X-ray spectroscopy

Revealing the atomic dance

Photon correlation spectroscopy with coherent X-rays reveals the elementary diffusive motion of atoms.

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On an atomic scale it has been difficult to directly observe relatively slow equilibrium fluctuations such as the diffusion of atoms in solids. The time scales of such processes are too long for experimental techniques that rely on high energy resolution, such as inelastic scattering, and the length scales are too short for coherent visible light techniques such as photon correlation spectroscopy. On page 717 of this issue, Michael Leitner and co-workers[1] report on a technique based on the diffuse scattering of a coherent X-ray beam that is capable of revealing the dynamics of atoms diffusing in a Cu-Au alloy crystal. Their achievement opens the way for studies of equilibrium dynamics at the atomic scale using the new high-coherent-flux X-ray facilities currently being built worldwide.

Diffusion of atoms in solids determines the rates and pathways of countless chemical reactions and structural transformations. Our understanding of the mechanisms of these non-equilibrium processes, and thus our ability to synthesize new materials with better properties and stability, is typically built upon models for the fundamental diffusion processes that take place even at equilibrium in solids. While standard time-resolved scattering techniques can be used to observe the changes in the average structure that occur during non-equilibrium processes, the underlying equilibrium diffusion processes are more difficult to study – from a macroscopic perspective, the equilibrium system is static, and the internal dynamics can only be revealed by a coherent, atomic-scale probe (Fig. 1).

Leitner *et al.* use X-ray photon correlation spectroscopy (XPCS) to observe the dynamics of diffusing atoms. Photon correlation spectroscopy is based on analysis of "speckle" patterns, which are fine-scale diffraction patterns that appear in scattering of coherent light from a disordered system. Speckle patterns, long known from laser light scattering[2] and more recently observed with coherent X-rays[3], are sensitive to the exact spatial arrangement of the disorder. As is usual for scattering techniques, the spatial structure in the system is not imaged directly, but length scales are resolved as Fourier wavevector components in reciprocal space. If the arrangement changes with time, the observed speckle pattern will also change, so that by observing the intensity fluctuations in the speckle pattern, the characteristic times of fluctuations in the system as a function of wavevector can be determined. Photon correlation spectroscopy is sensitive to dynamics even in systems at equilibrium, and the use of X-rays allows atomic-scale behavior to be observed. Such information about equilibrium dynamics is not accessible in an ordinary scattering experiment with incoherent light because the fine-scale speckle features are not resolved and only the changes in the ensemble-average structure of the sample can be determined.

While XPCS has been previously used to study dynamics occurring on longer length scales (> 10 nm), for example, in small-angle scattering from colloids and polymers[4-8] or near Bragg peaks of crystals[9], it has been a challenging task to carry out studies on atomic length scales because of the relatively low intensity of coherent X-ray beams available. The results of Leitner *et al.* are the first to extract correlation times from the diffuse X-ray scattering at sufficiently large wavevectors to contain the information about local atomic arrangements. The system chosen for study, a $Cu_{90}Au_{10}$ alloy at temperatures near 540 K, exhibits a tendency for the Au atoms to locally order on a certain set of sites in the crystal. The observed wavevector symmetry of the correlation time shows effects related both to this ordering tendency and to the directions of the elementary atomic jumps by which diffusion occurs. This study demonstrates for the first time the full potential of XPCS to reveal equilibrium dynamics in materials at the atomic scale. Still, the time scales that could be studied by Leitner *et al.* were restricted to be larger than about 10 seconds by the available coherent X-ray intensity at the ESRF, a state-of-the-art third-generation synchrotron radiation source. Sources under construction such as the PETRA-III ring in Hamburg, Germany or the NSLS-II facility in Brookhaven will provide 10-100 times more coherent flux and thus greatly facilitate this type of experiment.

A new type of coherent X-ray source is on the horizon, the free electron laser (FEL), that promises to extend the time range available with XPCS down to the sub-picosecond range, spanning the gap to inelastic scattering techniques. Projects are underway to build such facilities in the US, Europe, and Japan[10]. FELs are capable of producing sub-100-fs pulses of coherent light with each pulse carrying of order 10^{10} photons (the intensity available today in a second!). To enable ultrafast XPCS experiments without the need for ultrafast detectors, a split-and-delay technique has been proposed[11]. Here, the X-ray pulse from the FEL is split into two pulses which

travel different length paths, introducing an adjustable delay[12]. The correlation times are obtained by analyzing the contrast in the summed speckle pattern from the two pulses[13]. The Linac Coherent Light Source at SLAC produced the first hard X-ray laser beam in April of this year[14], and XPCS experiments using this technique will be possible beginning in early 2011.

With these new facilities, one can imagine investigation of transient short and medium range structures of molecular fluids. Liquids (or glasses) do not exhibit translational symmetry and in turn are able to accommodate different local symmetries in the same system. Among them is icosahedral local order, which belongs to the forbidden motifs in periodic structures. By using novel (higher order correlation function) techniques such as the newly developed X-ray cross correlation analysis[15] it may be possible to analyze the transient local structure of liquids (in particular also water) from single laser shot speckle diffraction patterns and follow their temporal evolution.

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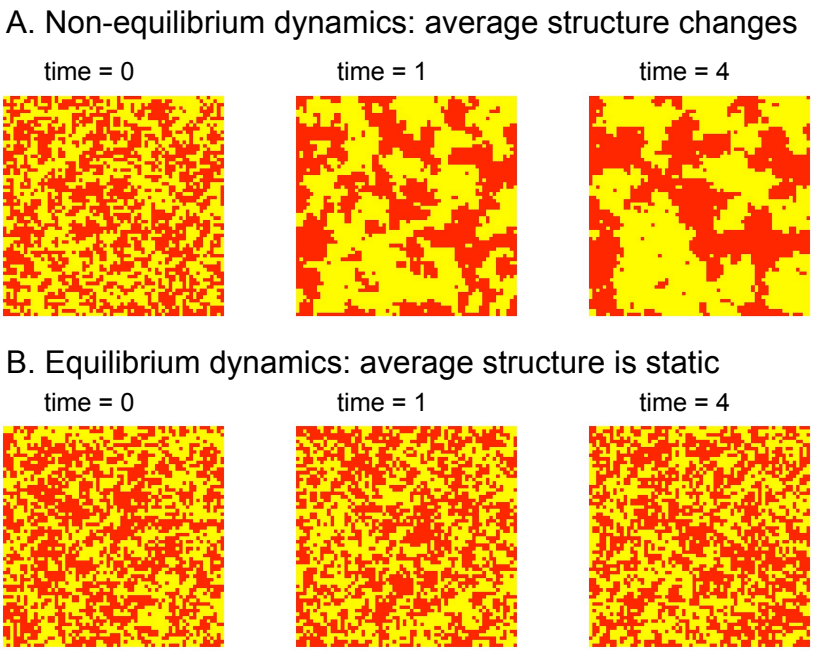

Figure 1. Schematic images of atomic ordering onto two sublattices in an alloy, showing difference between non-equilibrium and equilibrium dynamics. A: After changing the temperature from above to below the critical point, ordered domains grow and the average structure changes with time. Such dynamics can be observed by standard time-resolved scattering. B: At constant temperature equilibrium, the exact atomic arrangements constantly change with time, even though the average structure is static. Coherent techniques such as XPCS are required to observe these fundamental equilibrium dynamics.

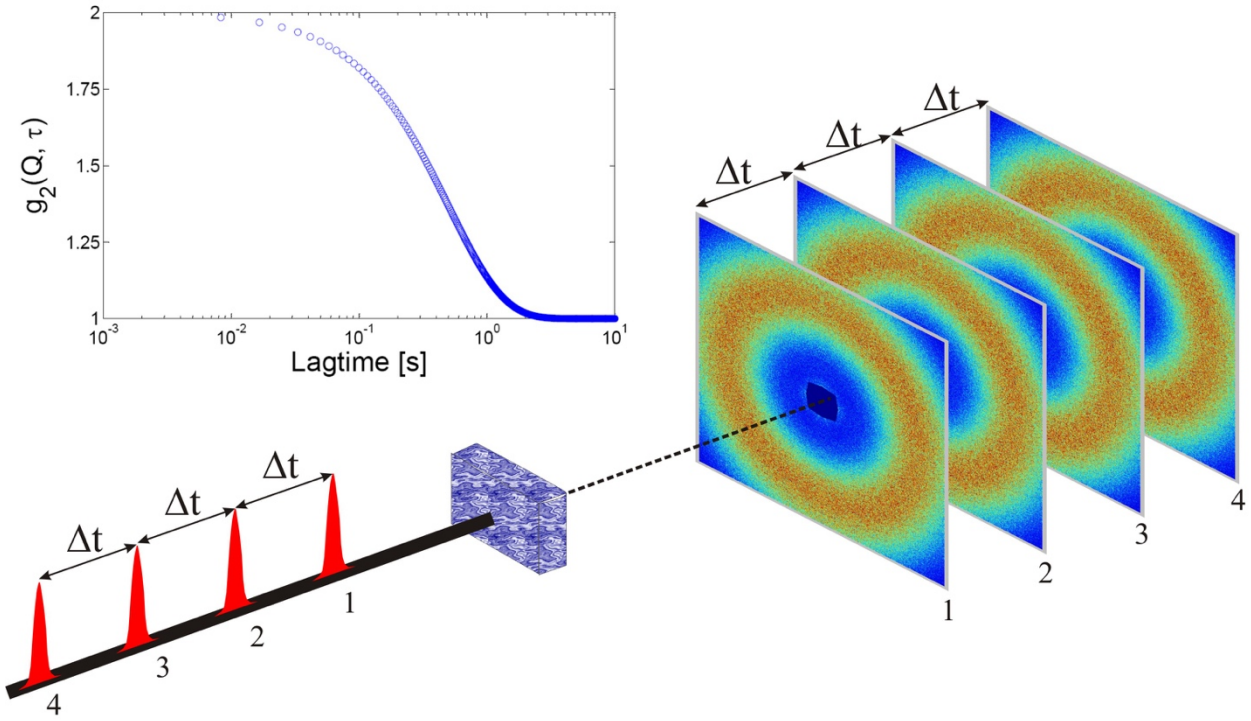

Figure 2. The X-ray photon correlation spectroscopy (XPCS) technique for observing equilibrium dynamics. Typically, a sequence of speckle patterns is recorded and the intensity at each point is autocorrelated to characterize the dynamics on time scales as short as the time spacing Δt of the sequence. To investigate times faster than the readout time of the detector, speckle patterns from two pulses can be summed and the decay in contrast used to determine the correlation times.