

Coherent X-Ray Study of Fluctuations during Domain Coarsening

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We report observations of the dynamics of the exact structure factor (speckle pattern) during phase separation in a sodium borosilicate glass, measured using intensity fluctuation spectroscopy with a coherent x-ray beam. Nonequilibrium fluctuations in the structure factor are analyzed using a two-time correlation function to extract the time-dependent and wave-number-dependent correlation time. The behavior of the correlation time is in agreement with a scaling law previously found in simulations. [S0031-9007(98)08014-4]

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The growth of domains driven by boundary energy reduction is a ubiquitous process in the approach to equilibrium. General theories of such domain coarsening have been developed based on the idea that, although the domain structure is evolving, it remains statistically self-similar at all times [1]. This leads to the concept of dynamic scaling [2], in which the average structure factor does not change if length scales are measured in units of the average domain size R . In the dynamic scaling regime, R is found to grow as a power law in time, with an exponent n which depends on dimensionality and the character of the order parameter. In recent years, increasing theoretical attention [3–5] has been focused on the statistics of fluctuations about this average behavior, which differs from classical fluctuation statistics. Fluctuations about the ensemble average are (almost) “frozen in” to each instance of a coarsening system, leading to domain arrangements at later times which are strongly correlated with those at earlier times. A previous experimental study of two-dimensional domains in a liquid crystal [6] employed real-time microscopy to observe the large-time-difference limit of the two-time correlation function of the order parameter in real space. In the present paper we use a new technique, scattering with coherent x rays, to observe a complementary quantity, the short-time-difference limit of the two-time correlation function of the exact structure factor in reciprocal space. It has been predicted that the exact structure factor exhibits fluctuations which are persistent [3] and which have correlation times obeying a scaling law with the wave number [5].

The scattering of a conventional incoherent x-ray beam from a random arrangement of domains measures the average structure factor $\langle I \rangle(q, t)$. To measure the exact structure factor $I(\vec{q}, t)$, a coherent incident beam must be employed [7]. With the very high brilliance now available from third generation synchrotron sources, it has become feasible to produce a sufficiently intense coherent x-ray beam to perform such measurements dynamically. This technique, x-ray intensity fluctuation spectroscopy (XIFS),

probes the dynamics of fluctuations on short length scales (<100 nm) and long time scales ($>10^{-4}$ s). In the past few years, XIFS has been demonstrated in studies of equilibrium dynamics such as fluctuations near a critical point and diffusion in colloids and micellar systems [8]. In this paper we apply the technique to a nonequilibrium process, domain coarsening. An earlier XIFS study of order-disorder domain coarsening in Cu_3Au indicated that the correlation times for fluctuations may be large [9]. Here we study the coarsening of phase domains in a sodium borosilicate glass undergoing phase separation. For this type of system, the average structure factor has been found to exhibit dynamic scaling behavior [10]. In this Letter we report that the correlation times of fluctuations about this average behavior also obey a scaling law.

The XIFS experiments were performed in a small-angle scattering geometry at the MIT-McGill-IBM undulator beam line (8-ID) of the Advanced Photon Source. In order to obtain a sufficiently intense coherent x-ray beam, the full 2.5% energy bandwidth of the undulator first harmonic was used [11]. The undulator magnet gap was set to 18.00 mm, giving a first harmonic energy of 7.66 keV. A silicon mirror was used to reject the higher harmonics of the undulator spectrum. A transversely coherent incident beam was produced using slits with highly polished edges, set to an 11 μm vertical by 6 μm horizontal aperture. A detailed description of the production and characterization of x-ray speckle using this beam line was reported earlier [12]. The sample was held in a small (2-mm inside diameter) quartz tube furnace in a helium atmosphere. The supports were water cooled to minimize thermal motion. A helium-filled ion chamber was used to monitor the total intensity transmitted by the sample. The scattered x-ray signal was recorded using a direct-detection charge-coupled device (CCD) camera with 22 μm square pixels, located 254 cm downstream of the sample. Samples consisted of ~ 100 - μm -thick polished glass disks of composition $(\text{Na}_2\text{O})_{0.07}(\text{B}_2\text{O}_3)_{0.22}(\text{SiO}_2)_{0.71}$, which is at the

critical composition for separation into B_2O_3 -rich and SiO_2 -rich phases ($T_c = 1026$ K) [13]. In a typical experiment, the sample was heated to $T = 1033$ K for 10 s to equilibrate it in the single-phase state, and then rapidly (within 10 s) quenched to and held at a temperature below T_c so that phase separation occurred isothermally. During this process, scattering patterns were recorded at a rate of one frame per 1.24 s (1 s counting time and 0.24 s readout time). We present data for phase separation occurring at two temperatures, 943 and 963 K.

When phase separation is initiated, a ring of scattering appears at large wave numbers. As the domains coarsen, the ring moves to smaller wave numbers and becomes more intense with time. Typical scattering data at 3 times after a quench are shown in Fig. 1. The speckles apparent in these patterns are a manifestation of the coherent illumination of the sample. Time correlations in the intensity of these speckles characterize the fluctuations about the average structure factor.

In order to set the characteristic time scales for the fluctuations, we first analyze the scaling behavior of the average scattering. The dynamic scaling limit for $\langle I \rangle(q, t)$ can be written as [2]

$$\langle I \rangle(q, t) = \langle I \rangle_{\max}(t) F(y), \quad (1)$$

where the wave number has been rescaled as $y \equiv q/q_{\max}$ using q_{\max} , the wave number at which $\langle I \rangle$ is maximum for a given time. It is expected [1] to evolve in time as $q_{\max} = [A(t - t_0)]^{-n}$, where $n = 1/3$ for a system with a conserved order parameter (the current case), A is a constant, and t_0 sets the initial condition for the scaling law. To apply this analysis to our data, the average structure factor, $\langle I \rangle(q, t)$, was calculated by circularly averaging

each CCD image around the direct beam position and normalizing it to the total intensity. Estimates of $\langle I \rangle_{\max}(t)$ and $q_{\max}(t)$ were first obtained by fitting the near-peak regions of $\langle I \rangle(q)$ at each time with a Gaussian. The average scaling form F was then obtained by averaging all of the $\langle I \rangle(q)$ curves scaled using Eq. (1). The $\langle I \rangle(q)$ curves were then refit to this average scaling form F to extract final values for $q_{\max}(t)$ and $\langle I \rangle_{\max}(t)$. After scaling, the data at all times fall on the same master curve (inset of Fig. 2a), indicating that the wave-number scaling law (1) works well. We also found that the same scaling form F could be used for both quench temperatures. The $q_{\max}(t)$ extracted for each temperature is plotted in Fig. 2a. At early times, q_{\max}^{-3} deviates from linear behavior prior to reaching the dynamic scaling limit. The lines are linear fits to the data at $t > 400$ s. The time intercepts of these lines give values for t_0 of 68 and 81 s at 943 and 963 K, respectively.

One may alternatively write the dynamic scaling form for $\langle I \rangle(q, t)$ as a scaling law in time (rather than a wave number) of the form

$$\langle I \rangle(q, t) = \langle I \rangle'_{\max}(q) F'(x), \quad (2)$$

where time has been rescaled as $x \equiv (t - t_0)/[t_{\max}(q) - t_0]$ using t_{\max} , the time at which $\langle I \rangle$ is maximum for a given wave number. In this case, the q dependence of t_{\max} can be expressed as the power law $B(t_{\max} - t_0) = q^{-1/n}$, where B is a constant. Using values of t_0 from the wave-number scaling, the functions $F'(x)$, $\langle I \rangle'_{\max}(q)$, and $t_{\max}(q)$ were extracted following a method analogous to that described above. As shown in Fig. 2b, the time scaling works well except at the highest wave numbers, and the values of t_{\max} follow the predicted power law.

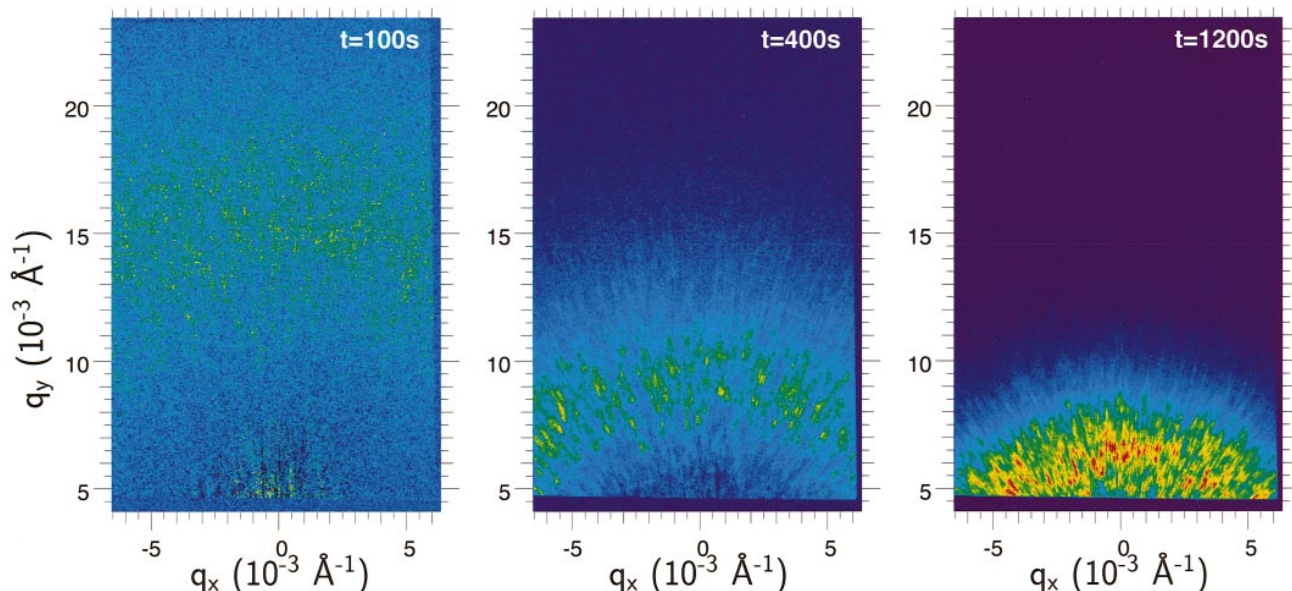


FIG. 1(color). Speckle patterns produced by a coherent x-ray beam scattering from a sodium borosilicate glass sample undergoing phase separation at 963 K. One-second exposures at 100, 400, and 1200 s after a quench from 1033 K are shown. Red indicates higher intensity; q_y and q_x are the horizontal and vertical components of q .

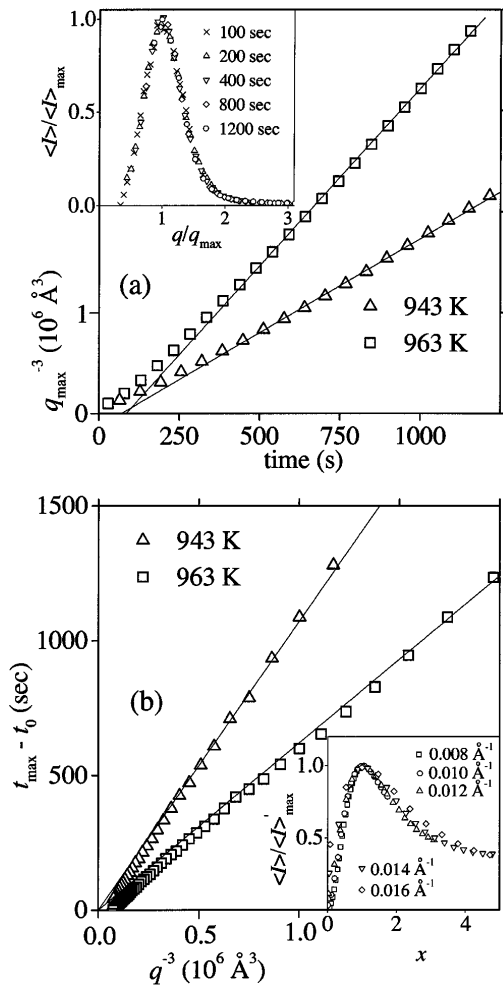


FIG. 2. (a) Values of $q_{\max}(t)$ extracted using the wave number scaling law. The inset shows $\langle I \rangle(q)$ at different times after the quench to 963 K scaled as in Eq. (1). (b) Values of $t_{\max}(q)$ extracted using the time scaling law. Linear fits give $B = 0.93 \times 10^3$ (1.61×10^3) $\text{\AA}^3/\text{s}$ at 943 K (963 K). The inset shows $\langle I \rangle(t)$ at different q scaled as in Eq. (2).

Following Ref. [5], to analyze the fluctuations in the exact structure factor we use a two-time correlation function defined by

$$C(q, t_1, t_2) = \frac{\langle I(t_1)I(t_2) \rangle - \langle I(t_1) \rangle \langle I(t_2) \rangle}{[\langle I^2(t_1) \rangle - \langle I(t_1) \rangle^2]^{1/2} [\langle I^2(t_2) \rangle - \langle I(t_2) \rangle^2]^{1/2}} \quad (3)$$

Here $I(t)$ is the intensity in the pixel corresponding to the wave vector \vec{q} at time t normalized to the total intensity. To calculate this function the CCD images were divided into 10-pixel-wide annuli such that all pixels in any annulus can be assumed to have the same $q \equiv |\vec{q}|$. The product $I(t_1)I(t_2)$ in the numerator was calculated at each pixel in the annulus and then averaged. Since the diagonal elements ($t_1 = t_2$) of this matrix contain a term from the Poisson statistics of photon counting, they were replaced by the average value of the four neighboring elements.

These new values were then used in the $I^2(t)$ to normalize the matrix elements [the denominator in Eq. (3)]. The value of this correlation function C along the diagonal is always unity by construction.

A typical two-time correlation function for a specific wave number is shown in Fig. 3. The coordinate along the direction of the central ridge is the average time after the quench $\bar{t} \equiv (t_1 + t_2)/2$. If one makes a cut across this ridge along the time-difference coordinate $\Delta t \equiv t_1 - t_2$, the short-time-difference behavior of C is characterized by the width of the peak, which gives the correlation time at \bar{t} . For an equilibrium system, this width would be constant as a function of \bar{t} . From Fig. 3, it is clear that the width increases with \bar{t} . The correlation time τ was evaluated for each \bar{t} by determining the value of $|\Delta t|$ which gives a correlation value $C = 0.5$. The resulting $\tau(\bar{t})$ at each q are shown in the inset in Fig. 4. The correlation times increase with time at each wave number, and decrease with wave number. In addition, τ is always a large fraction of \bar{t} , indicating that the speckles are persistent.

Simulations of domain coarsening using a Langevin model [5] have found that τ follows a scaling law, which we write as

$$\tau(q, t) = [t_{\max}(q) - t_0]W_2(x), \quad (4)$$

where t_{\max} , t_0 , and x are determined by the scaling behavior of the average structure factor $\langle I \rangle$. In the limit of large x , the scaling function W_2 is found to have a power-law form $W_2 = ax^p$ with the exponent $p = 1 - n$ [5]. Figure 4 shows this function W_2 obtained by normalizing the experimental correlation times by $t_{\max} - t_0$. The scaled correlation times at both temperatures fall along the same curve, indicating that proposed scaling works for this system. The relatively large and nonrandom deviations of the individual points reflect the non-Gaussian statistics of the speckle intensities for a single quench [3]. To test

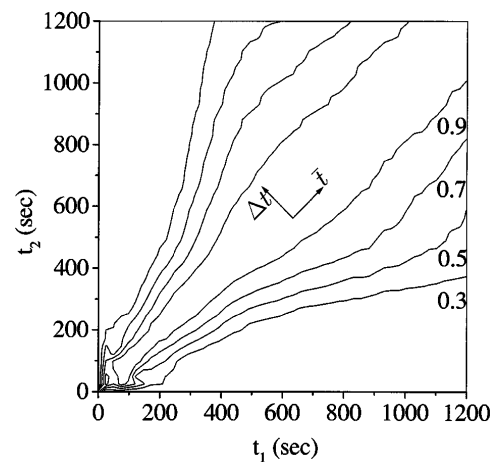


FIG. 3. Contour plot of two-time correlation function at $q = 0.01 \text{ \AA}$ for the 963 K quench. Values of C for each contour are shown. The directions of the alternative coordinates \bar{t} and Δt are indicated.

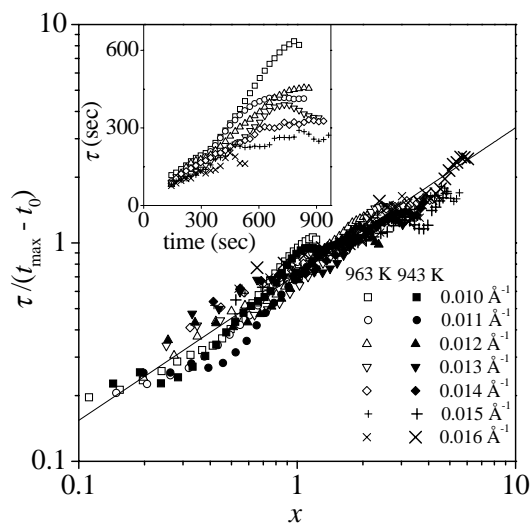


FIG. 4. Scaled correlation times for both quenches. The line is a power-law fit to the data. The unscaled correlation times for the 963 K quench are shown in the inset.

the prediction for W_2 , the experimental data were fit to the power law form, giving $a = 0.72 \pm 0.02$ and $p = 0.65 \pm 0.04$. The value of p agrees with the prediction of $1 - n = 2/3$. The near-unity value of a indicates that the speckles are quite persistent, and agrees within a factor of 2 with simulation results [5].

The scaled times covered in this study ($0.1 < x < 10$) are relatively small compared with those used to obtain the scaling law (4) in the simulation studies, even when differences in time normalization are considered. Experimentally, we are limited both by the range over which the intensity is sufficiently large and by the maximum time over which the apparatus is sufficiently stable (currently about 1500 s). In addition, the average structure factor shows some deviations from the dynamic scaling limit at short times and large wave numbers. Nevertheless, the observed scaling of the correlation time at both temperatures provides the first experimental confirmation of the scaling law (4) for τ , based on values of t_{\max} and n from the scaling of $\langle I \rangle$. This small- Δt behavior appears to be inde-

pendent of the large- Δt scaling of C characterized by the exponent λ , since λ is unrelated to n [4,6]. More generally, these results demonstrate the persistence of speckles during domain coarsening, behavior which differs qualitatively from that previously observed with XIFS in equilibrium systems. We believe that the two-time correlation function measured by XIFS can be a useful quantitative probe for understanding the dynamics of non-equilibrium systems.

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