

High-Frequency Acoustic Modes in Liquid Gallium at the Melting Point

T. Scopigno,¹ A. Filipponi,² M. Krisch,³ G. Monaco,³ G. Ruocco,¹ and F. Sette³

¹*Dipartimento di Fisica and INFN, Università di Roma "La Sapienza," I-00185, Roma, Italy*

²*Dipartimento di Fisica and INFN, Università di L'Aquila, I-67010, L'Aquila, Italy*

³*European Synchrotron Radiation Facility, B.P. 220 F-38043 Grenoble, Cedex France*

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The microscopic dynamics in liquid gallium at melting has been studied by inelastic x-ray scattering. We demonstrate the existence of acousticlike modes up to wave vectors above one-half of the first maximum of the static structure factor, at variance with earlier results from inelastic neutron scattering [F. J. Bermejo *et al.*, Phys. Rev. E **49**, 3133 (1994)]. Despite structural (extremely rich polymorphism) and electronic (mixed valence) peculiarities, the collective dynamics is strikingly similar to the one of van der Waals and metallic fluids. This result speaks in favor of the universality of the short time dynamics in monatomic liquids rather than of system-specific dynamics.

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The nature of the microscopic dynamics in simple fluids is nowadays one of the most lively debated topics in the condensed matter field. The provocative evidence of well-defined collective excitations outside the truly hydrodynamic region has attracted many experimentalists in the last three decades. In particular, several studies performed through inelastic neutron scattering (INS) revealed the presence of a Brillouin triplet in the dynamic structure factor of many monatomic liquids [1]. Together with numerical studies [2] these experiments provided us some pictures of the high frequency dynamics, although a deep comprehension of the ultimate nature of these excitations is still missing [3,4]. More recently, the advent of the new radiation sources has allowed the full development of the inelastic x-ray scattering (IXS) [5]. This technique, being sensitive to the coherent dynamics only and allowing to investigate the low exchanged momentum (Q) region inaccessible to INS, renewed the interest and the efforts in the field giving rise to a number of experiments [6]. More specifically, some light has been shed on the mesoscopic dynamics of different monatomic systems as van der Waals fluids (He, Ne), liquid alkali metals (Li, Na), and more complex liquid metals (Al). In particular, using the generalized Langevin equation formalism, the presence of two viscous relaxation processes has been experimentally proven in all these systems, and the relevant parameters have been quantitatively determined [7].

Among the elemental liquid metals, Ga exhibits peculiar structural and electronic properties. In addition to the low melting point ($T_m = 303$ K), it presents an extended solid phase polymorphism with complex crystal structures where a competition between metallic and covalent bonding character takes place [8]. Although the electronic density of states (DOS) in liquid gallium (l-Ga) is nearly free electron it still shows anomalies associated with some covalency residue. Moreover, the first peak of the $S(q)$ presents hump characteristics of non-close-

packed liquid structures [9]. As far as dynamical properties are concerned, again liquid gallium seems to show peculiarities that elude the picture of the high frequency dynamics emerging in all the monatomic liquids. In fact, earlier studies performed by INS showed somehow contradictory results [10,11]. At room temperature, although no collective modes were visible in the experimental data, the spectra were described by a damped harmonic oscillator model, and the excitation frequencies were found to lie above the hydrodynamic values. This effect was ascribed to the presence of high frequency optical modes that were supposed to contribute to the spectra. In these studies, the absence of acoustic excitations was explained with a high value of the longitudinal viscosity, even though on the basis of hydrodynamic arguments collective modes should have been expected [10]. A few years later, a new INS experiment was performed at higher temperature ($T = 973$ K), and collective modes were detected [11]. In particular, at low wave vectors an acoustic mode was found, while at high wave vectors the dispersion curve split into two branches that according to the authors should be associated with acoustic and optical excitations, respectively [11]. This picture (the absence of acousticlike excitations just above melting)—if verified—would stress the anomalous dynamical behavior of gallium, and would pose against the idea of a common high frequency dynamics of monatomic systems.

In this Letter, we report on an inelastic x-ray scattering study of the microscopic dynamics in liquid gallium just above the melting point ($T = 315$ K). The sensitivity of this technique to the purely collective motion only and the extended accessible kinematic region, allowed an accurate determination of the coherent dynamic structure factor. At variance with the results reported in [10] we find a clear indication of acousticlike excitations, whose properties parallel those of all the other investigated monatomic liquids. Moreover, the value of the transport coefficients derived by a generalized Langevin equation

description of the spectra, quantitatively agrees with the hydrodynamic expectations. The obtained results indicate that—despite its structural and electronic anomalies—liquid gallium shares with the other simple liquids (metals and nonmetals) the same features of the high frequency atomic dynamics.

The experiment has been performed at the ID28 beam line of the European Synchrotron Radiation Facility (ESRF) at fixed exchanged wave vector over a Q -region below the position of the main diffraction peak ($Q_M \approx 25 \text{ nm}^{-1}$). A typical energy scan ($-50 < E < 50 \text{ meV}$) took about 300 min, and was repeated for a total integration time of about 300 s/point. A five analyzers bench allowed us to collect simultaneously spectra at five different values of the exchanged wave vector Q for each single scan. The sample consisted of a gallium molten droplet kept in sandwich between two sapphire windows (thickness 0.25 mm). The sample thickness ($\approx 100 \mu\text{m}$) was chosen in order to match the absorption length at the incident energy of 17794 eV, corresponding to the (9 9 9) reflection from the silicon analyzers that we utilized ($\delta E \approx 3.0 \text{ meV}$) [5].

In Fig. 1 we report the measured IXS intensity for each investigated (fixed) Q value. The presence of an acoustic propagating mode clearly appears from the raw data. The spurious signal coming from the longitudinal and transverse phonons of the sapphire windows, due to the high value of their speed of sound, does not significantly over-

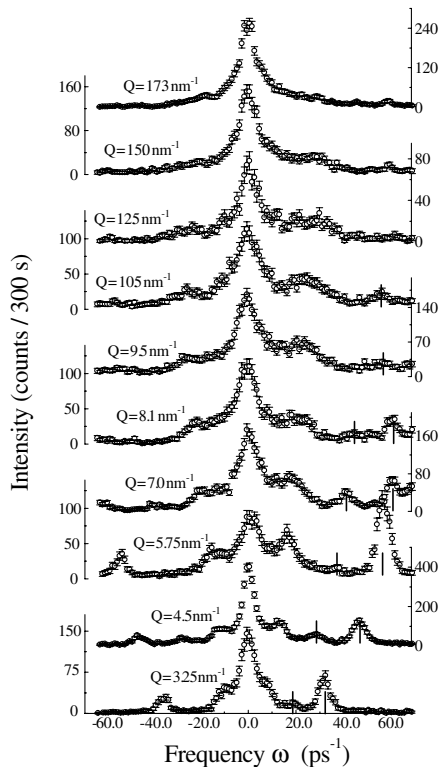


FIG. 1. IXS spectra of liquid Ga ($T = 315 \text{ K}$) at the indicated Q values. The vertical bars indicate the (Stokes side) energy positions of the L - and T -acoustic phonons of sapphire.

lap with the gallium spectra. In order to extract quantitative information on the reported excitations, a data analysis has been performed following a memory function approach that has been shown to be well footed on several simple fluids [3,7]. Within the generalized Langevin equation formalism, it is possible to express the *classical* dynamic structure factor in terms of a complex memory function $M(Q, t)$ related to the interaction details. In particular, in terms of the real and imaginary part of the Fourier-Laplace transform of $M(Q, t)$, it holds [3]:

$$S(Q, \omega) = \frac{S(Q)\pi^{-1}\omega_0^2(Q)\tilde{M}'(Q, \omega)}{[\omega^2 - \omega_0^2(Q) + \omega\tilde{M}''(Q, \omega)]^2 + [\omega\tilde{M}'(Q, \omega)]^2} \quad (1)$$

Here the quantity $\omega_0^2(Q) = KTQ^2/mS(Q)$ is related to the generalized isothermal sound speed through the relation $c_t(Q) = \omega_0(Q)/Q$, and can be calculated from the liquid structure once $S(Q)$ is known. In order to be used as a test function to fit the experimental data, the above expression has to be modified to satisfy the detailed balance condition and must be convoluted with the instrumental resolution function $R(\omega)$:

$$I_N^{\text{th}}(Q, \omega) = \int \frac{\hbar\omega'/KT}{1 - e^{-\hbar\omega'/KT}} S(Q, \omega') R(\omega - \omega') d\omega'.$$

Taking advantage of the results obtained in several other liquid metals (Li, Al, Na) [7,12] and fluids (noble gases) [13–15], we utilized a memory function composed by two relevant time scales associated to two processes of viscous origin, plus an exponential contribution that accounts for the thermal relaxation process. For the two viscous terms we adopted a simple Debye law (exponential decay) to account for the structural relaxation and an instantaneous approximation (delta function) for the faster, microscopic contribution. Consequently, the total memory function reads

$$M(Q, t) = (\gamma - 1)\omega_0^2(Q)e^{-D_T Q^2 t} + \Delta_\alpha^2(Q)e^{-t/\tau_\alpha(Q)} + 2\Gamma_\mu(Q)\delta(t).$$

Thus the free fitting parameters are τ_α (the structural relaxation time), $\Delta_\alpha(Q)$ (the structural relaxation strength) and $\Gamma(Q)$ (associated to the microscopic relaxation, and representing the Brillouin linewidth in the fully relaxed limit). The value of $\omega_0(Q)$ has been calculated using the $S(Q)$ data reported in [9], while the specific heat ratio γ and thermal diffusivity D_T are deduced by macroscopic data (their Q dependence have been neglected). The outcome of the fitting procedure for selected Q values, i.e., a comparison between the best fitting line shape and the experimental spectra, is reported in Fig. 2. Intensities have been normalized using the $S(Q)$ values of Ref. [9].

In Fig. 3 we report the apparent sound velocity [16] (full dots). At the lower accessible wave vector, the

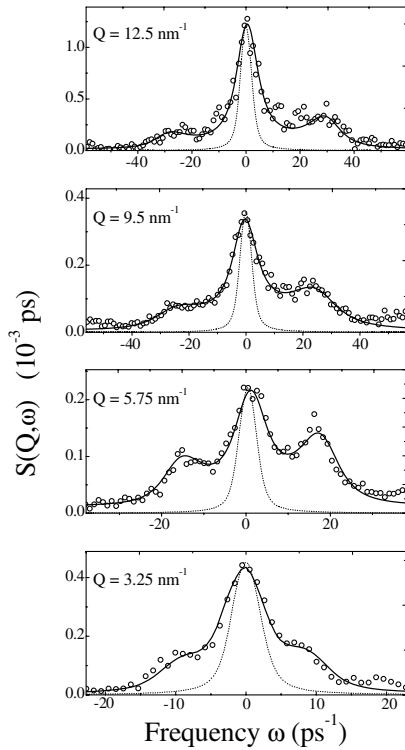


FIG. 2. Selection of IXS spectra (\circ) plotted with the fitting function (—) described in the text. The instrument resolution function ($\delta E \approx 3.0$ meV) is also shown (\cdots).

measured sound velocity (≈ 3000 m/s) still exceed the isothermal value (≈ 2800 m/s) as deduced by ultrasonic measurements [17], a behavior (the so-called positive dispersion of the sound velocity) that is common with many other simple fluids. In the same figure we report the generalized (Q -dependent) isothermal sound velocity [$\omega_0(Q)/Q$ as deduced by the $S(Q)$ [9]] (open triangles) that constitutes the low frequency limit of the sound speed, as well as the high frequency limit, $c_\infty(Q)$ (full line) numerically estimated through the structural data (pair distribution function, interaction potential) [10]. The full triangles come from the best fitted values of $\omega_0(Q)$ that—in a separate check fitting session—has been left as free parameters. The coincidence of the fitting-derived $\omega_0(Q)$ values with those derived from the $S(Q)$ data indicates the robustness of the fitting model. In the inset the Q dependence of the structural relaxation time as derived by the fit is reported. Apart from the very high value found at the lower Q point, mainly because the width of the central line becomes comparable to the instrument resolution, we find a slightly decreasing value in the range $0.25 > \tau_\alpha > 0.17$. It is worth pointing out that the relation $\omega(Q)\tau_\alpha(Q) > 1$ holds in the whole explored Q range, i.e., the structural relaxation is frozen over the probed time scale. As a consequence, the sound velocity tends to the value $c_{\infty\alpha}(Q) = \sqrt{\omega_0^2(Q) + \Delta_\alpha^2(Q)}/Q$ (dotted line in Fig. 3) which represents the contribution to $c_\infty(Q)$ associated to the structural process only, as can

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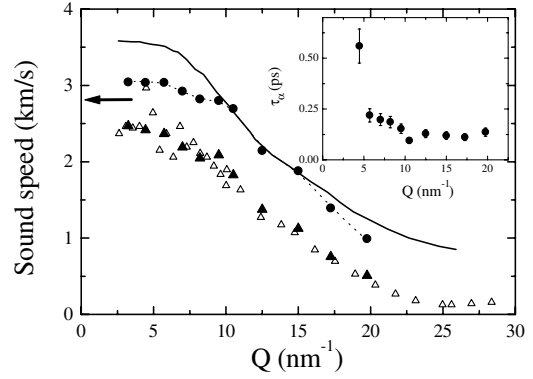


FIG. 3. Sound velocities deduced from the present data: apparent (\bullet) [16], $c_0(Q)$ (\blacktriangle) and $c_{\infty\alpha}(Q)$ (\cdots) (see text). Isothermal [$c_0(Q)$, \triangle] and unrelaxed [$c_\infty(Q)$, —] values are also reported from Refs. [9,10], along with $c_0(Q \rightarrow 0)$ estimated by ultrasonics (\leftarrow) [17]. In the inset we report the values of the α relaxation time as obtained by the fit.

be seen approximating by a constant the correspondent part of the memory function in the general expression of $S(Q, \omega)$ (1). On the other side, the “instantaneous” nature of the microscopic process [$\omega(Q)\tau_\mu(Q) \ll 1$] prevents the system from reaching the fully unrelaxed regime, thus explaining the gap observed at low Q between the sound velocity and the $c_\infty(Q)$.

A further relevant quantity that can be extracted from the fitting parameters is the generalized (Q dependent) longitudinal viscosity $\eta_L(Q)$, i.e., in the Langevin equation formalism, the total area of the memory function: $\eta_L[Q] = \rho(\Delta_\alpha^2\tau_\alpha + \Gamma_\mu(Q))/Q^2$, reported in Fig. 4. In the upper inset we show the two individual contributions $\Gamma(Q)$ and $\Delta_\alpha^2(Q)\tau_\alpha(Q)$: the viscosity associated with the structural rearrangement turns out to be dominant all over the entire explored Q range; the part coming from the microscopic process follows—at low Q —a Q^2

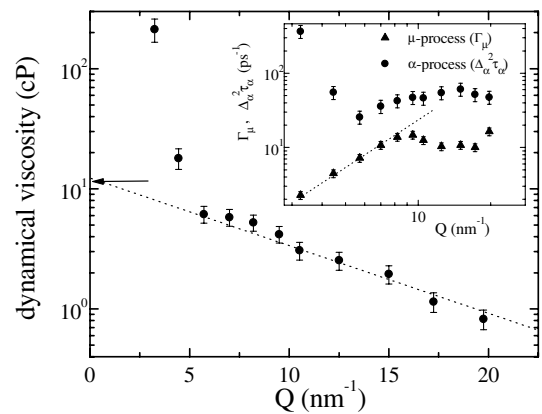


FIG. 4. Values of $\eta_L(Q)$ as determined by the memory function parameters for l-Ga (\bullet) [7]. The hydrodynamic value [10] is also reported (\leftarrow). Inset: partial contributions due to the α (\bullet) and μ (\blacktriangle) process, respectively. The dotted line emphasizes a noteworthy Q^2 behavior.

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behavior as already reported in other liquids and glasses [7,12,13]. This latter contribution is particularly relevant as it is the only one affecting the Brillouin linewidth in the present regime. The presence of nonoverdamped mode is, in fact, due to the condition $\Gamma(Q) \ll \omega_l(Q)$ holding over the explored Q range.

Apart from a low Q increase, an artifact due to the finite resolution effect and already observed in other systems [7], the total $\eta_L(Q)$ follows an exponential Q dependence, whose origin deserves further investigations. However, the low Q limit of $\eta_L(Q)$ can be obtained by extrapolation, and turns out to be in very good agreement with the value $\eta = 11.4$ cP, determined from the experimental value of the shear viscosity and from the shear-to-bulk viscosity ratio deduced by structural parameters [10].

In conclusion, we presented an experimental study of the collective high frequency dynamics in liquid gallium at the melting temperature. Evidence for collective acoustic modes has been found in a Q region extending beyond the hydrodynamic regime up to one-half of the structure factor main peak. A generalized hydrodynamic analysis allows a quantitative determination of relevant parameters such as the structural relaxation time and the generalized viscosities. More importantly, it reveals how the main features of the collective dynamics in this system are very similar to the ones reported in different elements such as Li, Na, Al [7] and noble gas fluids [14,15]. This is an important indication of how—despite *quantitative* differences—the high frequency dynamics in simple fluids exhibit universal features which go beyond system dependent details such as the electronic structure, bond nature, atomic interaction, and structural properties. Since on the observed time scale the structure of the liquid is frozen [$\omega_l(Q)\tau_\alpha(Q) \gg 1$], one can think of the high frequency dynamics as that of a system with well-defined equilibrium position (“glass”). Therefore, the details of the dynamics (microscopic relaxation times, residual viscosity) are fully determined by the vibrations of the disordered structure, explaining the observed universality [12,13]. Finally, although we did not find any evidence for additional modes in the explored Q range, on the basis of the findings of Ref. [11] we believe that further investigations should be devoted to the higher Q region.

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[16] It is worth recalling that the apparent sound velocity is defined as the ratio of the excitation frequency $\omega_l(Q)$ to the Q values. The quantity $\omega_l(Q)$, in turn, is the position of the maximum of the longitudinal current correlation spectrum $J^L(Q, \omega) = \omega^2/Q^2 S(Q, \omega)$, where $S(Q, \omega)$ is obtained by the best fitted parameters, and therefore is resolution deconvoluted.

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