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Section 14. Metallic liquids and glasses

Dynamic structure factor of liquid mercury

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Abstract

The low momentum dynamics of liquid mercury has been investigated by means of inelastic neutron scattering and molecular dynamics (MD) simulations. Due to the rather high incoherent cross-section and the high mass of mercury, the measured dynamic structure factor is dominated by the self-correlation function which has been studied in details. The low momentum collective dynamics are also made accessible by the very good energy resolution of the experiment. Collective modes are clearly visible against the incoherent scattering up to a momentum transfer of 0.6 $\mathring{A}^{-1}$. The self-dynamics, as resulting from either the experiment and MD simulations, turn out to be characterized by two time scales.

Keywords: 61.12.−q; 61.25.Mv; 71.10.Ca; 83.10.R

1. Introduction

The investigation of the dynamic properties of liquid metals has been constantly addressed over the years because of that richness of features in the excitation spectra and in the self-motion which enable to test different theories of the liquid state. In particular, liquid metals microdynamics cannot be simply interpreted by extending the description of the liquid from classical hydrodynamics [1]. Among liquid metals, the properties of molten alkali-metals have been largely studied by both inelastic scattering experiments [2–7] and molecular dynamics (MD) simulations [8–12] based on effective ion-pair potentials, like, for instance, that given by Price, Singwi and Tosi (PST potential) [13,14]. Indeed, the treatment of low electron density systems with a free-electron-like structure is simplified by the possibility of modeling the electron component by an interacting homogeneous electron gas at the suitable density. The results of

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these investigations show that systems quite different as to atomic mass and number density, all sustain density fluctuation modes characterized by a rather long lifetime and a dispersion relation extending up to a momentum transfer well outside the hydrodynamic regime.

A previous experimental study of liquid lead [15] has shown that long living collective excitations exist also in this polyvalent metal. This finding, coupled to the findings in alkali-metals, suggests that the interatomic interactions in simple and polyvalent liquid metals strongly favor the presence of long living collective excitations. However, due to the limited experimental data available on these systems, this statement cannot be considered as a definitive one. In this scenario, the study of the dynamics of a high-electron-density system would be fundamental to clarify the effects of strongly density dependent ion–ion interactions on microscopic dynamics. Mercury, which has a high-electron density and a rather low sound velocity, which enables inelastic neutron scattering measurements to be performed without tight cinematic constraints, is a particularly attractive system. Recent measurements in highly absorbing systems like liquid Cs [4] and $Cs_{50}K_{50}$ alloy [6] that liquid mercury can be studied on a similar accuracy level. Moreover, the presence of a rather high incoherent contribution allows one to approach also the self-dynamics of the system.

Most of the predictions of the liquid-metal dynamics, such as the persistence of well defined modes outside the strict hydrodynamic region or the occurrence of memory effects with a time scale of the order of the collision time in high density systems, have been provided by MD simulations and have been tested by inelastic neutron and X-ray scattering experiments. The simultaneous use of these two techniques and the comparison of experimental and numerical results allow a deeper understanding of the microscopic mechanisms at the basis of liquid-metal dynamics, the efficacy of this comparison being strictly related to the choice of a potential that reproduces in a realistic way the experimental data available for the studied system. Indeed, the reliability of MD findings depends on the capability of the interatomic potential, used to simulate the ion–ion interaction, in reproducing the real system. We have developed a new simple form for the ion–ion effective potential in liquid mercury which depends only on average conduction electron density of the system and reproduces quite well the static structure factor, the diffusion coefficient and the sound velocity of our system in a wide temperature and density range along the liquid-vapor coexistence curve [16,17]. We have performed large scale MD simulation, based on this potential, to obtain the collective and self-dynamics of liquid mercury to be compared with the measured total dynamic structure factor.

2. Experimental results

The measurements on liquid mercury were carried out at the three-axis spectrometer IN1 installed at the hot source of the High Flux Reactor ILL in Grenoble and the description of the experiment is given in a recent work [18]. Here we remind that a fixed final wave vector of 4.5 Å^{-1} was selected in order to obtain a final energy high enough to reduce the absorption cross-section of mercury as much as possible and to get, at the same time, a good energy resolution. The experimental setup was carefully chosen to optimize the measurement. High quality data were collected down to 1° scattering angle. All the measurements were carried out at 293 K on a 99.999 % pure mercury sample with natural isotopic composition. The scattered intensity from the sample was measured at seven wave vector transfers Q, namely at $Q = 0.25$, 0.3, 0.4, 0.6, 0.8, 1.0 and 1.2 Å^{-1}. The experimental data were corrected by applying the same procedure successfully used in previous experiments [6,19]. The sample intensity, corrected for background and multiple scattering, is shown in Fig. 1 versus energy at four of the measured wave vectors. Considering that the elastic resolution obtained from the vanadium measurement amounts to 1.16 meV, the features observed in Fig. 1 are expected to be related to the mercury dynamics. A close inspection of Fig. 1 suggests a wave vector-dependent structure of the inelastic signal. In particular, the analysis of the low Q-region, enables one to infer the velocity of the dispersive mode which turns out to be of the order of 2100 m/s [18]. Such a value is

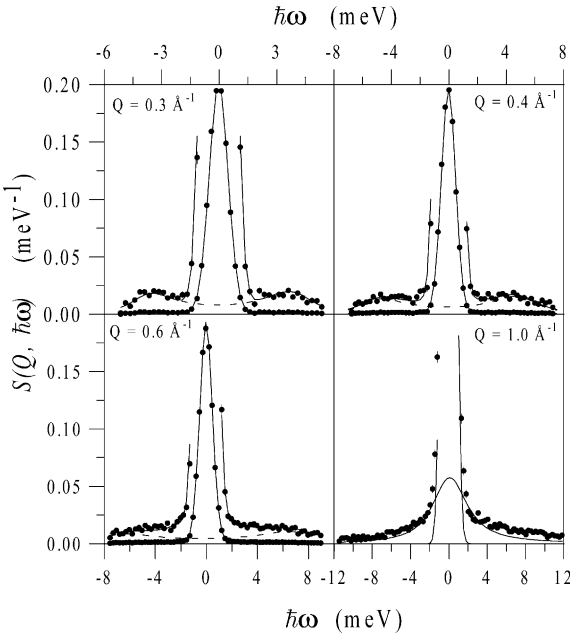

Fig. 1. Dynamic structure factor $S(Q,\hbar\omega)$ of liquid mercury as a function of energy transfer at four values of wave vector transfers. The experimental data (•) are also shown on a scale expanded by a factor ten to emphasize the inelastic structures. The full lines represent the curves calculated according to the fitting model described in the text. At $Q = 0.3$, 0.4 and 0.6 Å^{-1} the inelastic contribution (DHO) is also shown, whereas at $Q = 1.0$ Å^{-1} the two quasi-elastic (Lorentzian) contributions are shown.

much larger than the sound velocity in mercury at 293 K as measured by ultrasound spectroscopy [20], namely 1470 m/s. Actually, anomalous dispersion has been often observed in metals [7,15,21], but an impressively large effect as the present one has been reported only in water [19], that is in a profoundly different system. At high Q, a progressive merging of the collective mode signal into a quasi-elastic signal is observed and the extension of this quasi-elastic structure is well beyond the resolution-limited central peak, which is present at all wave vector transfer values.

3. MD simulation results

A large scale MD simulation, based on the simple analytic model for the effective ion–ion potential of liquid mercury presented in Ref [16], was carried out. The quality of the proposed potential had been previously tested against various measured static quantities and over a wide range of temperatures along the liquid-vapor coexisting curve. The base assumption is that the potential of mercury could, in a first approximation, be constructed by simply taking the sum of a long and a short range part. The short range part, representing the repulsive interaction due to the overlap of electron cores, was modeled by means of an inverse power law dependence, whereas the long range part was taken as the asymptotic form of the effective ion–ion interaction [22–25], screened by the conduction electrons. The effective ion–ion potential was therefore written as

$$V(r) = \frac{A}{r^{12}} + B\frac{\cos(2k_{\mathrm{F}}r + b)}{r^3}\exp(-k_{\mathrm{TF}}r) \qquad (1)$$

where r is the ion–ion distance, $2k_{\mathrm{F}}$ is the diameter of the Fermi sphere and k_{TF} is the Thomas–Fermi wave vector, i.e. the inverse of the Thomas–Fermi screening length. A, B, and b are parameters to be determined. The power of the repulsive short range part is borrowed from the Lennard-Jones potential of noble gases. An effective number of electrons per atom equal to Z^*, the effective ionic charge, was assumed to evaluate the electron number density and hence k_{F} and k_{TF}. The parameters A, B, b and Z^* were optimized by fitting the experimental data of the static structure factor $S(Q)$ [26,27], diffusion coefficient D [20] and (adiabatic) sound velocity c_{S} [28,29] of liquid mercury at room temperature, namely 298 K ($\rho = 13.55$ g cm^{-3}), to the corresponding classical MD results with the proposed potential [16].

Standard NVE simulations of a system of 87 808 atoms were performed by using a cubic box with periodic boundary conditions and leap-frog algorithm to integrate the equations of motion. Details of simulations are reported in a previous paper [17]. The total dynamic structure factor $S(Q,\omega)$ was obtained from the power spectrum (Welch method [30]) of the signal ranging from 0.1 to 1.2 Å^{-1} and by taking an average over all possible $\mathbf{Q}$ directions. Well defined collective modes, superimposed to a broad quasi-elastic contribution, are apparent [17].

4. Discussion

Considering that the incoherent cross-section of mercury is quite high as compared to the coherent contribution at small Q, the experimental data are better and more quantitatively analyzed by using a flexible model to account for the self-dynamic structure factor. As observed, the quasi-elastic peak shows a rather sharp component and a broader component which becomes dominant as Q increases. Following this observation, we modeled the dynamic structure factor using two Lorentzian functions to describe the self-dynamic structure factor and a damped harmonic oscillator to describe the coherent component. Therefore, the following equation has been used to fit the experimental dynamic structure factor:

$$S(Q,\omega) = \frac{\sigma_{\rm inc}/(4\pi)}{\sigma_{\rm inc}/(4\pi)+b^2}\,\frac{\hbar\omega/k_{\rm B}T}{1-\exp(-\hbar\omega/k_{\rm B}T)} \times\left[\frac{a_0(Q)}{\pi}\,\frac{\Gamma_0(Q)}{\omega^2+\Gamma_0^2(Q)}+\frac{a_1(Q)}{\pi}\,\frac{\Gamma_1(Q)}{\omega^2+\Gamma_1^2(Q)}\right] + \frac{b^2}{\sigma_{\rm inc}/(4\pi)+b^2}\,\frac{a_c(Q)}{1-\exp(-\hbar\omega/k_{\rm B}T)} \times\frac{\Gamma_c(Q,\omega)}{[\omega^2-\omega_c^2(Q)]^2+\Gamma_c^2(Q,\omega)}, \qquad (2)$$

where $\Gamma_0(Q)$ has been assumed to be equal to DQ^2, D being the self-diffusion constant [20], the damping function $\Gamma_c(Q,\omega)$, which is always an odd function of ω, has been approximated by $\Gamma_c \times (Q,\omega) = \alpha Q\omega$ and $\Gamma_1(Q)$, $\omega_c(Q)$, $a_0(Q)$, $a_1(Q)$ and $a_c(Q)$ have been left as free parameters. As shown in Fig. 1, the fit of the dynamic structure factor using Eq. (2) turned out to be satisfactory at all the wave vector transfers we measured. Looking at the behavior of the free parameters of the fit we observed that $\Gamma_1(Q)$ has a small, if any, Q dependence, while $\omega_c(Q)$ shows a rather linear trend up to $Q = 0.6$ Å^{-1}. Therefore, the fit was repeated assuming Γ_1 to be a constant and $\omega_c(Q) = c_0 Q$, c_0 being the collective mode velocity, using three nonlinear Q-independent parameters Γ_1, c_0 and α and three amplitudes $a_0(Q)$, $a_1(Q)$ and $a_c(Q)$, which are linear fitting parameters. We got the following results for the Q-independent parameters: $\hbar\Gamma_1 = 2.0 \pm 0.2$ meV, $\hbar c_0 = 13.8 \pm 0.5$ meV/Å^{-1} and $\hbar\alpha = 9 \pm 2$ meV Å. We found that the amplitude $a_1(Q)$ is an increasing function of Q and $a_c(Q)$ is almost constant in the region where the collective modes can be fitted to the present data. Considering that there exists also a resolution-limited quasi-elastic contribution, we think that this part of the mercury dynamics deserves a properly designed experiment. However, from the experimental data analysis, we obtained an indication of the presence of at least two time scales which characterize the mercury self-dynamics. We obtained a confirmation of this statement and a deeper understanding of the fast time process from MD simulations. To this aim we extracted the self-intermediate scattering function $F_{\rm s}(Q,t)$ from the simulation at all the experimental wave vectors. In Fig. 2 we show $F_{\rm s}(Q,t)$ at $Q = 0.3$ Å^{-1} in the time scale accessible to the experiment (≈4 ps). Looking at Fig. 2 we can see that $F_{\rm s}(Q,t)$ shows an additional process, other than the usual free diffusion, faster than the time window of the present experiment. We extracted this additional contribution modeling the self-intermediate scattering function in the following simple way:

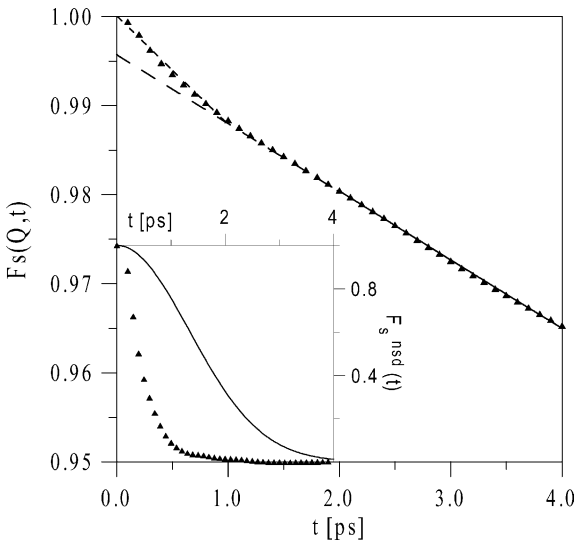

Fig. 2. Calculated self-intermediate scattering function at $Q = 0.3$ Å^{-1} as a function of time (▲), compared with a simple free diffusion model (– – –) and with a two time model (- - -). The short time contribution $F_{\rm s}^{\rm nd}$ is shown in the insert together with the experimental resolution.

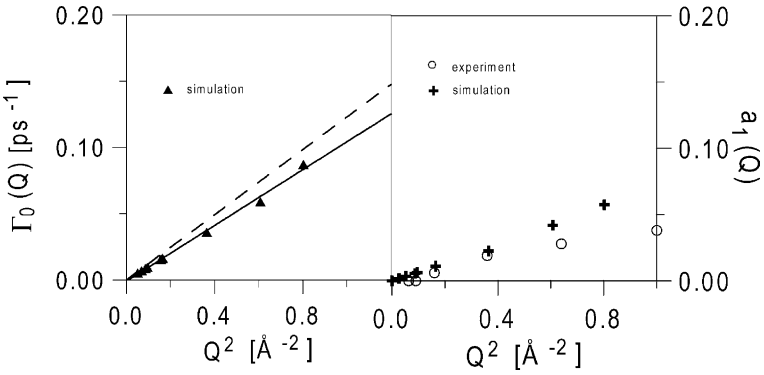

Fig. 3. The two parameters $\Gamma_0(Q)$ (▲) and $a_1(Q)$ (+), obtained from MD simulation are shown versus Q^2. In (a) the width of the free diffusion process $\Gamma_0(Q)$ is compared with that calculated from the mean square ionic displacement [16] (—) and with the experimental one (– – –). In (b) the amplitude of the short time process $a_1(Q)$ is compared with that obtained according to the fitting model of the experimental data (○). The experimental errors are smaller than symbols.

$$F_s(Q,t) = [1 - a_1(Q)]\exp[-\Gamma_0(Q)t] + a_1(Q)F_s^{nd}(t), \tag{3}$$

where the exponential term represents a free diffusive process and the second one a faster Q-independent process, fitted to the simulation results, whose time dependence is shown in the insert of Fig. 2. This additional contribution can be roughly approximated, in the time domain, by an exponential function, with a decay time of the same order as the experimental quasi-elastic contribution. In particular, we derived from the whole set of simulation data the two parameters $\Gamma_0(Q)$ and $a_1(Q)$ as a function of Q, thus obtaining that the time dependence of the additional process is Q independent while its strength is a function of Q. Both $\Gamma_0(Q)$ and $a_1(Q)$ depend on Q^2, as shown in Fig. 3. In particular from the relationship $\Gamma_0(Q) = DQ^2$ (triangles), which describes a free diffusion process, an estimate of the diffusion coefficient D was obtained and found to be in good agreement with the one calculated from the mean square ionic displacement by MD simulation [16] (full line), thus confirming the internal consistency of the calculations, and with the experimental one (dashed line). In Fig. 3 the values of $a_1(Q)$ obtained from simulations are compared with the fit results of the experimental data thus showing as the additional contribution amplitude is lower in the simulated system than in the real one. On the other end, the amplitudes of the simulated and experimental contribution are comparable.

5. Conclusion

As a conclusion, both the MD simulation and the experiment suggest the existence of two time scales in the self-dynamics of liquid mercury. In particular, the value of $\hbar\Gamma_1$ derived from the analysis of the experimental results indicates that there exists a contribution which is as fast as 1 ps, in agreement with the findings of the MD simulations. This process is essentially Q-independent, so that it should correspond to a localized diffusion and not a free diffusion in real space. This short time self-motion could be associated to the interactions between an atom and the *cage* of its nearest neighbors. This is confirmed by the behavior of particle trajectories obtained from simulations. In particular, the analysis of the displacements of a selection of particles from their initial configuration, shows that they are trapped for a time comparable with the decay time of the fast process in a cage of 2.5 Å, i.e. similar to the distance of first neighbours in mercury, before following a simple free diffusion.

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