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Applications and limitations of electron correlation microscopy to study relaxation dynamics in supercooled liquids

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ABSTRACT

Electron correlation microscopy (ECM) is a way to measure structural relaxation times, τ, of liquids with nanometer-scale spatial resolution using coherent electron scattering equivalent of photon correlation spectroscopy. We have applied ECM with a 3.5 nm diameter probe to $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$ amorphous nanorods and $Pd_{40}Ni_{40}P_{20}$ bulk metallic glass (BMG) heated inside the STEM into the supercooled liquid region. These data demonstrate that the ECM technique is limited by the characteristics of the time series, which must be at least 40τ to obtain a well-converged correlation function $g_2(t)$, and the time per frame, which must be less than 0.1τ to obtain sufficient sampling. A high-speed direct electron camera enables fast acquisition and affords reliable $g_2(t)$ data even with low signal per frame.

1. Introduction

Electron correlation microscopy uses time-resolved coherent electron nanodiffraction to measure atomic dynamics in materials [1]. It is modeled and named after photon correlation spectroscopy (PCS) [2], a similar technique using photons. Coherent scattering with either photons or electrons gives rise to speckle patterns, in which each speckle corresponds to a volume of the sample with sufficient internal order to create constructive interference of the scattered waves. The time of which the speckle intensity persists then corresponds to the time over which that particular structure persists. The persistence time can be measured statistically from the time autocorrelation function,

$$g_2(t) = \frac{\langle I(t')I(t'+t)\rangle}{\langle I(t')\rangle^2}, \quad (1)$$

where t' is the time of a frame in the diffraction time series, t is delay time after t', and $\langle\ \rangle$ denotes average over all t'.

The systems accessible to PCS and related techniques depend on the coherence length of the illumination and the wavelength of the radiation. PCS with optical lasers can produce large transverse coherence lengths, but the wavelength limits applications to systems like colloids with micron scale or larger particles. Coherent x-ray beams from synchrotron sources have enabled x-ray PCS (XPCS) [3], first with soft x-rays capable of studying smaller colloids and polymers [4,5], then with steadily harder x-rays that are now capable of studying atomic-scale motions [6–8]. In addition to studying particle dynamics, XPCS has been used to study atomic diffusion in alloys [9], and fluctuating ferromagnetic and ferroelectric domain structures [10,11].

The advantages of ECM over XPCS are the typical advantages of electron scattering over x-rays: high-quality lenses make nanometer-scale coherent probes easily accessible on any modern field-emission gun scanning transmission electron microscope (STEM) [12,13] and large elastic scattering factors create significant diffraction even from small volumes. The comparatively large signal may make it easier to measure fast dynamics from small structures in ECM than in XPCS. The disadvantages are also typical of electron microscopy: ECM requires thin samples without superficial oxidation, and maintaining sample and instrument stability over long experiments is a challenge. As a result, very slow dynamics are likely better measured using XPCS.

Our first experiments with ECM have focused on the atomic-scale dynamics in bulk metallic glass forming alloys heated above the glass transition temperature T_g and into the supercooled liquid [1]. Glassy dynamics occur *via* two general processes, called the α

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and β relaxations [14]. The α relaxation is associated with collective structural rearrangements in the liquid involving multiple atoms changing nearest neighbors. The β relaxation involves single-atom hopping or diffusion. As the temperature falls toward T_g, the α relaxation time τ_α diverges, but the β relaxation time τ_β does not. (This is a somewhat idealized picture. In some real glasses, the a and b relaxations are not easily distinguished from one another [15]). τ_α and τ_β are often measured by applying a time-varying stimulus to a material and measuring the out-of-phase response as a function of frequency. Different stimuli lead to different techniques, including dielectric relaxation [16], dynamic mechanical analysis [17–19], or modulated differential scanning calorimetry [20].

If $g_2(t)$ from ECM or XPCS is averaged over many speckles and many speckle lifetimes, it can be modeled by [21]

$$g_2(t)=1+A\ exp\left[-2\left(\frac{t}{\tau}\right)^{\beta}\right], \quad (2)$$

where τ is the structural relaxation time, usually identified with τ_α for supercooled liquids with a distinct τ_α and τ_β. β is a stretching exponent with the same physical meaning as β in the Kohlrausch-Williams-Watt equation often used to describe relaxation behavior in glasses: $\beta=1$ is exponential decay, and $\beta<1$ corresponds to the superposition of several relaxation processes with different characteristic times or rates. A depends on the contrast of the speckles above the incoherent background and noise which in turn depends on the coherence of the illumination and other experimental parameters. The value of ECM is the ability to measure $g_2(t)$ and thus τ with nanometer spatial resolution.

In this paper, we determine the experimental requirements for ECM technique through the measurement of the relaxation time in $Pd_{40}Ni_{40}P_{20}$ bulk metallic glass and $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$ metallic glass nanorods. We report first results from ECM experiments using a fast direct electron detection camera to improve the time resolution. Despite the low probe current required to achieve good coherence and the resulting low number of electrons detected in each diffraction pattern, the $g_2(t)$ data obtained from tens of thousands of patterns are low noise and an excellent match to Eq. (2). We also discuss the time resolution and total time series length required for ECM experiments to obtain reliable $g_2(t)$ results.

2. Experimental methods

2.1. Materials preparation

$Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$ glassy nanorods with diameter ~35 nm were synthesized by the nanomoulding method [22] which is based on thermoplastic forming of the BMG in its supercooled liquid region. In order to minimize the residual salts and anodized aluminum oxide from nanomoulding, we rinsed the plate with the rods attached in distilled water and isopropyl alcohol at least three times. Then the plate was immersed in methanol and the nanorods were released by sonication for 15–20 mins. A micro pipet was used to drop 1.5–1.8 μL of methanol containing nanorods onto a microhotplate *in situ* TEM heater chip from DENSSolutions [23]. Some of the nanorods attached to the SiN_x membrane of chip window after the evaporation of methanol. We repeated the drop process several times to increase the density of nanorods on the chip. To remove the fairly severe contamination induced by this preparation method, the sample holder with the chip was plasma cleaned at 20 psi $Ar+O_2$ mixture for 12–15 mins before ECM measurements.

A $Pd_{40}Ni_{40}P_{20}$ metallic glass ingot 1 mm diameter was synthesized by injection casting. The details for fabrication are described elsewhere [1]. TEM specimens were prepared by focused ion beam (FIB) lift-out in a Zeiss Auriga cross beam FIB. First, the ion beam and the electron beam were used to deposit a 2 μm thick Pt protection layer, then a $Pd_{40}Ni_{40}P_{20}$ lamella around 15 μm × 10 μm × 2.5 μm in size was extracted and attached to a copper grid with Pt deposition. The lamella was thinned to ~300 nm thick with 30 kV, 80 pA Ga+ ion, then the current was reduced to 20 pA for milling until the sample became electron transparent to 7 kV SEM imaging. Then a 5 kV, 20 pA ion beam was used for milling until sample was electron transparent to 3 kV SEM imaging. Finally, a 2 kV, 100 pA ion beam was used to remove surface damage. The stage was tilted by around 2° off the Ga emission direction during thinning. Next sample was transferred and attached over an empty window in a microhotplate heating chip window at a 13° incline angle to the chip surface using Pt deposition. Then 2 kV, 100 pA Ga+ ion was used to remove Pt redeposition on sample surface. These samples were plasma cleaned at 20 psi $Ar+O_2$ mixture for ~30 s before ECM measurements.

2.2. Electron correlation microscopy experiments

Low-speed ECM on the $Pd_{40}Ni_{40}P_{20}$ sample was performed in the University of Wisconsin-Madison FEI Titan STEM with probe aberration corrector at 200 kV in energy filtered "microprobe" STEM (μP-EFSTEM) mode. A camera length of 512 mm was used and the semi-convergence angle was adjusted to obtain probe with 3.5 nm diameter. The probe current was 1.6 pA. A Gatan BF_DF detector mounted on the 2.5 mm GIF entrance aperture was used to collect STEM images and Gatan US 1000 CCD camera inside a GIF 865ER energy filter was used to collect nanodiffraction patterns. The diffraction patterns were zero-loss energy filtered with a slit width of 10 eV. At binning factor 8 (256 by 256 pixel images) the readout time for the US1000 camera is 0.07 s. For lower temperatures from 328 °C and 332 °C, the exposure time 0.2 s for a total time per frame of 0.27 s. For temperatures from 336 °C to 352 °C, the exposure time was 0.1 s for a total time per frame of 0.17 s. Every series consists of 3000–4000 frames. The total electron dose on sample is 7.3×10^8–8.3×10^8 e^-/nm^2.

High-speed ECM experiments on the $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$ nanorods were obtained on the Brookhaven National Lab image-corrected Titan ETEM at 300 kV, a probe size of 3.5 nm, and a probe current of 10.5 pA, using a Gatan K2-IS direct electron detection camera, without energy filtering. The K2-IS acquires 1920 by 1856 pixel images at 2.5 ms total frame time (400 frames per second) and almost zero readout overhead time. Each time series of nanodiffraction patterns was two minutes long, so it contains 48,000 frames and occupies ~2.5 TB of data storage uncompressed. For each measurement, the total electron dose on sample is $\sim8.2\times10^8$ e^-/nm^2. The first step in the analysis was to crop each image to smaller size to include just the first amorphous ring which will be used to calculate the autocorrelation function. Since ECM does not require this high pixel count, the image was then binned by 10. Even after binning, each speckle covers 3–4 pixels. Large volume data analysis was performed using data storage and computing provided by the Brookhaven Center for Functional Nanomaterials and RHIC/ATLAS data center.

Samples were heated inside both microscopes using a DENSSolutions SH30 single-tilt heating holder, which provides temperature stability of ±0.03 °C and sample drift rates comparable to room temperature operation of the same microscope. The usable temperature range for these experiments is from T_g to the crystallization temperature T_x, which is 300–374 °C for $Pd_{40}Ni_{40}P_{20}$ and 230–265 °C for $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$. For both samples, initial heating from room temperature to above T_g was 20 °C/min. Then