A Peculiar Fluctuation in the Metal-nonmetal Transition Observed in the Supercritical Fluid Mercury

More than half a century ago, Landau, the winner of the 1962 Nobel Prize in physics, predicted that fluid Hg may undergo a first-order metal-nonmetal (M-NM) transition with volume expansion [1]. The M-NM transition in fluid Hg was later confirmed by electrical conductivity and thermopower measurements by Hensel and Frank in 1966. Fluid Hg is now known to undergo the M-NM transition with decreasing density, ρ, from 13.6 g·cm^{-3} under ambient conditions to 9 g·cm^{-3} near the critical point at a high temperature and high pressure (see the phase diagram in Fig. 1). However many experiments have indicated a gradual M-NM transition, *without* evidence of the first-order phase transition. Figure 1 shows the phase diagram of pressure-temperature plane for fluid Hg indicating the relation of the thermodynamic states between the M-NM transition and the critical point (critical data of Hg: T_C = 1751 K, P_C = 167.3 MPa, ρ_C = 5.8 g·cm^{-3}).

Here we report on our recent small-angle X-ray scattering (SAXS) measurements of fluid Hg under extreme conditions, where we found a fluctuation inherent to the M-NM transition [2] consistent with a first-order phase transition. The work was carried out at the high energy X-ray diffraction beamline **BL04B2** [3]. A monochromatized beam of X-rays at 37.8 keV energy was incident on the sample, and scattered

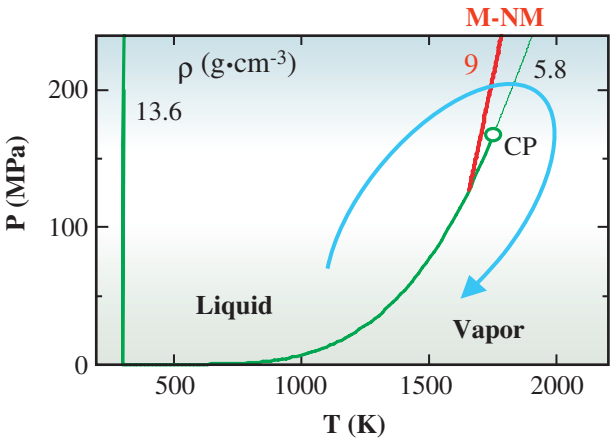

Fig. 1. Phase diagram of fluid Hg on pressure-temperature plane. The bold solid curve denotes the saturated-vapor pressure curve and the open circle at the end is the critical point. Also shown are the isochors of 13.6 g·cm^{-3} (thin solid line), 9 g·cm^{-3} (red bold line) and 5.8 g·cm^{-3} (thin solid line). Continuous volume expansion from liquid to vapor is possible through the supercritical region, as indicated by the light blue arrow.

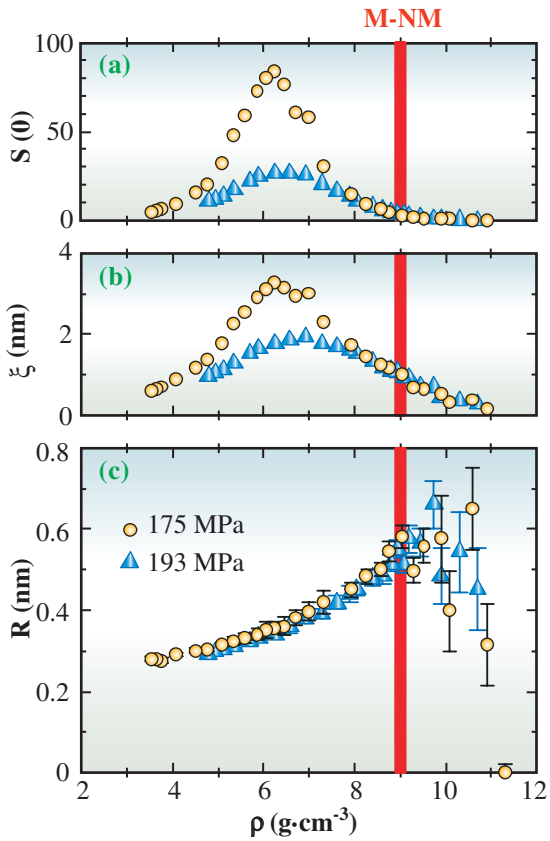

Fig. 2. Density fluctuation *S(0)* **(a)**, correlation length of the fluctuation ξ **(b)** and short-range correlation length *R* **(c)** of fluid Hg at 175 MPa and 193 MPa as a function of density ρ. The red band denotes the M-NM transition region at 9 g·cm^{-3}.

X-rays were detected by an imaging plate at a distance of approximately 3 m. The observable modulus of the scattering vector was from 0.4 nm^{-1} to 4 nm^{-1}. Details of the experiments have been described in [2].

A clear increase of SAXS intensity was observed at the M-NM transition region at 9 g·cm^{-3} for the first time. This means that a medium-range inhomogeneous structure appears at the M-NM transition. We analyzed the observed spectra using Ornstein-Zernike theory to understand the structure. Figures 2(a) and 2(b) show the density fluctuation *S(0)* and the correlation length of the fluctuation ξ as functions of density, ρ. Near the critical point of around 6 g·cm^{-3}, *S(0)* and ξ depend on pressure, and their values become small as the pressure is increased beyond the critical point. However in the M-NM transition region at 9 g·cm^{-3}, *S(0)* and ξ are nearly independent of pressure, which hints that the inhomogeneous structure has an origin different

from the critical fluctuation. Actually, the short-range correlation length R, which is deduced from $S(0)$ and ξ, indicates an anomaly in the M-NM transition as seen in Fig. 2(c). While ξ diverges as it approaches the critical point, R does not change much near the critical point at around 6 g·cm^{-3}. This is consistent with the central assumption in Ornstein-Zernike theory, that the direct correlation between particles is short-range. In contrast, R exhibits a maximum value in the M-NM transition while $S(0)$ and ξ decrease as the M-NM transition is approached. These results suggest that the fluctuation in the M-NM transition is different from the critical fluctuation and that the large R is strongly related to the first-order phase transition.

Further analysis shows that the fluctuation in the M-NM transition consists of slightly dense and slightly rarefied domains approximately 1 nm in diameter, and that these domains have a lifetime of several picoseconds [2]. The dense and rarefied domains have metallic and nonmetallic properties, respectively. Figure 3 shows a snapshot of the atomic configuration in expanded fluid Hg at (a) the M-NM transition and (b) near the critical point, obtained from Monte Carlo simulations using the effective pair potentials deduced from the measured static structure factors. Magenta and light blue particles in the figure show high and low density regions, respectively, calculated as an average over 1 nm spheres. In Fig. 3(a), the aggregates are mixed, as indicated by the yellow and white broken circles in the M-NM transition. This suggests that the first-order M-NM transition occurs as a fluctuation on a ~1 nm length scale. In contrast, the aggregates in Fig. 3(b) are almost all light blue, which suggests a nonmetallic property of the critical fluctuation. Thus, the present study clarifies that the M-NM transition in expanded fluid Hg exhibits the property of the first order phase transition as predicted by Landau.

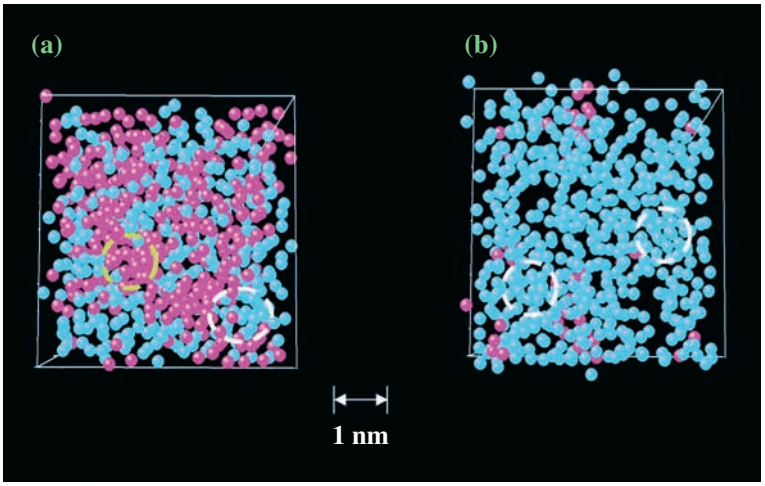

Fig. 3. Snapshot of atomic configuration in the M-NM transition **(a)** and near the critical point **(b)** in expanded fluid Hg. Magenta and light blue particles denote local densities higher and lower than 9 g·cm^{-3}, respectively.

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References

[1] L. Landau and G. Zeldovich: Acta Phys. Chem. USSR **18** (1943) 194.
[2] *M. Inui, K. Matsuda, D. Ishikawa, K. Tamura and Y. Ohishi: Phys. Rev. Lett.* ***98*** *(2007) 185504.*
[3] M. Isshiki *et al.*: Nucl. Instrum. Meth. Phys. Res. A **467-8** (2001) 663.