Collective excitations in a liquid semimetal: Molecular-dynamics simulation of the dynamics of liquid bismuth

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A molecular-dynamics simulation of liquid Bi at 578 K using a system of 16 384 particles, supported by neutron-scattering measurements, shows that the side peaks of its dynamical structure factor $S(Q\omega)$, attributed to the collective density excitations, are unobservable beyond wave vector $Q=0.6$ Å^{-1}. Being in contrast to what has so far been observed in liquid metals, the strong damping of the longitudinal modes we found is concluded to result from the anomalies in the liquid-Bi structure, typical for molten semimetals.

The existence of collective density modes in a classical monatomic liquid has been an issue of great interest for many years.[1,2] Early neutron-inelastic-scattering measurements on noble-gas liquids,[3] as well as later molecular-dynamics (MD) studies of the Lennard-Jones fluids[4] revealed the side peaks in the dynamic structure factor $S(Q,\omega)$, attributed to the propagating density waves at the Q region, below $\sim 0.15Q_0$ only, Q_0 being the position of the main peak of $S(Q)$. On the other hand, in a typical liquid metal the finite frequency peaks in $S(Q,\omega)$ have been observed for wave vectors up to $0.7Q_0$.[5,6] The peaks being well enough resolved, one can derive the collective modes' frequency variation with respect to Q, usually referred to as dispersion relation $\omega(Q)$. This was found to look similar to that of phonons in solids with its maximum at about $Q_0/2$. The well-known long oscillatory tail of the velocity correlation function, dominated by a well-defined frequency, is concluded[7] to be a manifestation of the spectral singularity resulting from the fact that the collective density modes are well defined around this wave-vector value. All the liquid metals studied thus far had been found to support the modes well beyond the described limit, which was thus assumed to be a distinctive dynamical feature of this class of simple liquids. It should, however, be mentioned that recent extensive measurements on the noble-gas fluids have been interpreted in terms of the revised Enskog theory thus yielding generalized sound modes well beyond the Q_0.[8]

The reasons for the described difference in dynamics of metallic and nonmetallic liquids are still not quite understood. It is widely believed that the damping of density waves mainly depends on the pair-potential shape at the close range: The repulsive part of the Lennard-Jones potential is considerably steeper than that of the interionic potential in an alkali metal.[9] Much less is known regarding the effects of the potential's shape beyond the nearest-neighbor distance. It was recently shown that the pair potentials in metallic liquids with strongly charged ions should be positive and repulsive well beyond that distance.[10,11] This makes the dynamics of these liquids to be an interesting subject of studies.

Bismuth is a typical semimetal and as such it exhibits a set of anomalous features in the molten state as compared with an ordinary liquid metal.[12] The most interesting one is the more or less pronounced shoulder on the high-Q side of the main peak of $S(Q)$ as well as some asymmetry in the subsequent peaks.[12] The shoulder was found to give rise to clearly visible effects in the spectral shape of $S(Q,\omega)$.[13] Another interesting feature reported by Dahlborg and Olsson[14] was the absence of structure in $S(Q,\omega)$ at small momentum transfers ($Q>0.6$ Å^{-1}). The result was questioned later by Shibata, Hoshino, and Fujishito.[15] The MD simulation technique enables us to obtain quantitatively reliable complementary information in the small momentum-transfer domain, which is hardly accessible experimentally. We report here the results of MD simulations of the liquid Bi dynamic scattering func-

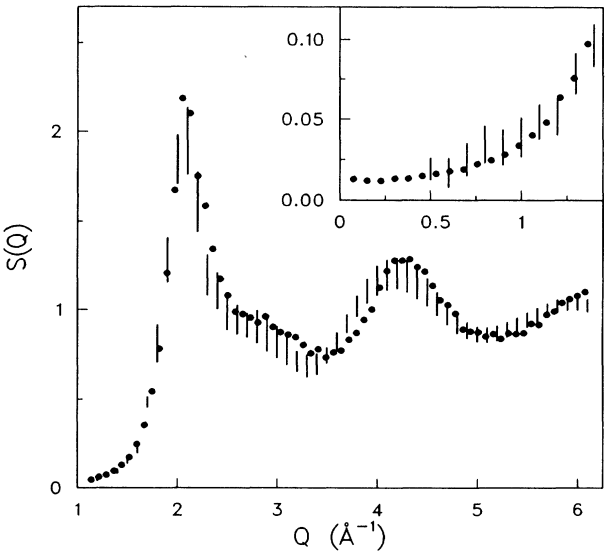

FIG. 1. Zeroth moments of the measured (Refs. 13 and 14) (error bars) and the MD-simulated $S(Q,\omega)$ (dots). The small-Q region is shown in the inset.

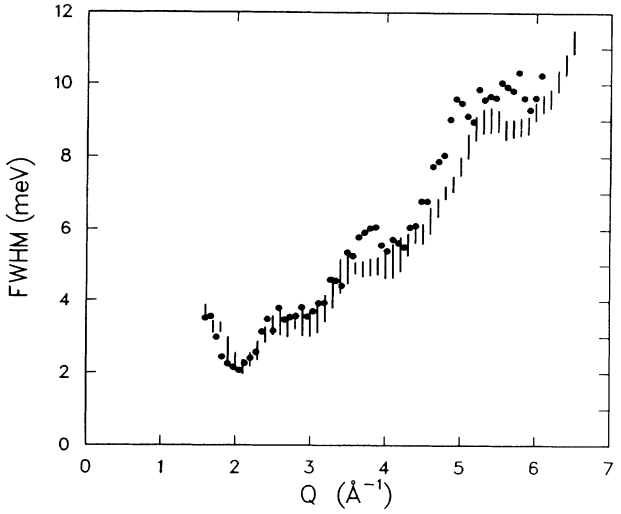

FIG. 2. Full width at half-maximum of the dynamic scattering function. Error bars, experimental data (Refs. 13 and 14); dots, the results of MD simulation. The MD-simulated $S(Q,\omega)$ has been convoluted with the experimental resolution function.

tion $S(Q,\omega)$, supported by the earlier published neutron-inelastic-scattering data. This new information provided from the long-wavelength region demonstrates that the collective density modes damping in liquid Bi is much stronger than in any metallic liquid studied thus far.

It was speculated that the structural anomalies in liquid Bi are due to the covalent effects presumably still prevailing in the system after melting.[12] Recent MD studies,[16] however, convincingly demonstrated that these effects either are negligible or may be incorporated into an effective pair potential. The parametrized phenomenological form of pair potential was optimized in an iterative procedure to fit to the experimental $S(Q)$. The scheme was based on the modified hypernetted-chain equation.[17] The $S(Q)$ simulated using the derived potential quite satisfactorily reproduces all the details of the measured structure factor including the small-Q region, which is important in light of the results being reported here. It should be noted that the potential remains positive and repulsive well beyond the first-neighbor distance.

Using the derived pair potential, we have carried out an extensive MD simulation of liquid Bi at 578 K and number density $n=0.0289$ Å^{-3} (that corresponds to the conditions near the melting point). A large MD system comprising 16 384 particles enabled us to reach the smallest Q value 0.078 Å^{-1}. The MD run of 15 000 integration time steps was carried out, the time step being chosen, 2×10^{-14} s. Following the usual routine, at every time point we calculated the Fourier transform of the N-particle system's density:

$$\rho(\mathbf{Q},t)=N^{-1/2}\sum_{j=1}^{N}\exp[i\mathbf{Q}\cdot\mathbf{R}_j(t)]\ . \tag{1}$$

$\mathbf{R}_j$ being the position of the particle j, and $\mathbf{Q}$ chosen consistent with the periodic boundary conditions imposed. The intermediate scattering function was then calculated

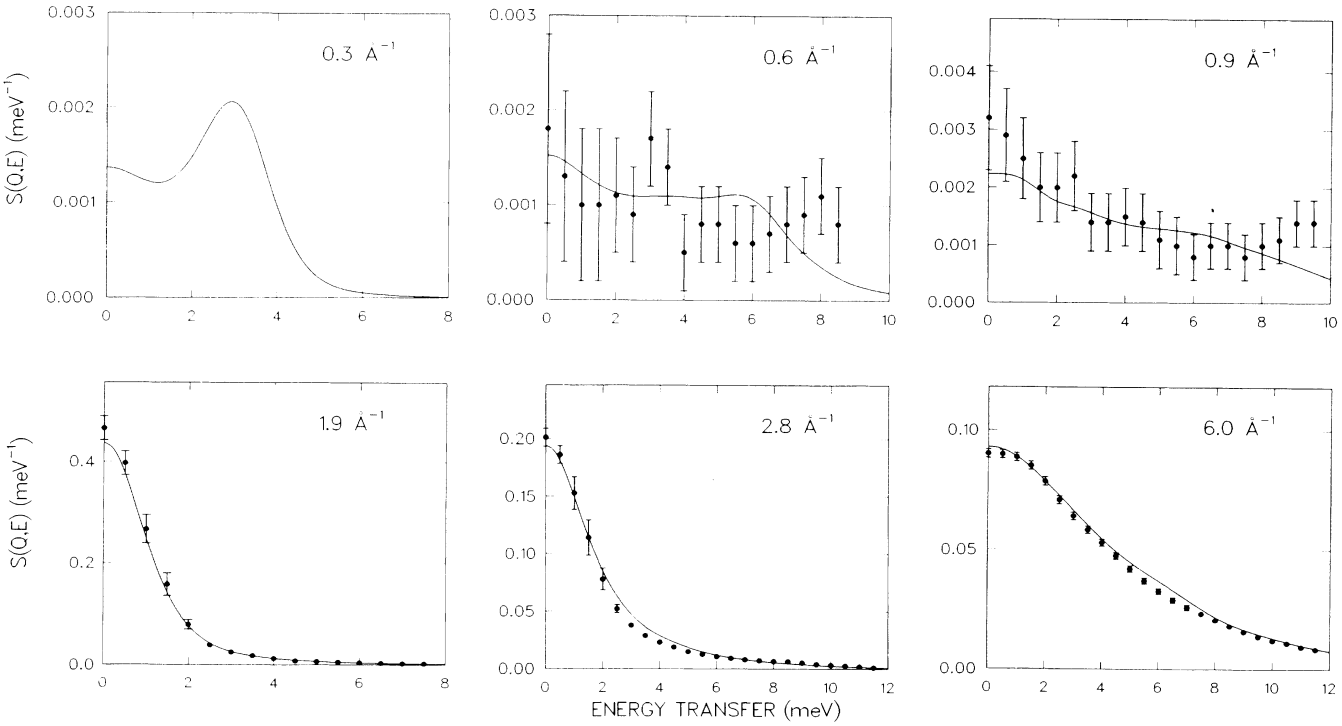

FIG. 3. Calculated and the measured $S(Q,\omega)$ plotted for several values of Q. Solid lines, MD simulation results; dots with error bars, the neutron-scattering results (Refs. 13 and 14).

according to definition

$$F(Q,t)=\langle \rho(\mathbf{Q},t)\rho^*(\mathbf{Q},0)\rangle \ , \tag{2}$$

and its cosine transform gives the dynamic scattering function

$$S(Q,\omega)=\pi^{-1}\int_0^\infty F(Q,t)\cos(\omega t)dt \ . \tag{3}$$

Since the calculated $S(Q,\omega)$ is to be used as a source of information in the Q region where reliable neutron measurements are not feasible, we first have to check its consistency with the experimental data available. In order to facilitate the comparison the MD-simulated $S(Q,\omega)$ was convoluted with the Gaussian representing the experimental resolution function.[13] The Gaussian approximation is not strictly accurate, but it is acceptable in this case. A good check of consistency between the measured and simulated results is to compare the corresponding zeroth moments of $S(Q,\omega)$. As it is obvious from Fig. 1, the agreement between the two sets of data does look quite satisfactory, also in the important small-Q region. Minor discrepancies are apparent though in the Q range from 2.5 to 4.0 Å^{-1}. The discrepancies are, however, consistent with those between the measured static structure factor and the MD-simulated one.[16]

Another quantity that gives a measure of spectral agreement between the measured and the simulated $S(Q,\omega)$ is the full width at half-maximum (FWHM), presented in Fig. 2. To avoid confusion, note that the experimental data in Fig. 2 are different from those in Fig. 7 of Ref. 13, where the resolution was deconvoluted. In spite of minor discrepancies, the agreement between the two sets of data in Fig. 1 is generally quite satisfactory. Therefore the four sets of independently obtained results, that is, the measured $S(Q)$, the measured $S(Q,\omega)$, and the two respective functions derived from MD simulation by different techniques, can thus be said to form a fully consistent piece of information.

The results on $S(Q,\omega)$ for several Q values, presented in Fig. 3, demonstrate that the simulation provides quite good agreement with the experimental data available. For the smallest wave vector reached by the experiment, the MD data lie well within the error bars. The most interesting new detail that emerges from the MD results is the finite frequency peak, clearly visible for $Q=0.3$ Å^{-1} in Fig. 3. The presence of pronounced collective density modes is found in the Q range below 0.6 Å^{-1}. The speed of sound, estimated as the hydrodynamic limit of $\omega(Q)/Q$, comes out as 1520 m/s, while the measured value is 1620 m/s.[18] Already at $Q=0.6$ Å^{-1}, however, the modes are damped so strongly that the maximum transforms into a plateau, so that no dominating frequency can be associated with this momentum-transfer value. It is clear that the structureless $S(Q,\omega)$ curves for the wave vector values beyond this limit presented here show no evidence for collective excitations. This result is supported by our previous neutron measurements and is in contrast to the conclusions made by Shibata, Hoshino, and Fujishita.[15]

It is interesting to note that the neutron-scattering measurements on liquid Pb,[19,20] supported by the recent MD studies (to be published), have not revealed the strong damping of density waves reported here. The ion mass and the melting point of Pb are close to those of Bi, so the anomalies reported here must have resulted from the more pronunced long-range interionic repulsion in liquid Bi as compared with that in liquid Pb (Fig. 4). The shoulder on the main peak of $S(Q)$ in liquid Bi is a manifestation of a set of distortions in its radial distribution function. The most important one in light of this analysis is the fact that its first peak occurs at 3.24 Å as compared with 3.37 Å in the case of the more dense liquid Pb (Fig. 4). Due to this paradoxical local-neighbors arrangement the ion-ion interaction in liquid Bi is dominated by the steeper shorter-range part of the potential, which makes the system less harmonic and its longitudinal modes more damped than in the case of liquid Pb.

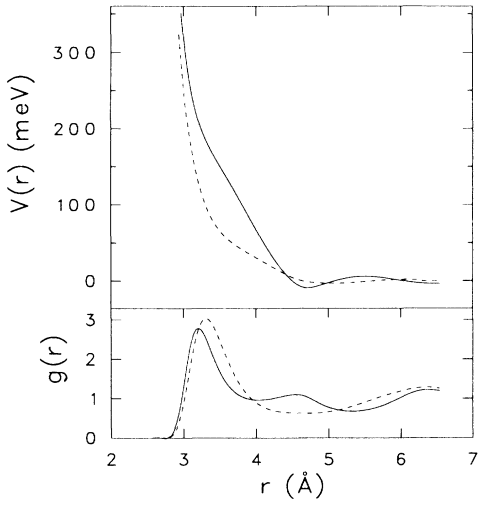

FIG. 4. Comparison of the pair potential $V(r)$ and the radial distribution function $g(r)$ in liquid Bi at 578 K (Ref. 16) (solid line) with those in liquid lead at 623 K (Ref. 10) (dashed line).

We conclude this Brief Report with the following remarks. It has been demonstrated that the MD model using the pair potential derived from the structure data adequately describes the dynamical properties of a molten semimetal. The existence of strong many-body effects cannot, therefore, be concluded from the anomalies observed in neutron diffraction on liquid Bi. We have found a pattern of collective dynamics that distinguishes it from the previously studied liquid metals as well as from the simple Lennard-Jones liquids. The density modes are found to be supported only for momentum transfer below $0.3Q_0$. The structural anomalies previously associated with the long-range repulsive part of the pair potential are concluded to cause this strong damping of the longitudinal waves. Therefore one can expect this distinctive feature of collective dynamics to be common for the whole group of polyvalent liquid metals exhibiting a shoulder on the high-Q side of the main peak of the structure factor $S(Q)$.

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