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Small-angle x-ray scattering of supercritical fluid Hg: Bi-impurity effect

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Abstract. We have carried out small-angle x-ray scattering and x-ray transmission measurements of supercritical fluid Hg-0.2%Bi and pure Hg systems at SPRing-8 in Japan. We have obtained the static structure factors $S(Q)$ in the low-momentum transfer region ($0.5 < Q < 3 \text{nm}^{-1}$) for both samples at temperatures and pressures up to $1600 \degree \text{C}$ and $200 \text{MPa}$. A Bi-impurity effect can be seen in both $S(Q)$ and density deduced from x-ray transmission, only in the high temperature and high pressure region; the sign of the phase separation is seen near the critical density for Hg-0.2%Bi sample. We have analyzed $S(Q)$ by Ornstein-Zernike formula and deduced the structure factors in the long-wavelength limit $S(0)$, correlation lengths $\xi$, and corresponding short-range correlation lengths $R \equiv \xi/\sqrt{S(0)}$. Temperature variation of $R$ is very similar to that of the density in each sample. This experimental fact hints that the variation of $R$ is highly dependent on its metallic nature because the density is the most relevant parameter for the electronic features in fluid Hg and its impurity systems.

1. Introduction

Fluid Hg has a critical point at the critical temperature $T_c = 1478 \degree \text{C}$ and the critical pressure $P_c = 167.3 \text{MPa}$. When it is expanded from the ambient conditions, it changes from metallic state to nonmetallic one at around the density $9 \text{g/cm}^3$, which is between $13.6 \text{g/cm}^3$ at ambient conditions and the critical density, $5.8 \text{g/cm}^3$. This metal-nonmetal (M-NM) transition of fluid Hg is confirmed by many experiments and some simulations [3]; electronic feature of fluid Hg depends on the density [3].

Electronic properties of fluid Hg are strongly affected by an impurity. Only about 1% metal-impurity, for example In [4, 5], Cd, Bi and so on [6], causes enhancement (or diminishment) of electrical conductivity by as much as one order of magnitude through the volume contraction (or expansion) [5]. The impurity effect in fluid Hg is clearly observed only near the critical point. This experimental fact means that the temperature and pressure where the M-NM transition occurs can be controlled by impurities.

Recently, we have carried out small-angle x-ray scattering (SAXS) measurements of supercritical fluid Hg and observed an enhancement of fluctuations near the metal-nonmetal (M-NM) transition region [1]. It is a new type of fluctuations and may be the long-waited evidence that the M-NM transition in fluid Hg is a first-order phase transition which was first proposed by Landau and Zeldovich more than half a century ago [2]. In order to confirm the phenomena and to discuss further details, we have studied the impurity effect on the fluctuations.
Figure 1. State points of the measurements for Hg-0.2% (open circles) and pure Hg (solid triangles) samples. Solid line is a vapour pressure curve and C.P. denotes the critical point of pure Hg. M-NM transition occurs at around the density 9g/cm³.

Figure 2. Densities estimated from the x-ray transmission data: open circles and solid triangles indicate Hg-0.2%Bi and pure Hg samples respectively. Difference between the two samples can be seen in the thin- and thick-hatched areas. Solid line indicates the density from $\rho$-PT data [8].

near the M-NM transition in fluid Hg. In this article, we report the results of SAXS and density measurements for fluid Hg and Hg-0.2%Bi.

2. Experiment
The experiments were carried out at the High Energy X-ray Diffraction beamline BL04B2 of SPring-8 in Japan. The energy of incident x-ray is 37.8keV and the scattered x-ray was detected with an imaging plate of 300×300 mm² located at 2.9 m distance from the sample position. In order to determine the sample density and to make absorption corrections, we also measured the intensity of transmitted x-ray with an ionization chamber.

Both Hg-0.2%Bi and pure Hg samples with a thickness of about 110 $\mu$m were contained in a poly-crystalline sapphire cells. Each cell was located in a high-pressure vessel equipped with single-crystalline diamond windows for both incident and scattered x-rays. The vessel was pressurized up to $P = 200$ MPa by He gas and heated up to $T = 1600$ °C by W heaters. Further details of the experiment were shown in [1, 7].

We measured SAXS spectra and density with increasing temperature. Open circles and solid triangles in Fig. 1 indicate the state points of the measurements for Hg-0.2%Bi and pure Hg samples, respectively. The measurements were done at almost the same state points for the two samples. Empty cell measurements were separately carried out for background (including scattering intensity from sapphire cell and He gas) subtraction. The structure factor $S(Q)$, where $Q$ is the momentum transfer defined by $Q = 4\pi \sin \theta / \lambda$ (the scattering angle $2\theta$ and the wavelength of x-ray $\lambda$), is deduced with the background subtraction and normalization using the scaling factor for the absolute SAXS intensity obtained from compressed He gas measurements.
Figure 3. $S(Q)$ of Hg-0.2%Bi. Each spectrum corresponds the one at the temperature indicated beside it. The spectra are displaced each other by 0.2 for clarity.

Figure 4. Temperature variations of (a) zero-Q-limit static structure factor, (b) correlation length and (c) short-range correlation length deduced from SAXS spectra. Each symbol denotes the value of each sample in the figure. Hatched regions correspond to those in Fig. 2.

3. Results and Discussion

Figure 2 shows the temperature dependence of the density estimated by the x-ray transmission measurements. Open circles and solid triangles are densities $\rho$ of Hg-0.2%Bi and pure Hg samples, respectively. Solid line indicates the density calculated from the phase diagram of pure Hg by Götzlaff [8], which is consistent with the solid triangles. Impurity effects can be seen only in the temperature region from 1450 to 1515 °C (thin- and thick hatched areas) where the density depends on temperature differently between the samples. From 1495 to 1515 °C (thick-hatched areas), the density abnormally increases with increasing temperature in Hg-0.2% sample, which is the sign of the phase separation. In this region, the increase of Bi ratio is proved by the x-ray fluorescence experiment [9] separately carried out.

Figure 3 shows $S(Q)$ of Hg-0.2%Bi at temperatures indicated beside it. With increasing temperature, $S(Q)$ at low-$Q$ increases and its slope becomes steeper from 25 to 1490 °C, the former exhibits the maximum at around 1490 °C, and the former decreases and the latter becomes moderate at higher temperatures.

We analyzed $S(Q)$ using Ornstein-Zernike equation [10] given as,

$$S(Q) = S(0)/(1 + \xi^2Q^2),$$

(1)
where $\xi$ is the correlation length and $S(0)$ is the zero-Q-limit of the static structure factor. The optimized $S(0)$ and $\xi$ are shown in Fig. 4(a) and (b), respectively. Open circles and solid triangles denote Hg-0.2%Bi and pure Hg, respectively. Solid line in Fig. 4(a) indicates $S(0)$ calculated from $\rho PT$ data of pure Hg [8] using the equation $S(0) = k_B T (d\rho/dP)_T$ ($k_B$: Boltzmann factor). Closed triangles and solid line in Fig. 4(a) are in fairly good agreement with each other. Figure 4(c) shows short-range correlation length $R$ [10] (Debye persistence length [11, 12]) defined by $R \equiv \xi/\sqrt{S(0)}$. $R$ is related to the second moment of the Ornstein-Zernike direct correlation function and expected to be constant for the ideal gas [12]. In the present results, $R$ changes moderately while $S(0)$ and $\xi$ diverges near the critical density in pure Hg, which is consistent with the central assumption that the direct correlation function is short-ranged even near the critical density. On the other hand, $R$ in Hg-0.2%Bi shows complicated behaviour probably due to phase separation. $R$ is twice larger at around 1450 $^\circ$C, where M-NM transition occurs in both samples, which is consistent with the previous result [1].

Here one can notice that the temperature dependencies of $R$ in both samples are very similar to those of $\rho$ in Fig. 2. To display it more clearly, we draw thin- and thick- hatched areas in 4, corresponding to those in Fig. 2: Differences in $S(0)$, $\xi$ and $R$ between the two samples can be seen only in these hatched areas. The present result that $R$ changes following $\rho$ suggests that $R$ represents the metallic nature of the sample because the electronic features (electrical conductivity) of Hg and its impurity systems are closely related to the density [3, 5].

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