Medium-Range Fluctuations Accompanying the Metal-Nonmetal Transition in Expanded Fluid Hg

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We have carried out small angle x-ray scattering experiments of expanded fluid Hg in the metal-nonmetal (M-NM) transition region around 9.0 $\mathrm{g\,cm^{-3}}$. Increase of small angle scattering intensity following the Ornstein-Zernike equation is clearly observed in the M-NM transition region as well as near the liquid-vapor critical point at 5.8 $\mathrm{g\,cm^{-3}}$. The short-range correlation length, R, becomes twice as large in the M-NM transition region as in the critical region. The enhancement of R in expanded fluid Hg suggests a new type of fluctuations reflecting a first-order M-NM transition.

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More than half a century ago, Landau and Zeldovich [1] pointed out that fluid Hg is a probable candidate that undergoes a "first-order" metal-nonmetal (M-NM) transition with volume expansion besides the M-NM transition on evaporation. Theoretical investigations on metallic fluids have actually reported that the volume dependence of free energy indicates the first-order M-NM transition [2,3]. However, there has been so far no experimental evidence of the first-order M-NM transition. In fact, the first indication of the M-NM transition in expanded fluid Hg was electric conductivity data by Hensel and Frank [4], which showed a gradual decrease of the conductivity in the transition. Many experimental results [5] suggest that fluid Hg transforms to a nonmetallic state continuously with decreasing density, ρ, from 13.6 $\mathrm{g\,cm^{-3}}$ at the ambient conditions to 9 $\mathrm{g\,cm^{-3}}$ near the critical point (the critical temperature, pressure, and density of Hg are $T_c = 1751$ K, $P_c = 1673$ bar, $\rho_c = 5.8\,\mathrm{g\,cm^{-3}}$, respectively [6]). Strong thermal agitation at high temperature has been believed to obscure discontinuous nature in the first-order transition. Thus the prediction by Landau and Zeldovich has been left without further investigations.

Recent technical developments have made accurate structural studies under extreme conditions at high temperature and high pressure possible. Inelastic x-ray scattering (IXS) technique has been used to study dynamics of expanded fluid Hg and an anomaly has been observed that the dynamical sound velocity at low momentum transfer from 0.2 to 0.4 $\mathrm{Å^{-1}}$ is triple as fast as the adiabatic sound velocity in the close vicinity of the M-NM transition at 9 $\mathrm{g\,cm^{-3}}$ [7]. Now small angle X-ray scattering (SAXS) intensity has increased clearly in the M-NM transition in expanded fluid Hg. These experimental facts as well as local structure obtained from wide-angle x-ray scattering (WAXS) measurements [8,9] indicate that the M-NM transition in expanded fluid Hg is strongly correlated with fluctuations and structural instability. It is quite timely to reconsider the Landau-Zeldovich's prediction to understand the real mechanism of the M-NM transition in expanded fluid Hg.

The experiments were carried out on the high-energy x-ray diffraction beam line (BL04B2) at SPring-8 in Japan. The details of the beam line are given in the literature [10]. For SAXS measurements at high temperature and high pressure, 38 keV ($\lambda = 0.329$ Å) x rays monochromatized using flat Si(1 1 1) surface were incident on the sample and the scattered x rays were detected with an imaging plate of $300 \times 300\ \mathrm{mm^2}$ located at 2.9 m from the sample position. The accessible Q is from 0.04 to 0.4 $\mathrm{Å^{-1}}$, where Q, the modulus of the scattering vector, is $4\pi \sin\theta/\lambda$, and 2θ is the scattering angle. A vacuum path was mounted between the sample stage and the imaging plate to reduce the background from the air. The imaging plate was exposed for 20 minutes per pattern. To make absorption corrections, the intensity of the transmitted x ray was monitored using an ionization chamber before and after each SAXS measurement. We estimated ρ of the fluid sample using the transmission data.

The Hg sample of 99.999% purity and 100 μm thickness was loaded in a sapphire cell [11]. No parasitic scattering was observed from the cell even at high temperature. He gas of 99.9999% purity was used as a pressurizing medium. The high-pressure vessel, which can be operated up to 2000 K and 2000 bar, had diamond windows of 6 mm diameter and 2.5 mm thickness for scattered x rays and 3 mm diameter and 2 mm thickness for an incident beam. Using synthetic diamond of the highest quality, the background from the windows was much reduced compared to the previous high-pressure vessel with a Be window [12]. We measured SAXS spectra for expanded fluid Hg at 1750, 1800, and 1930 bar at temperatures from 1273 to 1860 K. The backgrounds were measured at the same pressures and temperatures. By comparing the observed SAXS spectra of He gas with the calculated one, we could determine a scaling factor of the absolute scattering intensity and deduce the structure factor, $S(Q)$, of fluid Hg [12].

Several $S(Q)$'s of fluid Hg in the M-NM transition region at 1930 bar are shown in Fig. 1. $S(Q)$ has no small angle scattering from 13.6 $\mathrm{g\,cm^{-3}}$ at the ambient conditions to 11.4 $\mathrm{g\,cm^{-3}}$, where the electronic property of fluid Hg is known to be metallic. With decreasing ρ, $S(Q)$ at small Q starts to increase around 10 $\mathrm{g\,cm^{-3}}$. It becomes gradually large when the M-NM transition is approached. Clear increase at small Q was observed in $S(Q)$ around 9.0 $\mathrm{g\,cm^{-3}}$ in the M-NM transition.

With further volume expansion, the critical opalescence was observed near ρ_c. We analyzed the spectra using Ornstein-Zernike equation [13].

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

where ξ is the correlation length of a density fluctuation, and $S(0)$ corresponds to fluctuations in a particle number $\langle(\Delta N)^2\rangle/\langle N\rangle$, where $\Delta N = N - \langle N\rangle$ and $\langle\rangle$ denotes the average. The inset in Fig. 1 shows Ornstein-Zernike plots of $S(Q)$ at 6.3 and 9.1 $\mathrm{g\,cm^{-3}}$. The spectra satisfy the scattering law of Eq. (1) in the M-NM transition region as well as in the critical region.

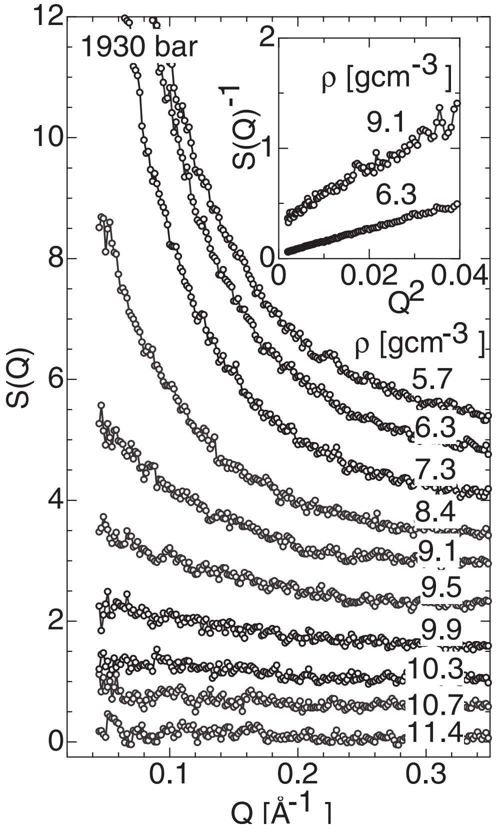

FIG. 1. Selected structure factor $S(Q)$ in the M-NM transition region of fluid Hg at densities from 11.4 to 5.7 $\mathrm{g\,cm^{-3}}$ at 1930 bar. The successive spectra are displaced by 0.5 for clarity. The inset shows Ornstein-Zernike plots of $S(Q)$ at 6.3 and 9.1 $\mathrm{g\,cm^{-3}}$.

We carried out least-square fits for the Ornstein-Zernike plots from 0.04 to 0.15 Å^{-1} using Eq. (1). The optimized parameters, $S(0)$ and ξ, are shown as a function of ρ in Fig. 2. The $S(0)$ and ξ at 1750 bar take a maximum at 6.2 $\mathrm{g\,cm^{-3}}$ around ρ_c. With increasing pressure the maximum become small. This is a self-evident fact that the critical scattering becomes weak when the critical point is remote. Note that the maximum positions shift towards larger ρ with increasing pressure and the shift is more remarkable in ξ than $S(0)$. It should be noticed that $S(0)$ and ξ do not depend on pressure at all in $8 < \rho < 10\ \mathrm{g\,cm^{-3}}$. This behavior is in contrast to that in molecular fluids such as water and carbon dioxides. In molecular fluids plots of $S(0)$ and ξ as a function of ρ are almost symmetrical with respect to ρ_c [14].

We estimate microscopic fluctuations in the M-NM transition quantitatively. $\langle N\rangle$ in the sphere of ξ in radius is about 100 and $\langle\Delta N\rangle$ is about 17, deduced from $\xi = 10$ Å and $S(0) = 3$ at 9 $\mathrm{g\,cm^{-3}}$. An estimation indicates that ρ in the sphere is fluctuating from 7.5 to 10.5 $\mathrm{g\,cm^{-3}}$. Kresse and Hafner [15] pointed out from their first-principles molecular dynamics simulation that 6*s* and 6*p* bands open at 8.8 $\mathrm{g\,cm^{-3}}$. Experimental results of a cluster beam for Hg reported by Rademann *et al.* [16] revealed that an isolated Hg_{20} cluster has a sign of metal. Then aggregate of about a hundred atoms is enough to be a real metal. These facts suggest that the electronic property in the sphere is fluctuating between metallic and nonmetallic ones in the M-NM transition. On the other hand, the same estimation indicates that ρ in the sphere is fluctuating from 5.2 to 7.3 $\mathrm{g\,cm^{-3}}$ at ρ_c, suggesting that it remains insulating.

To obtain further information on the fluctuations in the M-NM transition, we deduce the short-range correlation

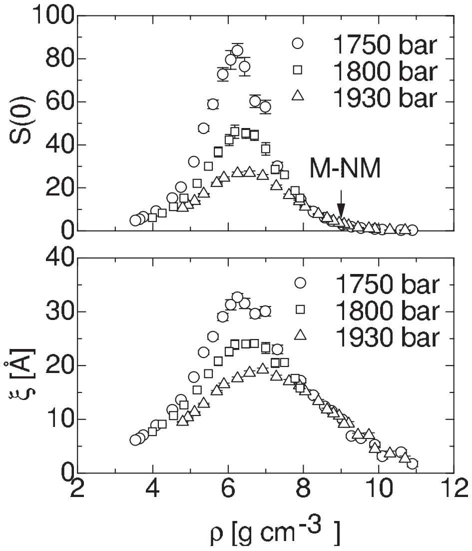

FIG. 2. The optimized fluctuations in a particle number $S(0)$ (upper panel) and the correlation length ξ (lower panel) at 1750 bar (○), 1800 bar (□), and 1930 bar (△).

length, $R\ [=\xi/\sqrt{S(0)}]$ [13]. R is related to the second moment of the Ornstein-Zernike direct correlation function, $c(r)$, as $R=\sqrt{-n\alpha}$, where n is number density and α, the coefficient of Q^2, in the expansion of $c(Q)$, the Fourier transform of $c(r)$. Here $c(Q)$ is related to $S(Q)$ by $1-nc(Q)=S(Q)^{-1}$. Figure 3 shows R as a function of reduced density ρ/ρ_c. $S(0)$ and ξ in fluid Hg depend on pressure clearly as shown in Fig. 2 but R hardly depends on it. In general, ρ dependence of R is moderate in molecular fluids, as an example of supercritical water [17,18] in Fig. 3. Near ρ_c, R in the supercritical water is close to the nearest intermolecular (O-O) distance. Similarly R in expanded fluid Hg corresponds to the nearest neighbor distance as seen in the pair distribution function, $g(r)$, at ρ_c [8,9]. These facts are consistent with the central assumption by Ornstein-Zernike that $c(r)$ is strictly short ranged at the critical point [13] and suggest that the primitive length describing the divergence of ξ is the nearest neighbor distance in the fluids. However, with increasing density, R in expanded fluid Hg increases gradually and shows a maximum in the M-NM transition region around 9 g cm^{-3}. The maximum value corresponds to the second peak position in $g(r)$.

The anomaly in R arises from the fact that $S(0)$ and ξ in $\rho>\rho_c$ have pressure dependence completely different from those in molecular fluids as seen in Fig. 2. Thanks to the careful studies of the pressure dependence of SAXS in the wide density region, we could show the origin of SAXS in $8<\rho<10$ g cm^{-3} different from the critical scattering around 5.8 g cm^{-3}. The present results indicate that the SAXS observed in $8<\rho<10$ g cm^{-3} is closely connected with the M-NM transition. The fluctuation in the M-NM transition region does not vary with pressure and the distinct SAXS is characterized by the small values of $S(0)$ of about 3 and ξ of about 10 Å. We carefully investigated $S(0)$ values from SAXS and the thermodynamic rule and concluded that they are consistent with each other within their experimental accuracy. In addition, the profile of SAXS spectra in the M-NM transition follows the Ornstein-Zernike scattering law. These results suggest that the ionic structure and the isothermal compressibility are determined self-consistently with the fluctuations in the M-NM transition.

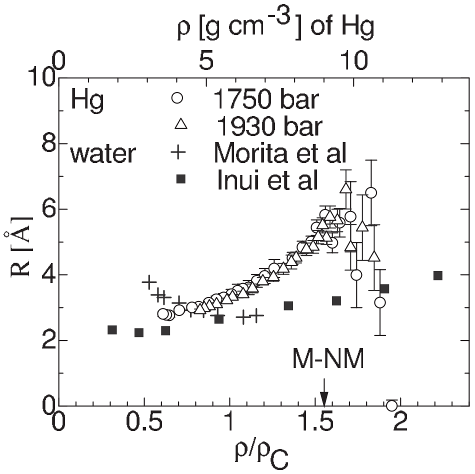

FIG. 3. The short-range correlation length R as a function of reduced density, ρ/ρ_c. ○ and △ denote data from SAXS at 1750 and 1930 bar, respectively. Also shown are R of supercritical water at constant temperature at 663 K (+) [17] and at constant pressure at 400 bar (■) [18].

R is a crucial parameter because it is related to the thermodynamic stability of fluids. For an inhomogeneous fluid where the local number density of particles, $n(r)$, exhibits slow spatial variation, the deviation in the free energy, δF, as a function of $\delta n(r)$ may be expressed by [13],

$$\delta F=\int d\mathbf{r}\{a_0\delta n(r)^2+(-\alpha k_BT)[\nabla\delta n(r)]^2+\cdots\}, \quad (2)$$

where $-\alpha=R^2/n$ and k_B the Boltzmann constant. a_0 is a constant depending on thermodynamic states. $-\alpha>0$ means the increase of free energy with increasing spatial variations in $\delta n(r)$ and a large magnitude of $-\alpha$ corresponding to large R acts as promoting phase separation. Kitamura [3] investigated the M-NM transition in expanded fluid Hg by varying $-\alpha$ and reported that the M-NM transition behaves like a first-order phase transition when $-\alpha$ is large. The result shown in Fig. 3 gives the experimental evidence.

The origin of large R in the M-NM transition must be related to the variation of electronic properties in domains induced by the fluctuations. Although SAXS does not observe the electronic properties in expanded fluid Hg, the effective pair potential, $\varphi(r)$, deduced from $S(Q)$ by WAXS and SAXS measurements may give the information on the electronic properties. We estimated $\varphi(r)$ by means of the inverse method proposed by Reatto *et al.* [19] based on the modified hypernetted chain approximation [20]. We iterated a Monte Carlo simulation using 3375 or 4096 particles varying $\varphi(r)$ until the experimental and simulated $g(r)$'s agree with each other. Figure 4 shows $\varphi(r)$ obtained at several densities. In the vapor phase ($\rho<5.7$ g cm^{-3}),

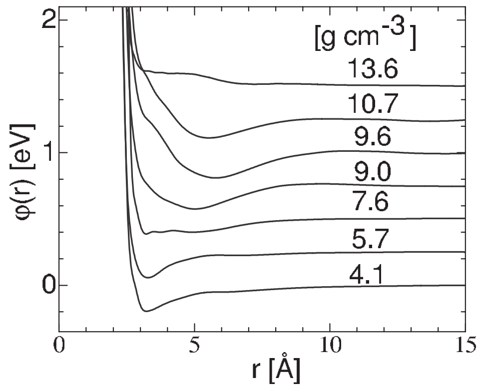

FIG. 4. The effective pair potential $\varphi(r)$ at densities indicated in the figure deduced from $S(Q)$ obtained experimentally. Each $\varphi(r)$ is shifted by 0.25 eV for clarity.

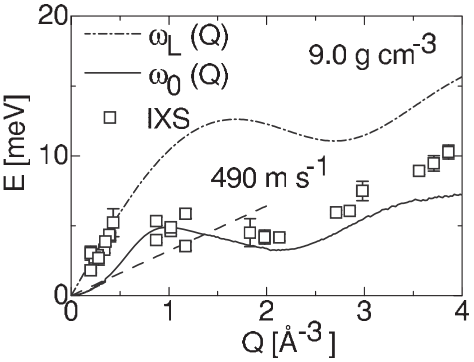

FIG. 5. The normalized second and fourth frequency moments, $\omega_0(Q)$ and $\omega_L(Q)$, calculated from $S(Q)$ and the $\varphi(r)$ at 9 g cm^{-3}, respectively. Also shown are the excitation energy obtained from IXS and the adiabatic sound velocity by squares and a broken line, respectively.

$\varphi(r)$ has a profile like a Lennard-Jones potential as reported by Munejiri *et al.* [21]. With increasing ρ, the minimum at 3.2 Å in the vapor phase becomes shallow and changes to a repulsive soft core while there appears a broad minimum at 5 Å in the M-NM transition at 9 g cm^{-3}. $\varphi(r)$ in the metallic state in liquid Hg at the ambient conditions is much different from that in the expanded states but it seems consistent with a reported one which has a purely repulsive profile [22]. These results indicate that the variation of the attractive part in $\varphi(r)$ is closely correlated with ρ dependence of R.

When the phase separation of metallic and insulating domains occurs as indicated by large R in the M-NM transition region, the lifetime of the domains is expected to be long. To estimate the lifetime we examined the fast sound in the M-NM transition [7]. When $\varphi(r)$ is known one can calculate the normalized fourth frequency moment, $\omega_L(Q)$. By taking the approximation in the review article [23], we obtained the Einstein frequency of 8.8 meV from $d^2\varphi(r)/dr^2$ and $\omega_L(Q)$ as shown in Fig. 5. As clearly seen in the figure the excitation energy of the fast sound disperses as fast as $\omega_L(Q)$ at small Q. This fact suggests that the fast sound in the M-NM transition is regarded as the high-frequency sound speed defined in the viscoelastic theory [24] which should appear when the condition in the simple Debye approximation, $\omega\tau \gg 1$, is satisfied, where ω is the angular frequency of the collective mode and τ the relaxation time. The estimation from the excitation energy at 0.2 Å^{-1} in Fig. 5 allows τ much longer than 0.8 ps. Since the relaxation process of the high-frequency sound mode is strongly correlated with the persistency of the domains, the lifetime of domains is considered to be equivalent with τ and must be much longer than 1 ps.

In conclusion, the enhancement of SAXS intensity in the M-NM transition in expanded fluid Hg is strongly related to a new style of fluctuations between metallic and nonmetallic domains. Large R in the M-NM transition obtained from the present SAXS data must be a first evidence of the first-order M-NM transition while thermodynamically the discontinuous change in the first-order transition is disrupted by strong thermal agitation. These results clarify a real picture of the first-order M-NM transition in fluid Hg predicted by Landau and Zeldovich [1].

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