c \sqrt{\frac{T}{\tau_c} N_{\text{sp}}} \\ &= \beta I_0 \sqrt{\tau_c T N_{\text{sp}}} \end{aligned} \quad (11)$$

This demonstrates that the  $s/n$  is linear in intensity and that for a given total time  $T$  any  $m$ -fold increase in intensity will allow one to measure coherence times which are  $1/m^2$  times shorter. It also shows the improvement by using area detectors. Typically the scatterer has something equivalent to azimuthal symmetry implying that many wave-vectors fluctuate with the same correlation function and can be measured in parallel. This is particularly important for measuring in systems which have large correlation times (many minutes) as the whole correlation functions can be measured in several correlation times.

Secondly, we can relate the number of photons per speckle to the incident intensity and the scattering cross-section density  $(1/V) d\sigma/d\Omega$ . The incident intensity is related to the brilliance  $B_0$  of the incident beam. Brilliance has units of photons per area per angular spread per energy spread and is a direct measure of coherence. It is useful to scale the diffraction volume in terms of the coherence volume. For the  $x$  direction, the coherence volume has a spatial size times an angular spread of  $dx dx' = \lambda/2$  ( $\lambda$  is its wavelength). Thus, the  $x$  direction's contribution to the scattering volume can be written as  $\alpha_x \lambda/2$  and the full diffraction volume becomes  $\alpha_x \alpha_y \alpha_z \lambda^3/8$ . As mentioned above,  $\beta = 1/(\alpha_x \alpha_y \alpha_z)$ . There is one caveat, however, if any  $\alpha_i$  is less than one it will not contribute  $1/\alpha_i$  but only 1 to  $\beta$ . More explicitly and putting in the scattering cross-section density to give the scattered intensity ( $\Delta E/E$  is energy spread and  $L$  is the remaining length defining the diffraction volume):

$$\begin{aligned} \frac{s}{n} &\approx \beta B_0 dx dx' dy dy' \frac{\Delta E}{E} \frac{1}{V} \frac{d\sigma}{d\Omega} L \sqrt{N} \\ &\approx \frac{f B_0 \lambda^3}{8} \frac{1}{V} \frac{d\sigma}{d\Omega} \sqrt{N} \end{aligned}$$

The factor  $f$ , which is  $\leq 1$ , accounts for any diffraction volume length being less than the corresponding coherence length. It will be 1 if all three diffraction volume dimensions are larger than the coherence lengths.

This version for the  $s/n$  shows that there is no penalty for choosing your diffraction volume a little too large but there is a penalty if you chose it too small ( $f$ ). The multi-tau algorithm used for calculating correlation functions optimizes this to give increased signal to noise by summing intensities before autocorrelating [20]. However, one cannot make the diffraction volume arbitrarily large. For large diffraction volumes, the count rates increase but the amplitudes of the intensity fluctuations decrease. At some point, instrumental errors in the detector will dominate. Typically, one uses  $\beta$  between 0.01 and 0.3 for XIFS measurements (remember a  $\beta = 0.01$  corresponds to intensity fluctuations of 10%).

Other articles [21,22,12] give details on the conditions for coherence. Here simplified conditions to perform an XIFS measurement are simply listed:

- (i) The scattering volume should be comparable in size to the coherence volume (diffraction limited scattering which is resolved by the detector).
- (ii) The scattering should be broad enough (i.e. enough disorder so there is interesting structure within the scattering volume and thus lots of speckles). See Ref. [23] for what happens in the limit of only a few speckles.
- (iii) There should be sufficient counts per correlation time (a good rule of thumb is at least one count per speckle).
- (iv) A sufficient number of correlation times need to be measured to get good enough statistics. This can be achieved by some combination of measuring many times on one speckle or measuring many speckles which all have the same time constant.

XIFS is ideally suited to study the relationship between kinetics and structure and this gives insight into the type of measurements where IFS can play an important role. Obvious examples are systems that have a microstructure, heterogeneous materials, polymers, non-Newtonian fluids, colloids and other systems where one expects kinetics to be different on different length scales. Often in solid materials the time scales are longer and X-ray count rates are sufficient when using an undulator source at a third generation synchrotron. The excitement of the technique is that one can directly measure the thermodynamic fluctuations in the structure and it is these fluctuations which allow the structure to evolve in time.

### 3. SAXS

The size of the coherence volume depends on the path-length difference and so for small angle X-ray scattering (SAXS), the longitudinal coherence length can be millimeters. Thus SAXS geometry is particularly advantageous for XIFS both because the scattering volume can be large and the scattering power increases as the wave-vector is reduced. Generally, the coherence volume gets smaller with increasing wave-vector and high-angle coherent diffraction becomes increasingly count rate limited.

First, I would like point out four papers [24–27] in which X-ray and light IFS have been compared on the same or similar samples and in similar wave-vector ranges. These articles confirm that DLS and XIFS measure the same thing aside from their differences in wavelength and scattering power. Even when the accessible time ranges and wave-vector ranges overlap, XIFS often has the advantage due to the lack of multiple scattering. Reise et al. [24], by measurements on index matched particles, make a direct comparison between light scattering and X-ray scattering correlation functions in colloidal suspensions, showing the agreement between the two techniques. In contrast, by slightly changing the liquid, a very similar but non-indexed matched suspension is obtained. This mismatched system shows strong multiple scattering effects for light scattering but none for X-ray scattering.

Geissler et al. [25], compare light and X-ray scattering in polymer colloidal systems which have long time constants. By using an area detector for both types of measurements, they were able to measure these long time constants.

In the reference by de Jeu et al. [26] light and X-ray scattering are compared to help understand heterodyne and homodyne effects in smectic-A membranes of the compound 4-octyl-4'-cyanobiphenyl (8CB). We will discuss heterodyne measurements later in the article.

Constantin et al. [27], compare the lamellar fluctuations of a lyotropic liquid crystal by both light and X-ray scattering. They measure time constants as short as several microseconds. By measuring the in-plane wavevector dependence of the time constants they infer elastic constants (compression and bending moduli) and the sliding viscosity of a sample with a composition of 19.3% sodium dodecyl sulfate (SDS), 29.9% pentanol, and 50.8% glycerol/water by volume.

From the beginning, XIFS measurements have emphasized colloidal systems [28–31]. This is in part because in the low concentration limit, these systems provide an ideal model system to demonstrate and test IFS techniques. The interesting physics, though, occurs at high concentrations. The ability to directly compare the time constants versus wave-vector through the peak in the structure factor has turned out to be difficult by light scattering but straightforward by X-rays. The nature of the cross-over from weakly interacting to strongly interacting particles [32,33] is providing stringent tests of statistical mechanics particularly in polar liquids where Coulombic forces play an important role [34] and the challenging physics of what happens as the concentration is increased can be addressed. Recent work has demonstrated the feasibility of the technique using magnetic colloidal particles [35–37], but as of yet no results on the magnetic field dependence has been reported.

Polymers are another example of a class of systems in which equilibrium motions are not well understood. Although the scattering from a homogeneous polymer is probably too weak to allow XIFS measurements with current sources, the kinetics in a homopolymer blend can be seen by XIFS [38]. These measurements show nondiffusive relaxation at high wave vectors, consistent with compositional fluctuations associated with the reptation model.

Equilibrium fluctuations of other aspects of polymers systems are also being pursued. One group of studies shows the dynamics in block co-polymer micellar systems [39–41]. Ref. [42] explores the possibility of using XIFS for microrheology measurements. Another article demonstrates aging effects in filled polymer systems [25]. In this work, two systems are compared. One has an untreated filler of fumed silica well dispersed in poly(dimethyl siloxane) (PDMS) giving a viscous fluid suspension and a second has a similar but differently treated silica particles to make a thixotropic liquid suspension. Both systems show an aging effect which leads to a novel wave-vector dependence in the time constants measured by IFS. An explanation in terms of flocculation of the silica aggregates is proposed.

In general, XIFS is well suited to understanding the nature of colloidal particles and polymer systems. Considering their technical importance, this will continue to be an active topic for future experiments.

I would like to point out one aspect of some recent measurements of particles in polymers or gels [43–47] and of a polymer-based sponge phase [41]. It appears that for many systems, the correlation functions have a compressed exponential form, a correlation function proposed by Cipelletti et al. [48,49] to address jamming in systems. The correlations are based on a specific random distribution of microscopic velocities. Averaging over the displacement fields of such a distribution gives

$$g^{(2)}(\tau) = 1 + \beta e^{-2(\tau/\tau_c)^{3/2}} \quad (12)$$

or, more generally, a compressed exponential with a power greater than one. This lineshape seems to be appearing in many slow systems. This is, in part, because the large wave-vectors used by XIFS make it sensitive to velocity distributions on the scale of nanometers per second. One can imagine that in highly viscous systems, any slow relaxation of stress would ultimately lead to such behaviour.

One of the advantages of SAXS is that the wavelength spread of the incident beam can be relaxed and still maintain sufficient coherence requirements to perform XIFS. One example is given by a critical scattering in a binary mixture of hexane-nitrobenzene [50], a second is in Ref. [51], looking at phase separation below the critical point of a sodium-borosilicate glass. By using the full first harmonic of the undulator, both were performed with *pink* beams having  $\delta\lambda/\lambda \approx 2.5\%$ .

Here I also mention some other XIFS measurements using SAXS [51–56] but as these are non-equilibrium measurements I will discuss them later on in the article.

#### 4. Reflectivity

Non-specular X-ray reflectivity measurements have turned out to be another fruitful type of diffuse scattering for XIFS. Measurements of thermally excited capillary waves at surfaces are presented in Refs. [57–61]. By using glancing incident X-ray diffraction, the wavevector dependence of the time constants for overdamped capillary waves are shown to agree with theoretical predictions. More detailed discussions are given in Madsen et al. [62], in particular they present a detailed discussion of the effects of coherence on diffuse reflectivity measurements.

Another class of systems, studied by XIFS in diffuse reflectivity mode are capillary fluctuations in thin polymer films. Experiments [63] have measured the time, thickness and wave-vector dependence of capillary waves fluctuations on the free surface of a thin film of a polymer confirming theory [64]. Furthermore the measurements are in good agreement with the bulk viscosity measurements [63,65–67]. Besides the intrinsic interest of the statistical mechanics in these systems, part of the original motivation for these experiments was the reported dramatic decrease (more than 50 K) of the glass transition as polymer films become thinner [68]. It appears that it is not viscosity or the glass transition of the film which are changing but that mechanical properties of the surface are anomalous and it is still unclear as to why.

These studies have been extended to include measurements of thin bi-layer films. By using the nature of the electric fields inside a thin film below the critical angle for total external reflection, it is possible to selectively discriminate the dynamics of the top polymer interface from that of the buried polymer–polymer interface [69,70].

Another effect discovered by these type of measurements is that near the specular ridge of reflection, the finite size of the resolution function needed for XIFS means that the reflected beam and the diffuse beam must overlap

and an interference between these two beams (heterodyning) must be accounted for to understand the correlation functions [60]. More about heterodyning will be discussed below.

## 5. Bragg scattering

One of the great advantages of X-ray diffraction is that any periodicity in a material leads to sharp peaks in the scattering. Typically, this periodicity arises from an underlying three dimensional lattice and these peaks are called Bragg peaks. X-ray crystallography is the science of using these Bragg peaks to measure the molecular structure of the repeating unit. Most types of disorder in the underlying lattice leads to the Bragg peak being broadened. Under coherent illumination, this diffuse scattering gives rise to speckle patterns. As mentioned above, the larger the wave-vector the smaller the coherence volume for diffraction. The initial demonstration of X-ray speckle and a discussion of the feasibility of XIFS were performed on the disordered (100) Bragg peak of  $\text{Cu}_3\text{Au}$  [11].

Large lattice constants such as those in the layer spacings of liquid crystals are ideal for XIFS measurements. If the lattice constants are large enough, softer X-rays can be used. Naively, the  $\lambda^3$  dependence of the  $s/n$  shown above should favour this approach. However, the much larger absorption cross-sections and the larger radiation damage of softer X-rays often counteract any advantage. For films thinner than the absorption length one might expect to win.

Thermally excited fluctuations in smectic thin films were measured in Ref. [71] using soft X-rays with a wavelength of 44 Å. The strong Bragg scattering from the smectic layer spacing allowed the authors to measure the very short time constants (1 to 50  $\mu\text{s}$ ) associated with short wavelength modes in freely suspended thin films (0.3 to 50  $\mu\text{m}$ ). Since then similar results have been obtained with hard X-rays [72–74]. They observe a cross-over from oscillatory correlation functions to damped behaviour associated with increasing the thickness of the smectic films. Care must be taken to also separate heterodyne and homodyne effects [75].

Equilibrium fluctuations seen in disordered Bragg peaks are shown for  $\text{Fe}_3\text{Al}$  [76] and in quasi-crystals [77,78]. The paper on  $\text{Fe}_3\text{Al}$  only shows that near the phase transitions dynamics exists but it is one of the first papers directly demonstrating the feasibility of XIFS. The work on quasi-crystals measures the dynamics of the long-wavelength phasons in the *i*-Al-Pd-Mn quasicrystal. The diffusive character of these phason modes, as predicted by hydrodynamic theory, is experimentally confirmed.

Equilibrium measurements constitute but one class of experiments where IFS can provide useful information, extending XIFS to non-equilibrium systems is also under way. If a non-equilibrium system is in steady state, stationarity may still apply, but typically the intensity correlations are not stationary and must depend on two time arguments (time from perturbation and time between measurement points). With the use of area detectors, correlation times can be estimated in much shorter times. Thus XIFS can be used to measure two-time correlation functions [79]. The theory of dynamical scaling can be used to calculate these two-time correlations [80,81] and the agreement with experiment has been nicely demonstrated in conserved order parameter systems (Model A) [51,52] and non-conserved (Model B) [82,83]. By measuring the fluctuations about the average domain growth, these experiments have provided a new test of dynamical scaling. These ideas should be more generally useful in other non-equilibrium systems.

Another approach for using XIFS with non-equilibrium studies is presented in [53–56,84]. The authors use a detrending analysis to understand how the fluctuations evolve. It is not clear how to relate these detrending results to the underlying equation of motion but good success have been obtained in comparing results with computer simulations [85] to help decide between underlying mechanisms.

## 6. New techniques

DLS can be measured in two modes, homodyne or heterodyne. In homodyne measurements the correlation functions decay (or decorrelate) because of the random movements of one part of the sample with respect to the other parts. Heterodyne measurements are performed by mixing a reference signal, usually a fraction of the incident light, with the signal scattered from the sample. With light, this is easily done with simple optical elements. Heterodyne measurements give one access to phase information through the relative phase between the reference beam and the sample beam. As mentioned above, reflectivity XIFS measurements at small transverse momentum transfer result in heterodyne measurements where the specularly reflected beam interferes with the fluctuating diffusely reflected beam [60,26,74,75]. A more controlled heterodyne technique is demonstrated in Ref. [44]. Simply by placing a static reference sample in the coherence volume with the sample, heterodyne SAXS measurements can be performed. By

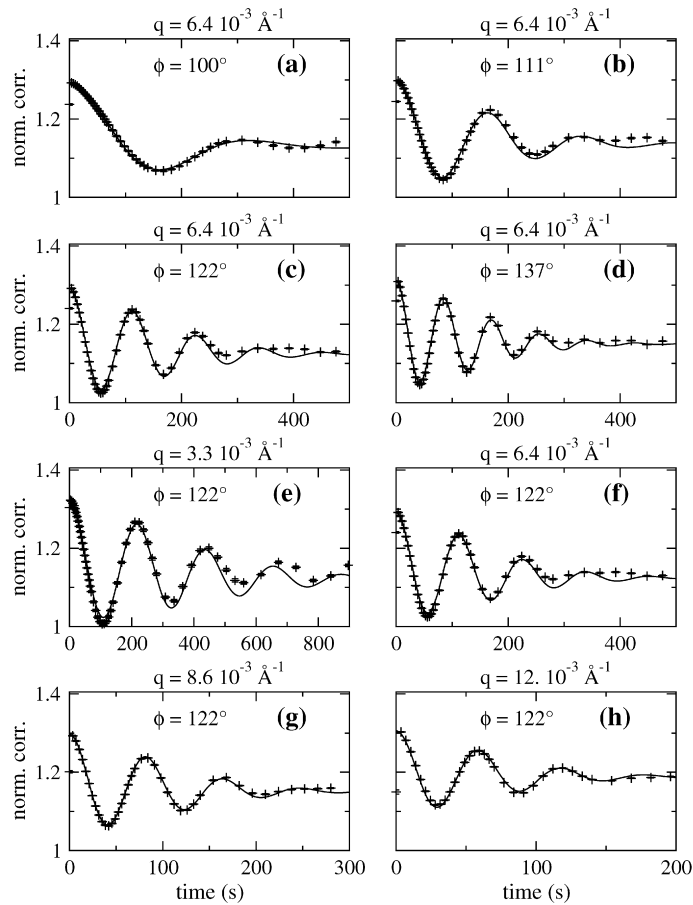


Fig. 1. Heterodyne correlations obtained from a cross-linked EPR rubber sample. (a)–(d): various azimuthal angles  $\phi$  for  $q = 6.4 \times 10^{-3} \text{ \AA}^{-1}$ , (e)–(h): various  $q$ -values for  $\phi = 122^\circ$ . The continuous curves correspond to fits using a compressed exponential correlation multiplied by  $\cos(\omega t)$ .

changing the reference material or simply its thickness, the amount of mixing signal can be controlled. One example given is the contraction of rubber after a 100% extension. This provides a relative phase of  $\exp(-i\vec{q} \cdot \vec{v}t)$  between the reference sample and the contracting rubber. The large wave-vectors of X-ray diffraction makes the measurement sensitive to small velocities and the experiment measured velocities of 10–100  $\text{\AA}/\text{s}$ . In the correct regions of parameter space (velocity slow enough), the time dependence is  $\text{Re}(g^{(1)}(\tau)) \cos(\vec{q} \cdot \vec{v}t)$ . Fig. 1 shows typical heterodyne correlations. The correlations have an oscillatory part determined by the velocity ( $\omega = \vec{q} \cdot \vec{v}t$ ) and envelopes which measure the random or dissipative part ( $g^{(1)}(\tau)$ ). The figure demonstrates the dependence on the angle between  $\vec{v}$  and  $\vec{q}$  and on the magnitude of  $\vec{q}$ . Interestingly, the oscillations in the correlation functions are the Doppler shifts of the X-rays scattered off the moving sample (for the figure the velocity is around 15  $\text{\AA}/\text{s}$ ). The ability of this technique to separate the loss of correlations as the sample flows out of the beam from their loss due to random dissipation makes it ideal to directly study visco-elasticity such as exhibited in materials like polymers and rubbers.

XIFS uses only one aspect of coherence but it does enable the measurements of time dependent correlations in condensed matter systems. I would like to mention some other uses of speckle measurements.

A speckle pattern is a high resolution diffraction pattern, so even in a very disordered material, it can be used as a sensitive measure of small changes. A *speckle* or coherent diffraction measurement, in blue-bronze, has shown scattering from a single dislocation in a charge density wave (CDW) satellite peak [86] found by comparing the diffraction from various positions in a high quality crystal. Speckle has also been used to give information about disorder in the CDW system  $\text{Nb}_3\text{Se}$  [87]. A speckle pattern is observed in the slightly disordered incommensurate CDW peak below the threshold electric field. Above threshold, when current is flowing, a conventional incoherent diffraction peak is seen. This demonstrates that the disorder is static below threshold but that the fluctuation times are



a lot shorter than the fastest measurement time above threshold implying that the broadening above threshold arises from dynamic fluctuations.

Similarly, recent measurements on SrTiO<sub>3</sub> show speckle in the short range order central peak just above its continuous phase transition. Thus the X-ray *central peak* is static. Furthermore, this disorder disappears below the phase transition temperature where the peak becomes a *single speckle* [88,89]. This clearly demonstrates a static mixture of high and low temperature structures just above  $T_c$ .

Another interesting use of a speckle pattern as a sensitive measure of disorder is in the study of the return point memory in Co/Pt magnetic multilayers [90]. By using X-rays at the L<sub>3</sub> resonance of Co (778 eV) the authors measure the diffraction pattern of the random magnetic domains while the magnetic field is swept through the sample's hysteresis loop. By correlating the speckle patterns as a function of magnetic field they were able to separate the reversible and irreversible aspects of the hysteresis loop. An interesting aspect of the measurements is that for the sample with a rougher surface the saturation field does not completely erase the memory whereas for the sample with a smoother surface it does.

In principle, the speckle pattern can be inverted to obtain complete structural information [91]. This aspect of coherence will not be addressed in this article, but the above examples show that unique and useful information can be measured from straightforward analysis of the speckle pattern.

## 7. Conclusions

XIFS is in the process of becoming a routine tool in the growing arsenal of diffraction techniques. Synchrotrons around the world are designing beamlines dedicated to this technique. This review has tried to give some idea of the variety of problems this new technique has been addressing. I hope the review gives you a better flavour for what can be measured and how XIFS could address problems of interest to you.

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