High frequency dynamics in liquid nickel: An inelastic x-ray scattering study

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Owing to their large relatively thermal conductivity, peculiar, nonhydrodynamic features are expected to characterize the acousticlike excitations observed in liquid metals. We report here an experimental study of collective modes in molten nickel, a case of exceptional geophysical interest for its relevance in earth interior science. Our result shed light on previously reported contrasting evidences: In the explored energy-momentum region, no deviation from the generalized hydrodynamic picture describing nonconductive fluids is observed. Implications for high frequency transport properties in metallic fluids are discussed. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2925256]

I. INTRODUCTION

Half a century of inelastic neutron scattering experiments, recently complemented by similar investigations with x rays, has clearly shown that acousticlike excitations can be sustained by simple liquids down to wavelengths comparable to the mean interparticle distances and frequencies extending up to the terahertz region.[1–3] In ordinary, nonconductive fluids, such collective modes can be roughly described in terms of adiabatic sound waves of energy $E=\hbar\Omega$ propagating with sound velocity $c_s=\lim_{Q\to 0}\Omega(Q)/Q$. This is a well known, immediate consequence of the hydrodynamic treatment when the condition $\Omega \gg D_T Q^2$ holds, where D_T is the thermal diffusion coefficient for the system under study and Q the exchanged momentum between the probe and the sample.[1,3] A deeper analysis reveals that such acoustic waves are actually subject to relaxation processes related to the frequency dependent viscosity. The origin of such processes is twofold: the structural relaxation, responsible for dynamical arrest in those systems capable of supercooling, and a microscopic process which induces an additional damping of the sound waves due to the non-plane-wave nature of the instantaneous vibrational eigenmodes. Both these processes manifest themselves at wavevectors $Q \approx 1/10 Q_M$, Q_M being the principal maximum of the static structure factor. This region, unfortunately, represents the technical limit for both neutron and x-ray inelastic spectroscopy, hindering the complete understanding of the underlying dynamical processes which are still controversially debated.[3]

In liquid metals, an additional complication arises. The hydrodynamic condition $\Omega(Q) \gg D_T Q^2$ breaks down in the range $0.1 \lesssim Q \lesssim 1$ nm^{-1}, an estimate obtained neglecting the Q dependence of the thermal conductivity. Consequently, an isothermal regime may be expected to occur above the $\Omega(Q) \approx D_T Q^2$ crossover, with the adiabatic limit attained only below this value.[3–5] Among the implications of such an isothermal regime on the sound waves propagation, noteworthy features would be a reduced value of the sound velocity $c_t = c_s/\sqrt{\gamma}$, with $\gamma = C_P/C_V$, the ratio of constant pressure to constant volume specific heats and a different expression for the thermal contribution to the acoustic attenuation: $(\gamma-1)c_t^2/\gamma D_T$ instead of $(\gamma-1)D_T Q^2$.

To address this issue, we present here an investigation of the high frequency dynamics in liquid nickel performed by inelastic x-ray scattering (IXS), a technique which has proven, since the early 1990s, to be an invaluable tool for deepening our comprehension of the dynamics of simple liquids on the microscopic scale, since it allows, on one hand, to overcome the kinematic limitations due to the lower incident energies of the neutrons and their specific energy-momentum relation and, on the other hand, provides direct access to the coherent cross section of the scattering process.[3]

In this respect, previous investigations performed by means of inelastic neutron scattering (INS) and molecular dynamics (MD) have shown contrasting results.[6–9] In the former study, the sound velocity attains indeed the isothermal value at the longest accessible wavelength ($Q \approx 8$ nm^{-1}), while in the latter the numerically estimated sound velocity is always larger than the adiabatic value. Recently, an interesting study involving both quasielastic neutron scattering and MD has pointed out how the simulation data for the speed of sound of liquid Ni attain the adiabatic value c_S at the lower accessed Q's ($Q \approx 2$ nm^{-1}).[10]

Liquid Ni, indeed, is characterized by the largest specific heat ratio among monatomic liquids, a property which should emphasize any nonhydrodynamic results. In addition, Ni is a system of paramount relevance in geophysical science

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due to its presence in the Earth's interior.[11] Indeed, the fact that the Earth outer core is mostly iron was established beyond reasonable doubt already in the early 1960s, when it was confirmed that the density of the core was about 10% lower than the density of iron and that the seismic parameter $\Phi = K/\rho$, K being the bulk modulus and ρ the density, was higher than that of iron.[12] About 4% Ni is thought to be present in the core, and although it does not appreciably change the density of liquid Fe, its presence should not be forgotten as phase diagrams of systems Fe-Ni-light elements may be significantly different from those of systems without Ni.[13,14] Among the most favorite candidates as lighter alloying elements with Fe and Ni, sulfur is perhaps the most addressed one.[11] In this respect, recently a high anomalous behavior of the ultrasonic sound velocity $c_S(T)$ and attenuation $\Gamma(T)$ as functions of temperature was reported in the mixture 85%Fe–5%Ni–10%S, for temperatures above melting ($T_m = 1650$ K) up to 2000 K, at ambient pressure conditions.[15] In fact, and contrary to the data of pure liquid metal components, the acoustic velocity is found to increase with temperature, as well as attenuation. A complete understanding of the underlying behavior of the alloy requires, in our opinion, to ascertain the nature of acoustic excitations in pure liquid Ni.

TABLE I. Thermal properties of selected liquid metals near the melting point. γ, the ratio of specific heats, and D_T, the thermal diffusion coefficient, are reported at those temperatures T, near the melting point, where data are available. For a more extensive summary of data on thermal as well as dynamical properties of liquid metals, see Ref. 3.

Sample	T (K)	γ	D_T (nm^2/ps)
Li	453	1.08,[a,b]1.065[c]	19.1,[d]20.3[d]
Na	371	1.12,[e]1.091[c]	68.8[d]
Mg	923	1.29[a]	39.8[d]
Al	933	1.4[a]	35.2[d]
K	336.7	1.11,[e]1.102[c]	81.4[d]
Fe	1808	1.8[a]	7.3[a]
Co	1765	1.8[a]	
Ni	1728	1.98[a]	9.6[a]
	1763	1.88[f]	
Cu	1356	1.33[a]	42.1[d]
Zn	693	1.25,[e]1.26[a]	15.7[d]
Ga	303	1.08[e]	11.6[d]
Ge	1253	1.18[a,g]	
Rb	312	1.15,[e]1.097[c]	61.5[d]
Ag	1233	1.32[a]	66.5[d]
Sn	505	1.11[e]	17.3[d]
Cs	302		44.6[d]
	308	1.102[h]	
Au	1336	1.28[a]	40.4[d]
Hg	293	1.14[i]	4.41[d]
Pb	623	1.19[a,b]	9.89[d]

[a]Reference 23.
[b]Reference 24.
[c]Reference 25.
[d]Reference 26.
[e]Reference 27.
[f]Reference 6.
[g]Reference 28.
[h]Reference 29.
[i]Reference 30.

II. THEORETICAL BACKGROUND: EXPECTED HYDRODYNAMIC BEHAVIOR FOR LIQUID METALS

In an IXS experiment, the double differential cross section, which depends on the exchanged momentum Q and energy E, is proportional to the so called dynamic structure factor $S(Q,\omega)$, which, in turn, is the Fourier transform of the time dependent intermediate scattering function

$$F(Q,t) = \frac{1}{N}\sum_{i,j} \langle e^{-iQ\cdot r_i(0)} e^{iQ\cdot r_j(t)} \rangle. \quad (1)$$

Here, N is the total number of particles constituting the system, and $r_i(t)$ the position of particle i at time t.[3] In particular, the zero time value of the intermediate scattering function is directly related to the structural features of the system, being $F(Q,0)=S(Q)$, i.e., the static structure factor. In the hydrodynamic limit, for low values of Q, the dynamic structure factor displays three distinct peaks. A quasielastic one, located at zero energy exchange, whose width $\Gamma_c = D_T Q^2$ is related to the thermal diffusion coefficient D_T, and two inelastic peaks—the so called Brillouin doublet—located at frequencies $\omega = \pm c_S Q$,[16] with c_S being the adiabatic speed of sound, and whose width depends mostly on kinematic viscosity, which is the main mechanism driving sound damping. On the basis of linear hydrodynamics, the dispersive behavior, i.e., the dependence of the frequency ω of propagating collective modes on Q, is well known to display a transition between a linear adiabatic regime to a linear isothermal one, characterized by an isothermal speed of sound c_T, at Q values such that $\omega\tau_{\text{th}} \sim 1$, where τ_{th} is the characteristic decay time of thermal fluctuations ($\tau_{\text{th}} \sim 1/D_T Q^2$).[3,4] In other words, at sufficiently high Q values, thermal fluctuations are expected to decay on a time scale much shorter than the time scale of sound propagation, which now takes place in a thermalized environment. If we look at the line shape of the dynamic structure factor, the linewidth of the quasielastic line will increase, ultimately overwhelming the Brillouin doublet and causing a shift of the inelastic peaks position. The adiabatic and isothermal speeds of sound, as we already pointed out in Sec. I, are related by the specific heat ratio γ, and we many call $Q_0 \sim c_S/D_T$ the value at which the adiabatic to isothermal transition takes place. In this scenario, liquid metals constitute a particularly interesting class of simple liquids, because of their high thermal diffusivity with values of about ten times larger than c_S, shifting the Q range of the isothermal region down to values between 0.1 and 3 nm^{-1} provided that, (1) the Q dependence of transport coefficients can be neglected below at least 3 nm^{-1}, as is the case encountered in most liquid metals. (2) The system interaction with radiation can be described within an effective single-component model, in which only the core electrons from the metallic ions interact with the electromagnetic radiation. However, transport coefficients are supposed to take an effective value also carrying the net effect due to valence electrons.

The second assumption has been on the basis of a recent

debate focused on the interpretation of IXS data on liquid alkali metals and aluminum.[17–19] The main difficulty in ascertaining the existence of sound propagation with lower than adiabatic sound velocity value lies in the fact that γ is for most metallic systems very close to unity, as can be seen from the specific heats ratios reported for a selection of liquid metals near their melting point in Table I.

For alkali metals, $\gamma \sim 1$ as well as for the great majority of liquid metals. Among the systems exhibiting a comparably high value of the specific heat ratio (Fe, Co and Ni), liquid nickel has been chosen, also in view of its lower—despite still very high—melting temperature.

III. THE EXPERIMENT

The experiment reported in this work was carried out at the high resolution beamline ID16 of the European Synchrotron Radiation Facility (Grenoble, France).

The backscattering monochromator and analyzer crystals, operating at the (11, 11, 11) silicon reflections, gave a total energy resolution of 1.5 meV, while energy scans were performed by varying the temperature of the monochromator with respect to that of the analyzer crystals. The sample, in the shape of a 100 μm thick foil, was 99.993% purity nickel, purchased by Rare Metallic Co. Ltd. (Japan), and was hold in a sapphire cell obtained from a single monocrystal, which was a slight modification of the so called Tamura-type cell.[20,21] The use of sapphire prevented the sample interaction with container, still providing a good cell transmission, with a total cell thickness of 500 μm seen by the scattered beam. The cell was lodged in a molybdenum holder and heated up by means of a properly isolated tungsten resistance. The nickel absorption length at an energy of the incoming beam of 21 keV is about 50 μm; thus, in our condition, a 15% sample transmission was expected. A selection of IXS spectra from liquid Ni at 1767 K is reported in Fig. 1 as open circles at the lowest accessed Q values. Dotted lines report the experimental resolution. Phonon modes from the sapphire cell (speed of sound of about 7 km s^{-1}) are well recognizable up to 3 nm^{-1}; however, they are well separated from inelastic features from the sample at Q greater than 1 nm^{-1}.

IV. RESULTS AND DISCUSSION

Experimental data have been analyzed with a damped harmonic oscillator (DHO) function centered at frequency ω_L and of width Γ_L modeling inelastic contributions from the metal. The elastic features have been represented by a Lorentzian of full width at half maximum Γ_C. Such an approximation is expected to work well for not too high Q's, i.e., until there is a clear separation between elastic and inelastic features, as is the present case for IXS measurements. At Q values approaching Q_M, corresponding to the static structure factor maximum, one has to resort to a model based on a so called extended heat mode and two extended sound modes, also incorporating the frequency sum rules.[22] The elastic contribution from the cell, supposed to be much

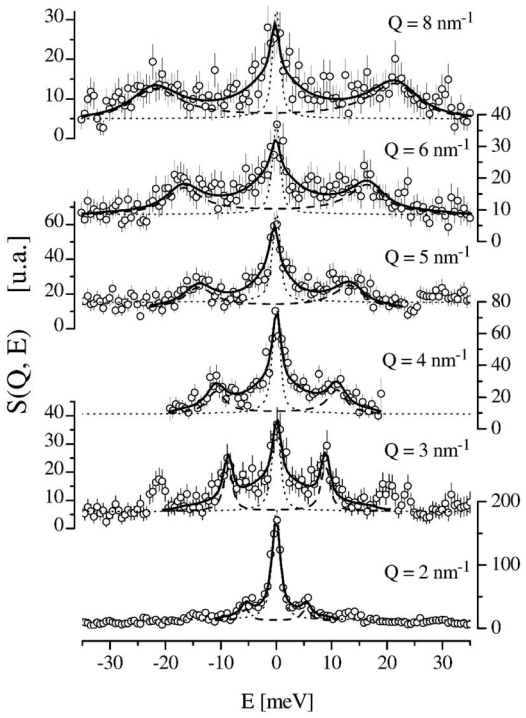

FIG. 1. A selection of IXS spectra from liquid Ni at 1767 K is reported (○) together with the experimental resolution (···). The model function, Eqs. (2) and (3), is also reported at each Q value (—), together with the DHO contribution (---). Phonon modes from the sapphire cell are recognizable up to 3 nm^{-1}; however, they are well separated from the inelastic features from the sample at Q greater than 1 nm^{-1}.

narrower than the experimental resolution, has been modeled with a Dirac delta function centered at zero frequency. Thus, the model for the $S(Q,\omega)$ can be written as

$$I_q(\omega) = I_{C,1}(Q)\delta(\omega) + I_{C,2}(Q)\frac{\Gamma_C(Q)}{\omega^2 + \Gamma_C(Q)^2} + I_L(Q)\frac{\omega_L^2(Q)\Gamma_L^2(Q)}{(\omega^2 - \omega_L^2(Q))^2 + (\omega\Gamma_L(Q))^2}. \quad (2)$$

Additionally, in order to properly reproduce the experimental spectra, the above expression has to be modified such as to be compliant with the detailed balance condition:

$$S(Q,\omega) = \frac{\beta\hbar\omega}{1 - e^{-\beta\hbar\omega}} I_q(\omega). \quad (3)$$

Before comparison with IXS data, the model is convoluted with the experimental resolution. This procedure results in the curves displayed as full lines in Fig. 1. Figure 2 reports the dispersion (a) and sound velocity (b) obtained for liquid Ni from the DHO model parameter ω_L at different Q values (□), while Fig. 3(a) reports sound damping as derived from the DHO parameter Γ_L (□). Sound speed and damping data are also reported from the cited INS experiment (▲),[6] as well as from MD experiments [○ (Ref. 7), –·–(Ref. 10)]. On one hand, our results (□) for the acoustic excitations frequency dependence on Q are in very good agreement with the data

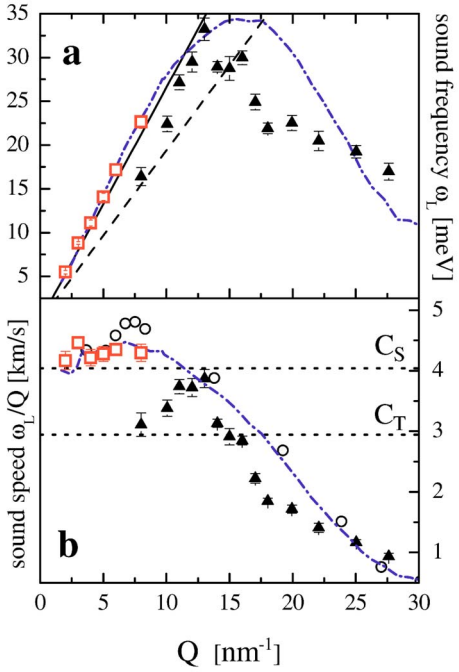

FIG. 2. (Color online) (a) Sound dispersion for liquid Ni: IXS (□) from the present work, an INS investigation by Bermejo *et al.* (Ref. 6) (▲), a MD simulation from Ruiz-Martín *et al.* (Ref. 10) (–·–). Adiabatic (—) and isothermal (---) sound dispersions are also reported. (b) Speed of sound reported from the present work (□) and from INS (Ref. 6) (▲) and MD [–·–(Ref. 10) and ○ (Ref. 7)] investigations. The adiabatic, c_S, and isothermal, c_T, speeds of sound are displayed (···).

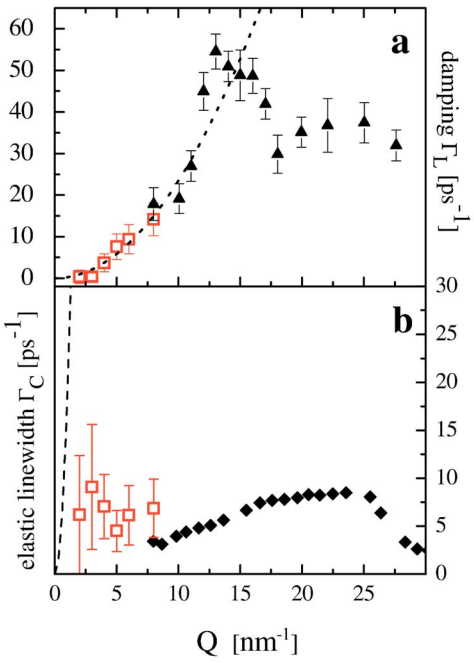

FIG. 3. (Color online) (a) Sound damping from the present work (□) and from INS (Ref. 6) (▲). The dashed line (---) is a quadratic best fit to the IXS data. (b) The quasielastic linewidth obtained in the present investigation of liquid Ni (□) and from a recent INS investigation (from the coherent dynamic structure factor) (Ref. 10) (◆). The expected hydrodynamic behavior is also reported (---), from the knowledge of the thermal diffusion coefficient D_T (Ref. 28).

obtained by Ruiz-Martín *et al.*[10] (–·–) in the most recent MD simulation on the subject, while, on the other hand, the experimental INS data (▲) are qualitatively different from both sets of data along the momentum range investigated.[6] This discrepancy is particularly evident in the region of $Q < 12$ nm^{-1}, where INS estimated sound speed reaches the isothermal value c_T (Fig. 2). This could be ascribed to the kinematic limitations to the energy accessible window at the lowest Q's which prevented the observation of the $S(Q,\omega)$ tail, and thus a reliable estimate of the DHO model parameters.[6]

In order to address the last issue, in Fig. 4, we report a comparison of IXS (○) and INS [▲ (Ref. 6)] dynamic structure factors at $Q=8$ nm^{-1}, corresponding to the lowest accessed Q-point for neutrons. The inelastic contribution to the IXS spectrum is emphasized by reporting the DHO function derived from the model [Eqs. (2) and (3)]. Beside the quasielastic peak, reflecting also the effect of incoherent scattering (which is not present in IXS in the case of monatomic systems), INS data show on the anti-Stokes side the presence of an inelastic peak around −16 meV. However, although the detailed balance condition would imply an even more pronounced peak on the Stokes side, its symmetric counterpart cannot be observed. Last but not least, the energy of propagating excitations found by means of IXS (22.6 meV) lies just at the edge of the accessed energy range for INS (−20 to 20 meV; see Fig. 4), corresponding to the energy and scattering angle configurations used in this experiment. Summing up, while at sufficiently high Q's, the sound dispersion of liquid Ni lies well inside the region of the momentum-energy range covered by INS, at Q values approaching wavevectors as low as 8 nm^{-1}, the reliability of the dispersion curve extracted by INS is questionable.

In Fig. 3(b), we report data for the elastic linewidth, compared with the expected hydrodynamic behavior, in which case the width of the quasielastic line is entirely due to thermal relaxation $\Gamma_C = D_T Q^2$ (- - -). Experimental INS values for Γ_C are also shown from a recent work (◆).[10] The present set of data [Fig. 3(b)] seems not to support the hypothesis of a weak Q dependence of transport coefficients.[3] Under this circumstance, the crossover to an isothermal re-

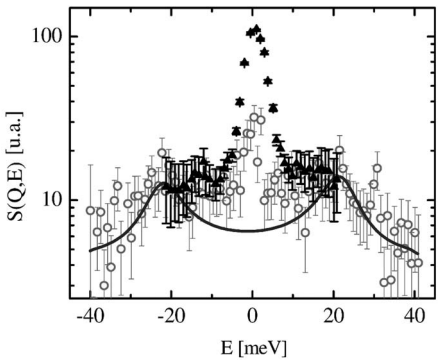

FIG. 4. Comparison of IXS (○) and INS (▲) (Ref. 6) dynamic structure factors for liquid Ni at $Q=8$ nm^{-1}. Data have been normalized to a constant factor in order to plot them on the same scale. The DHO function used to model IXS inelastic features is also reported (—, see also Fig. 1). The exchanged energy range covered by INS is narrower than that accessed by IXS, due to the kinematics of the scattering process for neutrons.

gime in liquid Ni may occur at values well below $1-2\ \mathrm{nm}^{-1}$, thus not accessible in the present experiment.

V. CONCLUSIONS

In conclusion, we performed an IXS experiment on liquid Ni at 1767 K, showing the ability of such system to sustain sound propagation over wavelengths comparable to the typical interparticle distance. Despite the indication from a previous INS investigation[6] suggesting the tendency of sound speed to attain the isothermal value at Q lower than $8\ \mathrm{nm}^{-1}$, we found the evidence of an adiabatic dynamical regime holding at Q as low as $2\ \mathrm{nm}^{-1}$, thus confirming MD results for the microscopic dynamics of this system.[7,10] The discrepancy, observed for $8<Q<12\ \mathrm{nm}^{-1}$ between INS data, on one hand, and results from IXS and MD, on the other hand, is probably related to the limitations imposed to the energy-momentum accessible region by the kinematics of the scattering process for neutrons. Even though an adiabatic regime still holds at the lowest accessed Q for liquid Ni, the weak Q dependence of the quasielastic linewidth clearly suggests that a generalized hydrodynamic picture should be invoked. The present result calls for further investigations with higher signal to noise ratio and at different temperatures to unambiguously ascertain the existence of an intermediate isothermal regime in liquid Ni in the explored momentum region.

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