

Coherent X-ray Scattering Studies of Fluctuation Dynamics in the Solid State

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by

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I. Introduction

Understanding the dynamics of fluctuations in solids has long been an important goal in materials physics from both fundamental scientific and technological viewpoints. The still-emerging technique of x-ray intensity fluctuation spectroscopy (XIFS) offers the promise of revealing unprecedented information about such fluctuations on length scales of $10^{-1} - 10^3$ nm¹. This is much smaller than the lengths probed by the analogous visible light technique of dynamic light scattering (DLS). With 3rd generation sources, significant progress has been made with XIFS, particularly in cases where the scattering from the sample is relatively strong and the time scales of interest are relatively long. This has particularly been the case in ordered macromolecular systems where mesoscopic structures give large scattering signals while evolving slowly.

There have been relatively fewer hard x-ray XIFS studies examining fluctuation dynamics in solids. Often it is the diffuse scattering, which is inherently weak, that is of most interest. By working very near the critical point, where correlation lengths (and hence critical scattering) are enhanced, Brauer *et al*². were able to examine ordering fluctuations in Fe₃Al. Francoual *et al.* were also able to study the dynamics of phason fluctuations in icosohedral AlPdMn³. There have been XIFS studies of coarsening kinetics in metallic alloys⁴, including one by the present PI⁵. These have examined theoretical predictions⁶ for the behavior of the two-time correlation function $C(q, t_1, t_2)$ during coarsening in phase ordering and phase separating systems. Such information is inaccessible in traditional “incoherent” x-ray scattering experiments. Despite these successes, however, 3rd generation x-ray sources have not had sufficient coherent intensity to examine the relevant diffuse scattering speckle dynamics in many systems of interest. The LCLS, however, offers the possibility of examining such processes in unprecedented detail. Below we discuss what might be learned in several kinds of solid state systems.

II. Fluctuation Dynamics in Substitutional Alloys

Substitutional alloys exhibiting atomic ordering or clustering have long been model systems for understanding dynamics and kinetics. The two tendencies of ordering and clustering differ fundamentally in their dynamical behavior. In clustering, there must be long-range transport of material, usually by atomic diffusion, while local motion alone is enough to produce an ordered alloy. This is reflected in the conservation laws for the relevant order parameters. The integrated order parameter in the clustering case, i.e. the atomic concentration, is “conserved” because the overall composition of the sample remains unchanged. In contrast, the order parameter in the atomic ordering case is “nonconserved” because it is typically a sublattice occupancy that is not constrained to be constant. The nonconserved and conserved cases are often referred to as “Model A” and “Model B” respectively in the nomenclature of Hohenberg and Halperin⁷. Another of their models is relevant to substitutional alloys as well, though much less investigated – “Model C”. In Model C there is a nonconserved order parameter coupled to a conserved order parameter. This is applicable to the case of ordering in an alloy that is not at its “ideal” ordering composition.

Our experience suggests that there will be sufficient scattered intensity from a single pulse at the LCLS to measure diffuse speckle patterns from alloys with statistical accuracies of a few percent. Thus the fluctuation dynamics in these systems will be accessible on the 120 Hz time scale of the pulse repetition. This will allow comprehensive studies of alloys both near critical points, and well away from them where fundamental diffusive processes come to the fore. It will be particularly interesting in the latter case to examine whether there exist any dynamic anisotropies associated with preferred crystallographic directions of diffusion.

Two ordering systems of special interest, and experience, for us are Fe-Co and Cu-Pd. The Fe-Co system offers a nearly “ideal” phase diagram with a long line of critical points. It is excellent for the study of the interrelationships between ordering and composition fluctuations in nonstoichiometric alloys. The Cu-Pd system is a classic long-period superlattice (LPS) alloy. Here there is a more complex ordering, with periodic antiphase domain boundaries forming “stripe” phases. The nature of the fluctuation dynamics in such complex cases is unexamined.

III. Glass Transitions in Plastic Crystals

Many molecular crystals exhibit plastic phases in which the molecules rotate while remaining on their lattice sites. With decreasing temperature, the orientations of neighboring molecules become more strongly correlated. The ground state is an orientationally ordered crystal, but this can often be bypassed to form an orientational glass. As is the case with structural glasses formed from supercooling liquids, these orientational glasses exhibit a loss of ergodicity and a drop in heat capacity relative to the disordered, high temperature phases. Like the structural glasses, they exhibit an “alpha-relaxation” as predicted by mode coupling theory⁸. However, because they don’t have the topological disorder found in structural glasses, they’re particularly intriguing. Well above the glass transition, orientational time scales can be quite short and have been investigated with dielectric relaxation and neutron scattering. However, XIFS at the LCLS offers the possibility of examining relaxational dynamics in unprecedented detail in the near vicinity of the glass transition.

IV. Other Solid State Systems of Potential XIFS Interest

The behavior of time scales in the above systems is sufficiently well understood to suggest that they are appropriate for XIFS study at the LCLS. Here we discuss two other important classes of materials for which we do not currently understand enough to know whether the relevant time scales will be appropriate for XIFS study at the LCLS or not.

The first category is systems exhibiting the well-known $\omega = 0$ “central peak” near displacive phase transitions. Neutron scattering experiments show in these cases that, as the transition is approached, the inelastic peaks associated with the soft phonon modes driving the transition stop moving inward, and a large central peak grows with the instrumental resolution at $\omega = 0$. It is generally believed that long-lived structural imperfections may interact with the softened phonon modes to cause the central peak. However, the time scales for the necessary relaxation remain unknown. XIFS offers the

possibility of examining atomic length-scale relaxation on much longer time scales than are accessible with inelastic neutron scattering. Indeed, a group from the Laboratoire de Physique des Solides in Orsay, France has already begun to attempt such studies at the ESRF⁹. However, the increased coherent intensity of the LCLS would allow such studies to be performed at higher temperatures (i.e. further from T_c) where the scattering is weaker but structural relaxations will be more rapid. We must acknowledge the distinct possibility, though, that the time scales for defect relaxation will always be much longer than we can measure at any temperature reasonably close to the transition.

Possibly related to the central peak problem is another potential opportunity for XIFS at LCLS: the examination of pre-martensitic fluctuations. Martensitic transformations are important, of course, for shape-memory materials and the tempering of steels¹⁰. Because of the change in shape between parent and daughter phases at the transition, elastic effects play a dominant role and classical ideas of fluctuation shape and of nucleation/growth are largely inapplicable. Fluctuations are probably often associated with “defects”, whether extended (e.g. statistical variations in local composition) or localized. In many cases, pretransitional behavior is observed as a “tweed” pattern in electron micrographs. These are typically long-lived and described as “glassy” states. However, the size and longevity of such fluctuations is believed to vary widely with temperature. Well above the martensitic transformation, it is quite possible that fluctuations occur with correlation times that are well suited for XIFS study.

V. Resources

Because of our extensive work in metallic alloys, we already possess a number of the necessary samples for this effort, as well as a high temperature furnace with hemispherical Be window for x-ray studies. For the research outlined here, we would ideally need to construct a two-stage furnace stable to within 1 mK. In addition, the studies of plastic crystals would require a stage able to reach 100 K, possibly using a dispex. Overall capital equipment costs, aside from a general diffractometer would be approximately \$50k. Applications for capital and operating funds would be made to DOE and NSF.

VI. References

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