

Remarkable dispersion of the acoustic mode in liquid Bi linked to Peierls distortion

More than 50 years ago, Peierls [1] suggested that in a one-dimensional metal with a half-filled band, a regular chain structure (see Fig. 1(a)) is not stable, and a structural distortion (see Fig. 1(b)) allows the reduction of the system energy accompanied by a metal-to-insulator transition. This structural instability, the Peierls distortion, is realized in crystalline materials, including elemental As, Sb and Bi with the A7 structure (see Fig. 1(c)), where a distortion of a simple cubic structure divides the six equal-length nearest-neighbor bonds into three short ones and three long ones. It is then interesting to consider the possibility of an analogous distortion in a liquid, and indeed hints of anisotropic bonding has been observed in liquid As. The nearest-neighbor coordination number for liquid Bi is in fact about 10, different from that of liquid As, so the analogy is not perfect. However, the structure factor of liquid Bi exhibits a shoulder on the high momentum transfer side of the first maximum, which suggests that there might be anisotropic bonding similar to in liquid As.

Considering previous investigations of liquid Bi, it is noted that very recent *ab initio* molecular dynamics (AIMD) simulations suggested that for liquid Bi the acoustic mode excitation energy should be almost constant for $8 \leq Q \leq 17 \text{ nm}^{-1}$ [2]. This is very different from the sinusoidal dispersion

observed in simple liquid metals. However, although the AIMD simulation [2] showed the acoustic mode excitation survived up to 17 nm^{-1} , inelastic neutron scattering (INS) results for liquid Bi suggested that the acoustic mode in liquid Bi disappeared for $Q > 6 \text{ nm}^{-1}$. As classical molecular dynamics (CMD) simulations for liquid Bi also exhibited no distinct acoustic excitation for $Q > 6 \text{ nm}^{-1}$, it was suggested that the disappearance of the inelastic excitation of the acoustic mode arises from an interatomic interaction unique to liquid Bi. However, other INS spectra measured in Japan suggested the excitation was visible for $Q \geq 6 \text{ nm}^{-1}$ [2]. In this context of unusual and possibly contradictory results from both experiments and calculations, it is then very interesting to make clear measurements of the dynamic structure factor, $S(Q, E)$, of liquid Bi, where Q and E are the momentum and energy transfers, respectively.

Inui *et al.* investigated $S(Q, E)$ of liquid Bi using inelastic X-ray scattering (IXS) [3]. The IXS technique avoids the kinematic constraints, which limit INS studies, so good spectra are obtained up to large energy transfers. The very high photoelectric X-ray absorption of Bi makes IXS experiments challenging, but they are possible by taking advantage of new powerful beamlines and improved sample cell techniques. Inui *et al.* [3] were then able to obtain high-quality IXS spectra which, when complemented by new AIMD and CMD simulations and compared carefully against previous data sets, allowed them to resolve previous discrepancies.

The experiments were conducted at the high-resolution IXS beamline **BL35XU** [4]. Liquid Bi of 99.999% purity was mounted in a Tamura-type single-crystal sapphire cell [5] that was carefully machined to provide a 0.04 mm sample thickness. IXS spectra of liquid Bi were measured at 573 K and 1023 K. After scaling for sample transmission, the backgrounds were subtracted from the data and $S(Q, E)$ was obtained, as shown for liquid Bi at 573 K in Fig. 2. The profile at the lowest Q exhibits a central peak with the inelastic excitation of the acoustic mode clearly visible on each side. Notably, with the relatively good quality data, the inelastic excitation is preserved even at 14.6 nm^{-1} , much larger than 6 nm^{-1} .

$S(Q, E)$ of liquid Bi was analyzed with the memory function formalism to determine the excitation energy of the acoustic mode. The results

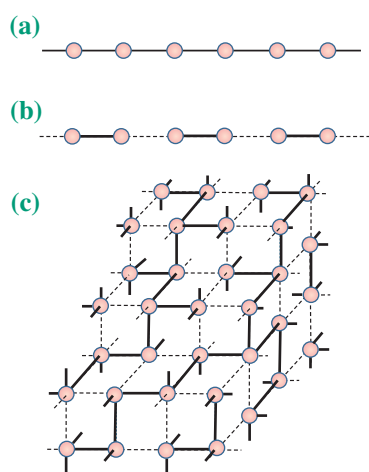


Fig. 1. (a) Regular chain. (b) Linear chain with a lattice distortion. Bold black lines denote shorter bonds. (c) Schematic structure of crystalline Bi on a simple cubic lattice. Bold black lines denote shorter bonds in the A7 structure.

are shown in Fig. 3 as a function of Q . The mode energy (black circles) disperses linearly for $Q \geq 7 \text{ nm}^{-1}$, whereas for $8 \leq Q \leq 15 \text{ nm}^{-1}$ the dispersion flattens and the energy remains approximately constant at 8.5 meV. The IXS results are consistent with previous AIMD predictions [2], and more recent calculations [3]. Thus, the anomalous dispersion of liquid Bi is real, and it now remains to obtain some understanding of its origin.

A linear chain model provides some insight into the origin of the anomalous dispersion, as discussed in [3], Figure 3 shows the excitation energy of the acoustic mode of a regular chain (see Fig. 1(a)) as a function of Q . A sinusoidal dispersion curve exhibiting a maximum at 10 nm^{-1} is not consistent with the IXS results. On the other hand, a linear chain model with a lattice distortion (see Fig. 1(b)) reproduces the flat dispersion curve well, as denoted by the red line in Fig. 3. In effect, an additional Fourier component is needed to model the dispersion, which Inui *et al.* linked to different length/strength bonds. This suggests that the medium-range structure of liquid Bi takes an atomic configuration with the Peierls distortion, similarly to crystalline Bi shown in Fig. 1(c).

The present IXS research on collective dynamics reveals that liquid Bi preserves anisotropic bonding. It might be difficult to demonstrate the anisotropic bonding from the radial distribution function obtained

by total scattering measurements. The present result suggests that the atomic configuration in the liquid state near the melting point is determined by the interatomic interaction on a nanometer length scale similarly to that in the solid state.

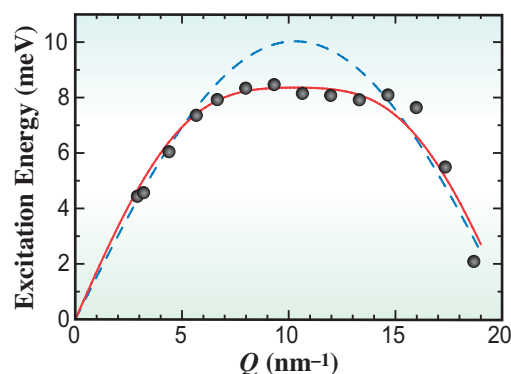


Fig. 3. Excitation energy of the acoustic mode in liquid Bi obtained by IXS (black circles). Also shown are the dispersion curve of the regular chain (blue broken line) and that of the distorted chain (red solid line) shown in Figs. 1(a) and 1(b), respectively.

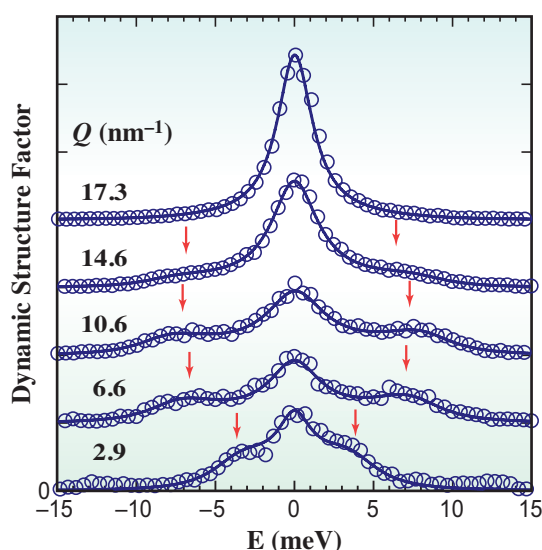


Fig. 2. Dynamic structure factor of liquid Bi at 573 K. Open circles and a bold line denote the IXS and the fitting results with the memory function, respectively. Red arrows indicate the inelastic excitations of the acoustic mode.

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