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High frequency dynamics of liquid bismuth

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Abstract

The dynamic structure factor $S(Q,\omega)$ of liquid Bi was measured at 580 K in the Q range from 0.15 to 0.6 Å^{-1} using inelastic neutron scattering. The obtained spectra clearly demonstrate the existence of well defined longitudinal propagating modes. A positive dispersion is found in the low Q region, where the mode velocity undergoes a transition between the hydrodynamic value and a high frequency value 20% larger. The damping of the excitations does not follow the hydrodynamic Q^2 trend and is stronger than in any metallic liquid investigated so far. The quasielastic lineshape contains a broad Q-independent Lorentzian contribution, other than a small sharp peak, which has yet been observed in liquid Hg and Ga.

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1. Introduction

The study of the high frequency dynamics of liquid metals has been an issue of great interest in the last years, due to the fundamental information it can provide on several basic topics such as the dynamics of topologically disordered systems, the effective pair potential between ions in a metal and the many-body screening phenomena in the interacting electron gas. Clarifying the mechanisms at the basis of the density fluctuations decay at the crossover between hydrodynamic and single particle regime would give a deeper knowledge of the effective interactions characterizing the ionic plasma embedded in an interacting electron gas.

Inelastic neutron scattering (INS) and inelastic X-rays scattering (IXS) experiments [1] have demonstrated that simple liquid metals are systems sustaining well-defined collective excitations, which are visible in the dynamic structure factor $S(Q,\omega)$ up to about $Q_0/2$, Q_0 marking the position of the first peak of the static structure factor, $S(Q)$. On the other hand, in Lennard-Jones (LJ) fluids, side peaks in the $S(Q,\omega)$ can only be observed in the region below $\sim 0.2Q_0$, being the excitations strongly over-damped [2] above this limit. The different dynamic behavior between metallic and LJ fluids has been connected with the difference in the pair potential at short range. In particular, the LJ potential is considerably steeper respect to the interionic pair potential in simple metals. The effects of the long-range behavior of the pair potential are still not well understood. However, it has been recently shown that strongly charged ions metals, characterized by a pair potential attractive well beyond the first-neighbor distance, sustain long living density fluctuations modes [3,4].

For liquid semimetals and semiconductors the presence of collective excitations in $S(Q,\omega)$ is still object of investigation [5]. For semimetallic liquid bismuth (l-Bi) previous INS measurements supported by MD simulations have shown that density fluctuation modes are unobservable in $S(Q,\omega)$ beyond $Q \sim 0.6$ Å^{-1} [6], in contrast to what has so far been observed for other liquid metals. Below $Q = 0.6$ Å^{-1}, the MD simulations foreseen the existence of density fluctuation modes propagating with a velocity of 1520 m/s, while

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the measured ultrasonic value is 1620 m/s [7]. No experimental data are available at such small Q values [6]. The strong damping of the longitudinal modes was connected with the anomalies in the l-Bi structure associated with the long-range repulsive part of the pair potential. In particular, l-Bi $S(Q)$ shows a pronounced shoulder on the main peak, as well as some asymmetry in the next peaks [8] which are a manifestation of a set of distortions in its radial distribution function, $g(r)$. This leads to an ion–ion interaction dominated by the steeper shorter-range part of the potential which was supposed [6] to determine the strong damping of the longitudinal waves. In the companion l-Pb, in spite of being more dense, the first peak of the $g(r)$ occurs at higher distances [9], and the distortions in the $S(Q)$ are less pronounced. As a consequence, its pair potential is characterized by a weaker long-range interionic repulsion resulting in the lower damping of the longitudinal waves [10]. Following this scheme, a common behavior in whole group of polyvalent liquid metals exhibiting a pronounced shoulder in the main peak of the structure factor, is expected. However, recent scattering experiments [4] on two polyvalent liquid metals, namely Hg and Ga, characterized by strong anomalies in the $S(Q)$ [11], pointed out at the presence of long living collective excitations in the dynamic structure factor. On a different ground, a recent generalized collective modes analysis [12] of l-Bi dynamics has shown that the spectrum of collective excitations contains three branches of propagating excitations: a generalized sound mode and two high frequency kinetic branches having extremely small weights to be visible in the dynamic structure factor. In addition the estimated mode-coupling effects in l-Bi at 578 K are found to be very small to affect the speed of sound, which was essentially coincident with the hydrodynamic value and the estimated damping of the generalized sound excitations departs from the hydrodynamic Q^2 behavior for $Q > 0.2\ \text{Å}^{-1}$ but do not support a strong over-damped regime.

The detailed investigation of l-Bi dynamics is an important piece of information in order to reach a deeper knowledge of the inter-atomic potential in metals and its related dynamical effects and in particular to enhance the possible relevance of the asymmetry of the first peak of $S(Q)$, which is a common feature of many polyvalent metals. In such a context we performed small Q INS measurements of l-Bi dynamic structure factor at melting, exploiting the best experimental performances now achievable with this technique.

2. Experimental details

The INS experiment was carried out at the thermal-neutron three-axis spectrometer IN8 installed at the high flux reactor of the Institut Laue Langevin (ILL), Grenoble, France. The spectrometer configuration was optimized to achieve high-energy resolution in conjunction with operation at low scattering angles (0.2°) in order to have access to the small Q region. Tight Soller collimations of 20′, 20′, 20′, and 30′ from the reactor to the detector were chosen in combination with two wide vertically focusing crystals, namely, a (200) Cu monochromator and a (111) Cu analyzer. The instrument was settled at fixed final energy with the analyzer set to select the neutron wave vector $k\ f = 4.1\ \text{Å}^{-1}$. A remarkable reduction of the background in the small angle configuration was accomplished by means of an evacuated flight path, namely, a 1-m-diameter chamber, around the sample and careful choice of diaphragms along the flight path. The sample was a 99.9% pure bismuth powder (Sigma, Aldrich) with natural isotopic composition. The cell was a slab shaped, vacuum tight aluminum container, $70 \times 40 \times 10\ \text{mm}^3$ size and 0.5 mm wall thickness.

The measurements were carried out at 580 K employing a standard ILL furnace. Inelastic scans from the sample were collected at six values of wave vector transfer, namely, $Q = 0.15\ \text{Å}^{-1}$, $0.2\ \text{Å}^{-1}$, $0.3\ \text{Å}^{-1}$, $0.4\ \text{Å}^{-1}$, $0.5\ \text{Å}^{-1}$, and $0.6\ \text{Å}^{-1}$. Background scans were carried out on a second identical, but empty, aluminum cell, at the same Q values as the sample, while the background produced outside the sample region was measured at $Q = 0.15\ \text{Å}^{-1}$ and $Q = 0.3\ \text{Å}^{-1}$ by shielding the cell with a 1 mm thick Cd plate. The contribution of the aluminum cell was dominated by the central peak, originating from elastic small angle processes, with inelastic tails of low intensity. The instrument background contribution was very low as shown by the data of the absorbing plate.

To measure the elastic resolution of the spectrometer and to normalize the intensity data, an inelastic scan at $Q = 0.3\ \text{Å}^{-1}$ was carried out on a standard vanadium plate having a thickness equal to 2 mm, inserted into the Al cell. The vanadium spectrum was very well reproduced by the theoretical resolution function, calculated for the specific configuration of the instrument according to Ref. [13]. It resulted in a Gaussian function with a full width at half maximum (FWHM) equal to 0.9 meV. The sample transmission was obtained by a direct measurement of the intensity transmitted throughout the aluminum cell, either empty or filled with the sample. For these measurements the incoming beam intensity was reduced by inserting an attenuator along the primary neutron path. The measured value of the transmission was $T = 0.79$ at 580 K, in good agreement with the estimate based on the tabulated values of Bi cross-sections.

3. Results and discussion

The data reduction was performed following the procedure successfully applied in similar investigations [14]. The single-scattering intensity was obtained by subtracting the multiple-scattering (MS) contribution from the background- and monitor-corrected data. The correction for MS contribution is a critical step of the data reduction. Indeed, even if the present sample is a fairly weak scatterer, the MS contribution is rather large at small Q since the single-scattering differential cross-section is quite low. In