A Study of Concentration Fluctuations in the Binary Mixture Hexane-Nitrobenzene with X-ray Photon Correlation Spectroscopy

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Introduction

X-ray Photon Correlation Spectroscopy (XPCS) has the potential to measure the relaxation rate of the dynamic structure factor of materials over a wide range of time scales (1μs-1000 s) in and out of thermodynamic equilibrium at wavevectors inaccessible to visible light (0.004-2 A^{-1}). XPCS experiments should expand our understanding of short length scale fluctuations, as well as enabling studies of opaque materials like metal alloys. Most of the results reported to date have been performed on systems with a large length scale microstructure which greatly enhances the scattered intensity due to the coherent addition of the scattering from the large number of atoms in the microstructure. This includes aggregate systems such as colloids [1-4] and polymer micelles [5], spinodally decomposing systems such as sodium borosilicate glass [6], and systems with anti-phase domains such as metal alloys [7-8]. Binary mixtures of small molecular weight fluids have much faster fluctuations (1μs to s), and they typically scatter more weakly than systems studied previously. As such, they represent an important test of the general applicability of XPCS to a wide variety of materials.

Here we report the first XPCS measurements done on a simple binary fluid, n-hexane (C_6H_{14}) and nitrobenzene ($C_6H_5NO_2$), near its critical point. We measured dynamic correlation functions with relaxation times as fast as 250 μs. Our measurements show that it is feasible to use XPCS to study the fast dynamics of even such weak scatterers as these low molecular weight hydrocarbon fluid mixtures. This further demonstrates the general applicability of XPCS to a wide variety of materials. Our results are also noteworthy in that the hexane/nitrobenzene mixtures showed no detectable signs of radiation damage even under the high intensity of a so-called 'pink' undulator beam at the APS. This is in contrast to observations on colloidal and polymer samples, which are typically quite sensitive to radiation damage or x-ray induced charging effects.

Methods and Materials

This experiment was performed on the undulator beamline at sector 7 of the Advanced Photon Source, operated by MHATT-CAT. With the undulator fundamental set at 9.0 keV, the white beam was collimated with white beam slits to 100 μm by 100 μm. In the experimental hutch 35 m from the source, two small Pt coated mirrors were used to produce a ''pink beam". The doubly reflected beam had a bandpass of $\Delta E/E = 2.55$ % and provided a coherent flux of 3.6 x 10^{10} ph/s in a $(5\ \mu m)^2$ beam incident on the sample. The speckle size in the detector plane was ~ 20 μm. The scattered x-rays in a single speckle were measured with an Amptek XR-100CR detector. A Brookhaven Instrument BI-30 hardware correlator was used to measure the dynamic correlation functions.

The sample was mixed at a critical composition and placed in a sample cell consisting of a 3 mm thick Al cylinder, sealed by two 2 mil Kapton windows. The sample temperature was stable to within 5 mK.

Results

The mixture studied, n-hexane (C_6H_{14}) and nitrobenzene ($C_6H_5NO_2$) has a relatively high X-ray contrast making it a good choice for XPCS. With a coherent flux of 8.7 keV X-rays equal to 3.6 x 10^{10} ph/s/$(5\ \mu m)^2$, we measured scattering rates of about 100-1000 photon/s/speckle for a temperature within 0.06° C of the critical temperature.

Fig. 1 shows the temperature dependence of the measured SAXS scattering rate for the critical composition. The data clearly show the expected divergence in the susceptibility of the composition fluctuations as the critical temperature is approached. The data are well fit by lorentzians with a $T_c = 19.12°$ C, a bare correlation length of 2.48 A and critical exponents $\nu = 0.635$ and $\gamma = 1.23$, in agreement with expectations for this Ising system.

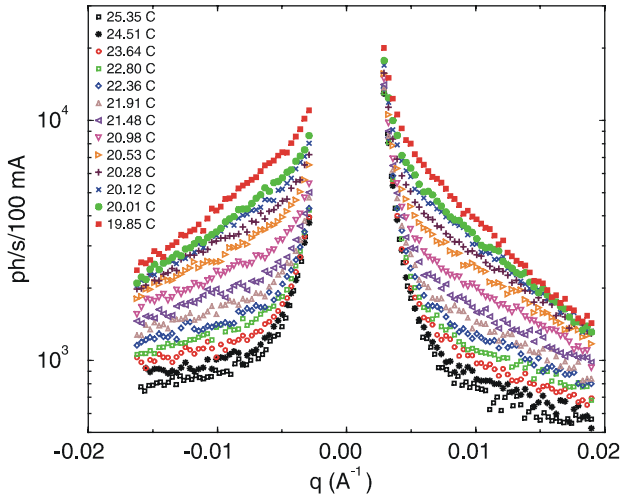

Figure 1. Temperature dependence of SAXS from composition fluctuations, measured under incoherent conditions.

When the scattering rate from the composition fluctuations is measured under coherent conditions, the count rate ranges from 10 to 1000 ph/sec/speckle, depending on the scattering wavevector and the temperature. However, a more meaningful figure of merit for an XPCS experiment is the count rate per speckle *per relaxation time*. The relaxation times for composition fluctuations in the binary fluid mixture are given by the Stokes-Einstein relation $\tau = 6\pi\eta\xi/(k_B T q^2)$, where η is the shear viscosity. The shear viscosity of the mixture is 0.0053 P. The relaxation time of the fluctuations 0.1° C away from T_c for a wavevector of 0.002 A^{-1} is 244 μs, which can be sampled with a standard hardware correlator.

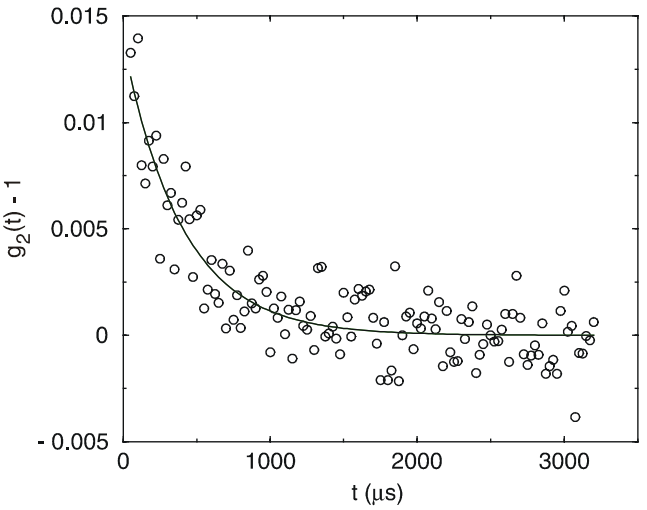

Figure 2. Typical dynamic correlation function for scattering from composition fluctuations.

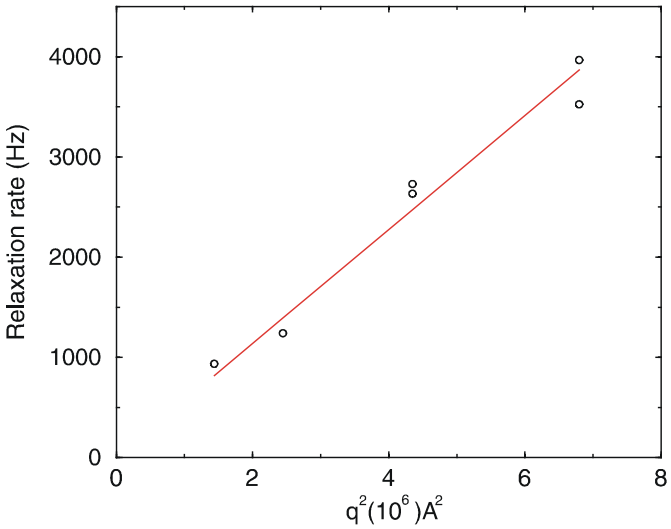

Figure 3. Scaling of the relaxation rate with q^2.

Figure 2 shows the dynamic correlation function of the scattered intensity versus the delay time of the correlator at $\Delta T = 0.063^{o}$ C and q = 0.00156 A^{-1}. The typical collection times to measure the correlation functions with the single channel correlator were on the order 30-60 minutes. The typical contrast measured was ~ 1.4 %.

The measured relaxation times were quite reproducible. This consistency shows that the sample was not easily damaged by the x-ray radiation. In fact, none of our observations indicated that the sample was affected by the x-ray beam. As noted in the introduction, this tolerance to high intensity x-ray beam is remarkable among soft condensed matter, organic systems, such as colloids or polymers, which are generally much more susceptible to radiation induced charging or damage effects. In this case, we speculate that the low viscosity of the mixture and resulting high diffusion coefficient contributes to alleviating the effects of any radiation damage which may occur.

Figure 3 shows the relaxation rate versus the square of the wavevector for the critical mixture at $\Delta T = 0.063^{o}$. The solid line is a fit to $\tau = Dq^2$ with a diffusion constantD = 5.69 x10^8 A^2/s. The data clearly shows simple diffusive relaxation for the range of wavevectors shown. The measure diffusion constant is in good agreement with that expected from the Stokes-Einstein relation and the known viscosity of the mixture.

Discussion

In summary, we have performed a SAXS and XPCS study of composition fluctuations in a critical binary mixture of hexane and nitrobenzene near its critical point. The measured critical exponents observed are consistent with expectations for this Ising system.

Using a hardware correlator we were able to measure the first XPCS dynamic correlation function on a simple binary fluid. Although rather fast (250 μs), we were able to measure the correlation functions with sufficient signal to noise within a single channel correlator with an hour of collection time. The diffusion constant deduced from our XPCS measurement is consistent with the Stokes-Einstein equation, the known viscosity of the mixture, and the measured correlation length.

These measurements demonstrate the feasibility of using XPCS to study the dynamics of even such a weak scatterer as this low molecular weight hydrocarbon fluid mixtures. This further demonstrates the general applicability of XPCS to a wide variety of materials. We found no detectable signs of radiation damage in these mixtures even under the high intensity of a 'pink' undulator beam at the APS.

Further developments in technique should permit future measurements to probe the relaxations on length scales much smaller than the correlation length, i..e, at large values of qξ. This is only possible in light scattering studies very near to the critical point, with very large correlation lengths. Studies of binary fluids in confined geometries should also benefit from this technique.

Acknowledgments

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