

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 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 Pd₄₀Ni₄₀P₂₀ bulk metallic glass (BMG) heated inside the STEM into the supercooled liquid region. In Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}, τ and β decreases when heating from the glassy state to higher temperatures in the supercooled liquid. In Pd₄₀Ni₄₀P₂₀ alloy, the measured τ decreases from $T_g + 28$ °C to $T_g + 48$ °C, then increases as the temperature approaches T_x . These data also demonstrate that the ECM technique is limited by the time series, which must be at least 40τ to obtain a well-converged $g_2(t)$, and the time per frame, which must be less than 0.1τ to obtain sufficient sampling.

Keywords: electron correlation microscopy, supercooled liquid, structural relaxation time, metallic glass, *in-situ* heating

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, 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 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 α and β 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 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 Equation (2). We report ECM data on Pd₄₀Ni₄₀P₂₀ bulk metallic glass and Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5} metallic glass nanorods, and we discuss the experimental requirements on time resolution and total time series length required to obtain reliable $g_2(t)$ results.

Experimental Methods

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 aluminium 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 by sonication for 15~20 mins. A micro pipet was used to drop 1.5 – 1.8 μ L 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 + O₂ mixture for 12 ~ 15 mins before ECM measurements.

A Pd₄₀Ni₄₀P₂₀ metallic glass ingot 1 mm diameter was synthesized by injection casting. The details for fabrication are described in detail 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 μ m thick Pt protection layer, then a Pd₄₀Ni₄₀P₂₀ lamella around 15 μ m \times 10 μ m \times 2.5 μ m 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 2kv, 100 pA ion beam was used to remove surface damage. The stage was tilted by around 2 degrees 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 2kv, 100 pA Ga⁺ ion was used to remove Pt redeposition on sample surface. These samples were plasma cleaned at 20 psi Ar + O₂ mixture for ~ 30 s before ECM measurements.

Electron Correlation Microscopy Experiments

Low-speed ECM on the Pd₄₀Ni₄₀P₂₀ sample was performed in the University of Wisconsin-Madison FEI Titan STEM with probe aberration corrector at 200 kV in energy filtered “microprobe” STEM (μ P-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 1.2 pA. A Gatan BF_DF detector mounted on the 2.5mm 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 10eV. 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 3200 frames.

High-speed ECM experiments on the $\text{Pt}_{57.5}\text{Cu}_{14.7}\text{Ni}_{5.3}\text{P}_{22.5}$ 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 3838 by 3710 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. ECM does not require this high pixel count, so the first step in the analysis was to crop each image, then bin by 10. 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 °C to 374 °C for $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ and 230 °C to 265 °C for $\text{Pt}_{57.5}\text{Cu}_{14.7}\text{Ni}_{5.3}\text{P}_{22.5}$. For both samples, initial heating from room temperature to above T_g was 20 °C/min. Then at each test temperature, the sample was held isothermally for 2 mins before data collection.

$g_2(t)$ was calculated from the diffraction data as

$$g_2(p) = \frac{(N-p) \sum_{i=0}^{N-p-1} I(i)I(i+p)}{[\sum_{i=0}^{N-p-1} I(i)][\sum_{i=0}^{N-p-1} I(i+p)]}, \quad (3)$$

where N is the total number of frames in the diffraction time series, and p is the frame / time index. $g_2(t)$ was calculated for every pixel (k_x, k_y) in the diffraction pattern, then averaged over the ring of pixels at constant $k = \sqrt{k_x^2 + k_y^2}$. All of the data reported here are for the first diffuse ring in the nanodiffraction pattern, which is $k \sim 0.45 \text{ \AA}^{-1}$ for $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ and 0.44 \AA^{-1} for $\text{Pt}_{57.5}\text{Cu}_{14.7}\text{Ni}_{5.3}\text{P}_{22.5}$. The averaged $g_2(t)$ was resampled logarithmically in time, then fit to Equation (2) using standard non-linear least-squares fitting.

Results and discussion

Figure 1(a) shows an example of single nanodiffraction pattern from a $\text{Pt}_{57.5}\text{Cu}_{14.7}\text{Ni}_{5.3}\text{P}_{22.5}$ nanorod at 250 °C acquired on the K2-IS camera after cropping and binning. Many of the pixels are zero, and the maximum intensity is $0.2 e^-$. The entire frame contains only ~ 30 detected e^- . Figure 1(b) is the normalized, resampled $g_2(t)$ extracted from the time series of nanodiffraction patterns like Figure 1(a). Although only a few e^- are recorded per frame, the aggregate statistics from the series of 48,000 frames are low noise and an excellent fit to Equation (2).

Figure 2(a) shows the change of structural relaxation time τ with temperature in the supercooled $\text{Pt}_{57.5}\text{Cu}_{14.7}\text{Ni}_{5.3}\text{P}_{22.5}$ nanowire measured with the K2-IS camera. The time series of nanodiffraction pattern was collected near the nanowire surfaces and the autocorrelation function

was calculated from $k \sim 0.44 \text{ \AA}^{-1}$. τ continually decreases with temperature increasing from 242 °C to 258 °C ($T_g + 12 \text{ °C}$ to $T_g + 28 \text{ °C}$). Since no report is available in the literature for the τ_α of bulk $\text{Pt}_{57.5}\text{Cu}_{14.7}\text{Ni}_{5.3}\text{P}_{22.5}$, there is no direct comparison between nanowire and bulk at the same composition. However, compared with the typical τ measured from BMGs [20,24–26], the τ is much shorter, indicating a higher mobility and faster dynamics in nanowire. The stretching exponent β in Figure 2(b) decreases with higher temperatures, indicating a wider distribution of relaxation time and more spatial heterogeneity of atomic dynamics when temperature approaching T_x .

Figure 3(a) and (b) shows the structural relaxation time τ and stretching exponent β in the supercooled liquid region of $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ BMG measured using the CCD camera. The time autocorrelation function $g_2(t)$ is derived from $k \sim 0.45 \text{ \AA}^{-1}$. τ shows a continuous decreasing with temperature increasing from 328 °C to 348 °C ($T_g + 28 \text{ °C}$ to $T_g + 48 \text{ °C}$). As the temperature approaches crystallization temperature T_x , there is an obvious increase of relaxation time, caused by the growth of nuclei and crystal from some pre-existing ordered structures possibly induced during sample preparation by FIB. Compared with the previous ECM measurement in $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ BMG by Li [1], a similar increasing of τ arising from crystallization was also reported when the temperature is above 340 °C, but from temperature 328 °C to 340 °C, τ measured here is generally larger (e.g. $\sim 25\text{s}$ at 328°C here compared with $\sim 11\text{s}$ at 325 °C in previous result), that is because a longer trajectory length was applied here to ensure the convergence of $g_2(t)$ and capture the whole relaxation behavior, which will be discussed in detail in Figure 5. According to the report by Wilde [20], τ measured at 340 °C from ECM experiment is very close to that obtained from modulated differential scanning calorimetry (MDSC). The stretching exponent β , an indicator of spatical heterogeneity of relaxation dynamics, is typically smaller than 1 in metallic glass systems. Figure 3(b) shows that the β is quite scattered with no obvious tendency with temperature change. The β averaged from the whole measured temperature region is around 0.44, which is comparable to other measurements [1,27,28].

Figure 4 shows that the A parameter in Equation (2) is effected by the probe coherence. The probe coherence can be controlled by varying the source demagnification using the excitation of the first condenser lens. This control is called “spot size” on FEI microscopes. Yi and Voyles have shown that varying spot size systematically changes the coherence length of the illumination field in the condenser aperture plane [13]. Figure 4 shows that A , measured from $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ metallic glass at 320 °C, increases with increasing coherence length and FEI spot number. Increasing spot number and coherence also decreases the probe current, showing quantitatively that ECM delivers higher signal at lower probe current.

The length of the time series is one significant factor that limits the application of the ECM technique. The time series must be much longer than τ for the $g_2(t)$ correlation function to converge, enabling reliable measurement of τ . Figure 5 shows that for both materials studied here (bulk $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ at 332 °C and $\text{Pt}_{57.5}\text{Cu}_{14.7}\text{Ni}_{5.3}\text{P}_{22.5}$ nanorods at 254 °C) a time series of at least 40τ is required to obtain reliable results. For bulk $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$, the calculated τ becomes 23% shorter with the data length of 20τ and 41% shorter with 10τ . A more dramatic decrease of calculated τ can be observed in $\text{Pt}_{57.5}\text{Cu}_{14.7}\text{Ni}_{5.3}\text{P}_{22.5}$ nanowire when the data length decreases to 20τ and 10τ . This observation is consistent with other similar convergence tests for time autocorrelation functions calculated from time series [29]. When the time series is too short, $g_2(t)$

fails to reach a limiting value of 1 by the maximum t (not shown). Thus, failure of $g_2(t)$ to converge to 1 is a practical indication of a time series that is too short.

This limitation can explain why our ECM measurements are comparable with results from macroscopic techniques at higher temperature when τ is short, but diverge at low temperatures for bulk $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ (not shown in figure 3). When the temperature is approaching T_g , the structural relaxation time is at the scale of several hundreds of seconds [18,20,24]. For ECM measurement, the required time series length would be hours to get converged data at low temperatures. Over such long times, the speckle lifetime will be dominated by drift of the sample, not intrinsic structural changes. Sample drift in the data in Figure 3 was ~ 0.1 nm/min and the entire drift for the longest time series (850 s) was ~ 1.5 nm, which is in tolerance with 3.5 nm spatial resolution.

A short time per frame is another requirement needed to be satisfied in ECM experiment. Figure 6 shows τ measured on $\text{Pt}_{57.5}\text{Cu}_{14.7}\text{Ni}_{5.3}\text{P}_{22.5}$ nanowire at 250 °C using the CCD camera as a function of time per frame. All measurements have identical length of the time series (300s). τ has only small fluctuations with time per frame $\leq 0.1\tau$, and the results are comparable to the results obtained with the K2 detector shown in Figure 2. With time per frame $> 0.1\tau$, the discrepancy from true relaxation time and the strong dependence of τ on the time per frame prove that the number of nanodiffraction patterns is insufficient to capture one relaxation time unit. Therefore, we conclude that the time per frame must be less than 0.1τ to guarantee sufficient sampling to obtain unreliable results. If τ is shorter than 1 s, such as in the high temperature regime of $\text{Pt}_{57.5}\text{Cu}_{14.7}\text{Ni}_{5.3}\text{P}_{22.5}$ nanowire in Figure 2, the conventional slow CCD camera cannot be used and a fast direct electron detector is necessary. Unlike the too-short time series, there is not a clear indicator in $g_2(t)$ for a too-slow camera, although there is some indication that $g_2(t)$ will show less of a flat plateau at short times than in Figure 1(b), and β may become anomalously low.

Conclusion

We report first results using a fast direct electron detection camera for electron correlation microscopy experiments to measure the relaxation time of metallic glass alloys in their supercooled liquid state. We have applied ECM to investigate the supercooled liquid region of $\text{Pt}_{57.5}\text{Cu}_{14.7}\text{Ni}_{5.3}\text{P}_{22.5}$ glassy nanowire and $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ BMG using fast K2 detector and CCD camera respectively. For $\text{Pt}_{57.5}\text{Cu}_{14.7}\text{Ni}_{5.3}\text{P}_{22.5}$, both τ and β decrease over the whole measured supercooled liquid regime. For $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$, the measured τ continuously decreases when temperature increases from $T_g + 28$ °C to $T_g + 48$ °C in the supercooled liquid and then slightly increases due to the onset of nucleation and crystallization. β is quite scattered without tendency as temperature changes. ECM technique significantly improves the spatial resolution of relaxation dynamics measurement down to the nanometer scale compared with macroscopic experiments, but it requires a length of time series at least 40 times the characteristic relaxation time and a time per diffraction pattern at most 0.1 times the relaxation time. These requirements impose limitations on the accessible time scales imposed by sample drift at long times and detector speed at short times.

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