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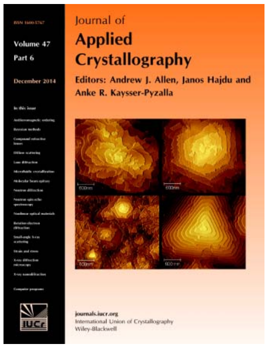

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# *In situ* small-angle X-ray scattering characterization of X-ray-induced local heating

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It is shown that small-angle X-ray scattering from binary liquid mixtures close to the critical point of demixing can be used for *in situ* characterization of beam-induced heating of liquid samples. For demonstration purposes, the proposed approach is applied on a well studied critical mixture of water and 2,6-lutidine. Given a typical incident X-ray flux at a third-generation synchrotron light source and using a 1.5 mm-diameter glass capillary as sample container, a beam-induced local temperature increase of 0.45 ± 0.10 K is observed.

## 1. Introduction

Small-angle X-ray scattering (SAXS) is a standard technique to study mesoscale fluids, yielding information on spatial electron density variations in the nanometre range (Glatter & Kratky, 1982). With the advent of third-generation synchrotron light sources and the ensuing increase in incident X-ray flux, the technique can today be applied to subsecond timescales or to minute sample volumes. Examples of the former include kinetic studies of surfactant self-assembly (Bressel *et al.*, 2012; Jensen *et al.*, 2013). Examples of the latter include *in situ* SAXS studies using microjets (Marmiroli *et al.*, 2009), microfluidic chips (Toft *et al.*, 2008) or, in certain cases, even 'nanofluidic' chips with a scattering volume as small as 30 pl (Nygård *et al.*, 2012).

The vastly increased flux may pose experimental problems. An obvious example is radiation damage in both natural and synthetic macromolecules. The incident X-ray beam will also heat up the sample locally, which should be a concern in studies of, for example, kinetics or phase transitions. For a typical SAXS setup at a modern synchrotron facility, the incident X-ray beam deposits energy with a power of ~1 mW in a volume of ~50–100 nl, assuming a sample thickness of about 1 mm. Given the ever increasing flux attainable at synchrotron light sources, this problem will become even more important in the future. In the case of millimetre-sized glass spheres, for example, thermal imaging has been applied to observe temperature increases of up to several degrees upon absorption of incident X-rays (Snell *et al.*, 2007). It is not trivial, however, to characterize the temperature of the liquid in the path of the X-ray beam. The question then remains, how much does the incident X-ray beam heat up the liquid sample locally?

In this short communication, we address the above-mentioned question. In particular, we demonstrate that SAXS from binary liquid mixtures close to the critical point of demixing, defined by the critical concentration $\varphi_{\rm C}$ and temperature $T_{\rm C}$, can be utilized to determine the X-ray-induced local temperature increase in liquid samples. With an incident X-ray flux typically attainable at a third-generation synchrotron light source ($10^{13}$ photons s$^{-1}$ mm$^{-2}$) and using a 1.5 mm-diameter glass capillary as sample container, we observe an X-ray-induced local temperature increase of $T_{\text{X-ray}}$ = 0.45 ± 0.10 K. In general, we briefly discuss the possibility of characterizing X-ray beam heating at room temperature using critical liquid mixtures.

## 2. Experimental details

For demonstration purposes, we collected SAXS data on a binary solvent composed of water (Milli-Q) and 2,6-lutidine (Sigma–Aldrich, purity $\geq$99%), which is a common system for studies of critical phenomena (Gambassi *et al.*, 2009). The chemicals were used as received, without any further purification or degassing. This mixture has a lower critical point at $T_{\rm C} \simeq 307$ K and a lutidine mass fraction $c_{\rm L} \simeq 0.286$ (Gülari *et al.*, 1972). Data were collected as a function of temperature $T$ in a range of $\Delta T = T_{\rm C} - T \simeq 0.5 - 4.0$ K below $T_{\rm C}$.

We carried out the experiment at the cSAXS beamline (X12SA; for details on cSAXS, we refer to the beamline web site, http://www.psi.ch/sls/csaxs) of the Swiss Light Source, using an incident X-ray energy of 12.4 keV. The X-ray beam was focused onto the detector plane in order to increase the angular resolution, and it had a size of 0.2 × 0.2 mm at the sample position. The X-rays impinged normal to the symmetry axis of the cylindrical sample container, and the scattered X-rays were detected 7 m behind the sample using a two-dimensional pixel detector (PILATUS 2M, 1461 × 1560 pixels with a size of 172 × 172 µm; Kraft *et al.*, 2009). In order to reduce parasitic scattering, we used an evacuated flight tube between the sample and the detector.

The sample was kept in a thin-walled (10 µm-thick) 1.5 mm-diameter borosilicate glass capillary mounted on a sample holder made of copper. The temperature of the sample holder was kept stable within ±0.05 K using a refrigerated/heating circulator (Julabo FP40-HE), as measured by a Pt-100 temperature sensor. The experiment was carried out as follows. For each temperature, the sample was allowed to stabilize for 60 s under X-ray irradiation, after which SAXS data were collected in six exposures of 10 s each. No temporal variation was observed in the SAXS data thus collected (see inset of Fig. 1). This procedure was repeated for eight different temperatures below $T_{\rm C}$. In total, the sample was therefore irradiated by X-rays for a duration of 960 s. Even during such lengthy X-ray irradiation, we do not expect any effects of beam damage in the critical fluctuations for the present system; in fact, no such effects were observed in a previous SAXS study on the same system at the same beamline, despite a three times longer total X-ray exposure period (Nellen *et al.*, 2011).

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Throughout this study, we divide the temperature of the sample into two parts, $T = T_{\rm X\text{-}ray} + T_{\rm nom}$, where $T_{\rm X\text{-}ray}$ is the X-ray-induced local temperature increase and $T_{\rm nom}$ the nominal temperature, that is, the temperature in the absence of X-ray irradiation. The nominal temperature was determined by slowly increasing the temperature, in the absence of X-ray exposure, and monitoring visually the onset of critical opalescence at $T_{\rm C}$. By this simple approach we could calibrate $T_{\rm nom}$ within ±0.10 K, as verified using several different samples.

## 3. Results and discussion

After subtracting the temperature-independent parasitic background scattering, the scattered intensity $I(q)$ was modeled using the classical Ornstein–Zernike (OZ) relation (Hansen & McDonald, 2006),

$$I(q) \propto \frac{\chi_T}{1+\xi^2 q^2}, \tag{1}$$

with $\xi$ denoting the correlation length describing the concentration fluctuations and $\chi_T$ the isothermal compressibility. By collecting SAXS data as a function of temperature $T$, we could thereby map the temperature-dependent correlation length $\xi(T)$.

Close to the critical point, binary liquid mixtures are known to follow the three-dimensional Ising-like universality class (Hansen & McDonald, 2006). In this case, the correlation length is given by

$$\xi = \xi_0 |\Delta T/T_{\rm C}|^{-\nu}, \tag{2}$$

with $\Delta T = T_{\rm C} - T$, $\nu \simeq 0.63$ a universal critical exponent and $\xi_0$ a sample-dependent constant. For the critical mixture of water and 2,6-lutidine, the latter constant has previously been found to be $\xi_0 = 0.20 \pm 0.02$ nm using light scattering (Gülari *et al.*, 1972) and SAXS (Nellen *et al.*, 2011).

To demonstrate our approach, we plot in Fig. 1 the scattered intensity $I(q)$ collected at two different temperatures, $T_{\rm C} - T \simeq 0.5$ and 3.6 K. Note that $I(q)$ is plotted on an arbitrary, but common, intensity scale. Also shown is the classical OZ model, obtained for each temperature by fitting equation (1) to the experimental data in the range $q = 0.15 - 1.5\ {\rm nm}^{-1}$, using $\xi$ and $\chi_T$ as free parameters. Both the shape and the magnitude of the scattering pattern are strongly temperature dependent, thus providing the basis for the approach suggested here.

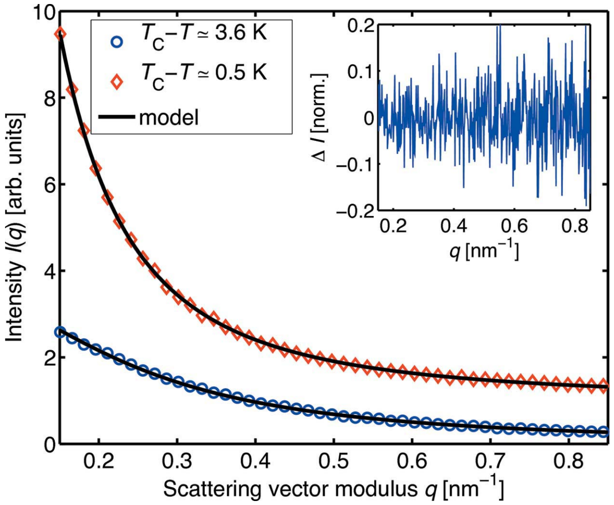

**Figure 1**
Scattered intensity $I(q)$ *versus* scattering vector modulus $q$, collected from a critical mixture of water and 2,6-lutidine (only every tenth data point is shown). Data are presented for two different temperatures, $T_{\rm C} - T \simeq 0.5$ and 3.6 K, and the former curve has been vertically offset by one unit for clarity. Note that the statistical inaccuracy is smaller than the symbol size. The best model fits using equation (1) are also shown. Inset: Temporally resolved low-$T$ data ($T_{\rm C} - T \simeq 3.6$ K), presented as $\Delta I(q) = [I(q;{\rm last}) - I(q;{\rm first})]/I(q;{\rm first})$, where $I(q;{\rm first})$ and $I(q;{\rm last})$ denote the scattering data collected during the first and last 10 s exposures, respectively.

By fitting the OZ model to the experimental data, we extract the correlation length $\xi = \xi(T)$. It is presented in Fig. 2 as a function of temperature $T = T_{\rm X\text{-}ray} + T_{\rm nom}$. The data of Fig. 2 can only be described using the well known three-dimensional Ising-like behavior if we assume $T_{\rm X\text{-}ray} = 0.45 \pm 0.10$ K. In this case, we obtain $\xi_0 = 0.25 \pm 0.06$ nm and $\nu = 0.63 \pm 0.05$, in good agreement with previous findings (Gülari *et al.*, 1972; Nellen *et al.*, 2011). It should be noted that the present approach is rather sensitive to $T_{\rm X\text{-}ray}$, as demonstrated by the strong effect of $T_{\rm X\text{-}ray}$ on the obtained $\nu$ shown in the inset of Fig. 2.

In order to obtain further support for our finding of $T_{\rm X\text{-}ray} = 0.45 \pm 0.10$ K, we can analyze the scaling of $\chi_T$ with temperature. Theory predicts that the isothermal compressibility scales as $\chi_T \propto |\Delta T/T_{\rm C}|^{-\gamma}$, with the critical exponent $\gamma \simeq 1.24$ (Hansen & McDonald, 2006). Indeed, light scattering experiments on the critical mixture of water and 2,6-lutidine have yielded $\gamma = 1.26 \pm 0.02$ (Gülari *et al.*, 1972). In the present study, we obtain $\gamma = 1.31 \pm 0.11$, assuming $T_{\rm X\text{-}ray} = 0.45 \pm 0.10$ K, in agreement with both theoretical predictions and light-scattering results.

The method proposed here differs from previously reported techniques for studying local X-ray beam heating as follows. First, while thermal imaging techniques (Snell *et al.*, 2007; Rosenthal *et al.*, 2014) measure absolute temperatures, our approach is probing an apparent shift in the phase transition temperature induced by X-ray heating. Second, whereas thermal imaging provides spatially resolved temperature maps (Snell *et al.*, 2007), our method measures an X-ray-induced temperature increase averaged over the scattering volume. Third, and most important for the present study, our scheme is directly applicable to liquids contained in typical sample cells routinely used at synchrotron SAXS instruments.

Finally, we comment on the applicability of the present scheme for characterizing X-ray beam heating. The beam heating will depend not only on X-ray flux but also on, for example, the geometry of the sample container and possible flow rate. Therefore, one would like to

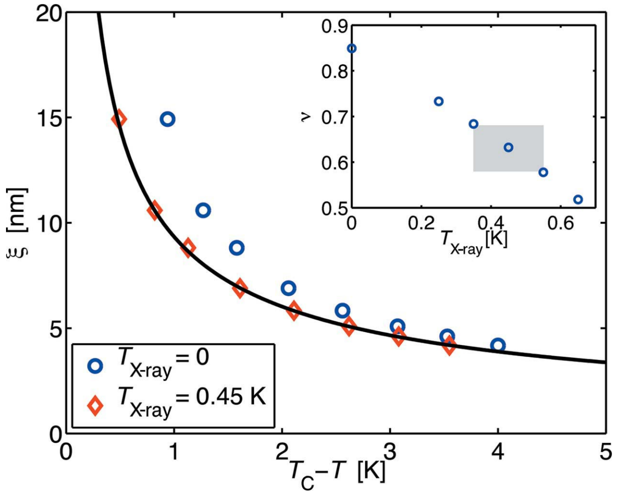

**Figure 2**
Correlation length $\xi$ as a function of temperature, $T = T_{\rm X\text{-}ray} + T_{\rm nom}$. The solid line corresponds to the theoretical prediction $\xi = \xi_0 |(T_{\rm C} - T)/T_{\rm C}|^{-\nu}$, with $\xi_0 = 0.25$ nm and $\nu = 0.63$ (see text for details). Inset: Critical exponent $\nu$ as a function of X-ray-induced local temperature increase $T_{\rm X\text{-}ray}$, obtained by fitting equations (1) and (2) to the SAXS data. The gray region demarcates $T_{\rm Xray} = 0.45 \pm 0.10$ K, which corresponds to fitted critical exponents $\nu = 0.63 \pm 0.05$.

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characterize the X-ray beam heating as close as possible to operating conditions. The present mixture of water and 2,6-lutidine has a critical temperature of $T_{\rm C} \simeq 307$ K, but by using different liquid mixtures one can expand the measurements to different temperature ranges. In particular, by suitable addition of an inorganic salt to the present system, one can shift the critical point to room temperature (Seah *et al.*, 1993).

## 4. Conclusions

The results of the present study are twofold: First, we have proposed that SAXS from binary solvents close to the critical point can be used to characterize X-ray-induced local heating in liquid samples. The proposed approach is straightforward and can readily be applied to different sample environments and operating conditions. Second, for demonstration purposes we have applied the method on a critical mixture of water and 2,6-lutidine in a 1.5 mm-diameter glass capillary, thereby observing a beam-induced temperature increase of 0.45 ± 0.10 K.

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