Collective dynamics of liquid Fe

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Abstract. The dynamic structure factor $S(Q, \omega)$ of liquid Fe was measured near the melting point of 1570 °C using high-resolution inelastic x-ray scattering spectrometer at BL35XU/SPRING-8. Although liquid Fe has large values of the ratio of heat capacities $\gamma$ and the viscosity $\eta$, the $S(Q, \omega)$ spectra show well-defined collective excitations. The excitation energy $\omega_Q$ of the inelastic excitation modes was obtained within the generalized Langevin formalism. A positive dispersion of the sound velocity, as compared to the hydrodynamic value by about 20 %, was found as in other liquid metals. The $\eta(Q)$ values decrease rapidly with $Q$, which may result in the well-defined collective excitations.

1. Introduction

In recent years, particle dynamics in liquid metals have intensively been investigated due to the extensive progress of inelastic x-ray scattering (IXS) technique using third-generation synchrotron radiation sources. The obtained high quality $S(Q, \omega)$ data have been analyzed using a damped harmonic oscillator model [1] or generalized Langevin formalism using memory functions [2]. In most liquid metals, energies of inelastic excitations are deviated from the hydrodynamic values obtained from the velocity of sound. This has been well discussed in context of generalized hydrodynamic theory [3], and usually explained by the hydrodynamic-to-viscoelastic transition. The acoustic excitation lifetimes are shortened by heat flow and viscous drag forces. Within the thermodynamic limit [2], the width of the inelastic excitation peaks, $\Gamma Q^2$, can be estimated from hydrodynamic equation,

$$\Gamma = \frac{[\gamma - 1]D_T + \eta/\rho]}{2}, \quad (1)$$

where $\gamma$ is the ratio of specific heats at constant pressure and constant volume, $D_T$ the thermal diffusivity, $\eta$ the longitudinal viscosity, and $\rho$ the density.

Liquid Fe has a large $\gamma$ value of 1.72 and a large shear viscosity ($\eta_s$) value of 5.5 mPas, from which a strong damping feature in the excitation modes was expected from the thermodynamic equation. However, the inelastic excitations obtained from the present IXS experiment near the melting point of 1570 °C are not overdamped, but well-defined excitation modes are visualized. In this paper, we report results of IXS spectra of liquid Fe, and discuss the feature of collective excitation modes.
2. Experimental procedure

The IXS experiments were performed at the beamline BL35XU of the SPring-8 using a high energy-resolution IXS spectrometer [4]. A monochromatized beam of 3.5 × 10^{9} photons/s was obtained from a cryogenically cooled Si(111) double crystal followed by an Si (11 11 11) monochromator operating in extremely backscattering geometry (89.975°, 21.75 keV). The same backscattering geometry of twelve two-dimensionally curved Si analyzers was used for the energy analysis of the scattered x-ray photons. The energy resolution was determined by the scattering from a Plexiglas sample and values of 1.6-1.9 meV (FWHM) were found for the detecting systems depending on the analyzer crystals. The Q resolution was set to be about ±0.30 nm^{-1}.

The sample thickness was about 100 µm, being slightly larger than an 1/e absorber. The purity of the sample was 99.9999 %. It was located in a single-crystal sapphire cell, which was a slight modification of the so-called Tamura-type cell [5]. The sample contained in the cell was placed in a vessel equipped with single-crystal Si windows. The very high temperature of 1570 °C was achieved using two W resistance heaters, and monitored with two W-5%Re/W-26%Re thermocouples. The IXS experiments were carried out at about twenty Q values between 1.3 and 21.3 nm^{-1} covering an energy transfer range of about ±40 or ±50 meV.

3. Results and discussion

Circles in figure 1 shows the selected IXS spectra normalized to the corresponding integral intensity, which is nearly identical to S(Q, ω)/S(Q) except the resolution broadening. Also given as a dashed line is a typical example of the resolution function. Clear inelastic excitations are seen as peaks or shoulders at both the side of the central line, and the energy of the inelastic contributions shifts with increasing Q. This result clearly demonstrates that the inelastic excitations originate from propagating modes.

A resolution correction was accomplished by noticing that the measured intensity is a convolution of a model S(Q, ω) and the experimentally determined resolution function. For the model, we used a generalized Langevin formalism with a memory function. The basic time correlation probing the collective dynamics in a monatomic fluid (N particles with a mass of m) is the intermediate scattering function, F(Q, t) = (1/N) \sum_{i,j} \langle e^{-iQr_{i}(0)e^{+iQr_{j}(t)}} \rangle, where r_{j}(t) denotes the position of j-th particle at time t. Since S(Q, ω) is the frequency spectrum of F(Q, t), it is in general possible to obtain the latter from experimental data with a sufficient quality. Within the generalized Langevin formalism, F(Q, t) is determined by

\[ \bar{F}(Q, t) + \omega_{0}^{2}(Q)F(Q, t) + \int_{0}^{t} M(Q, t - t')\bar{F}(Q, t')dt' = 0. \] (2)

Here, M(Q, t) is the memory function of the density fluctuations, and \( \omega_{0}^{2}(Q) = k_{B}TQ^{2}/mS(Q) \) is the reduced second frequency moment of S(Q, ω), which gives the lowest limit of the sound velocity at a finite Q as c_{0}(Q) = \omega_{0}(Q)/Q.

For M(Q, t), we used the well-known approximation containing an exponential for thermal relaxation and two exponential decay channels for viscous relaxation [8] given as,

\[ M(Q, t) = [\gamma(Q) - 1]\omega_{0}^{2}(Q)e^{-D\tau_{T}(Q)Q^{2}t} \]

\[ + [\omega_{0}^{2}(Q) - \gamma(Q)\omega_{0}^{2}(Q)][(1 - A(Q))e^{-t/\tau_{\mu}(Q)} + A(Q)e^{-t/\tau_{\alpha}(Q)}]. \] (3)

The Q → 0 limits of \( \gamma \) and \( D\tau_{T} \) values were used for the calculation at each finite Q. In the second term, \( \omega_{0}^{2}(Q) \) is the reduced forth moment of S(Q, ω), which characterizes the instantaneous collective response of the liquid at a finite Q, and determines the generalized infinite-frequency velocity (or highest limit of sound velocity in generalized hydrodynamics), c_{∞} = \omega_{1}(Q)/Q. \( \tau_{\mu} \) and \( \tau_{\alpha} \) are, respectively, relaxation rates for the so-called microscopic \( \mu \)-relaxation process.
as a faster relaxation dominant over a very short timescale and the $\alpha$-relaxation (structural relaxation) process as responsible for the long-lasting tail. $A(Q)$ measures the relative weight of the slow viscoelastic decay channel. For the simplicity, the viscoelastic term is written as $[9]$, $\Delta_\alpha(Q)e^{-t/\tau_\alpha(Q)} + \Delta_\beta(Q)e^{-t/\tau_\beta(Q)}$. The above approach has proven to be useful in describing results of computer simulation studies on simple liquids $[8]$, and also of experimental IXS data on many liquid metals $[7]$. Details of this model were described in Ref. $[9]$.

For each $Q$ value, the frequency spectrum of $F(Q, t)$ convoluted with the experimentally obtained resolution function was fitted to the present scattering intensity data. The model function fits well to the data, which are shown as the solid lines in figure 1. Then, the resolution-deconvoluted lineshapes of $S(Q, \omega)$ were built from the fitting parameters, and the corresponding longitudinal current correlation functions, $J(Q, \omega) = (\omega^2/Q^2)S(Q, \omega)$, were calculated from the obtained $S(Q, \omega)$ spectra. The maximum of the $J(Q, \omega)$ function, $\omega_Q$, was used for determining the dispersion relation of the inelastic modes at the finite $Q$ values.

Circles in figure 2 indicate the dynamical sound velocity $c_Q = \omega_Q/Q$ at various $Q$ values. The closed triangles indicate the generalized isothermal sound velocity $c_0(Q) = \omega_0/Q$, and the open triangles the high-frequency values $c_\infty = \omega_l/Q$. The arrow shows the hydrodynamic limit at $Q \to 0$, i.e., the adiabatic sound velocity of 3,800 m/s $[6]$. The $c_Q$ value already deviates from the hydrodynamic value by about 20% even at the lowest $Q$ values measured, reaches the high-frequency limit $c_\infty$ around $Q = 8-10$ nm$^{-1}$, and again approaches the lower limit $c_0$ when the $Q$ value reaches the $S(Q)$ maximum.

Figure 1. Selected IXS spectra (circles) normalized to the corresponding intensity. The dashed curve represents a typical resolution function, and solid curves indicate the best fits using the generalized Langevin formalism convoluted with the resolution function to the experimental data.
Figure 2. Dynamical sound velocity $c_Q$ obtained from this generalized Langevin analysis. The open triangles indicate $c_0(Q)$, and the closed triangles $c_\infty(Q)$. See the text for details.

Figure 3. The $Q$ dependence of longitudinal viscosity $\eta(Q)$ calculated from generalized Langevin analysis. The arrow shows the hydrodynamic shear viscosity $\eta_s$. The solid curve is guide for eyes.

The $Q$-dependent (generalized) longitudinal viscosity $\eta(Q)$ in the Langevin formalism is the total area of the memory function, expressed as, $\eta(Q) = (\Delta^2_\nu \tau_\mu + \Delta^2_\alpha \tau_\alpha)/Q^2$. Figure 3 shows the $\eta(Q)$ values, and the arrow indicates the hydrodynamic value of the shear viscosity obtained experimentally [10]. Noting that for liquid metals the shear viscosity part usually accounts for a half of the longitudinal viscosity, the agreement is satisfactory. The $\eta(Q)$ value decreases rapidly with increasing $Q$, which may qualitatively contribute the well-defined (not damped) feature of the inelastic excitation modes at finite $Q$ values in liquid Fe. It should be noted that even using the reduced $\eta(Q)$ values for the hydrodynamic equation (1), the results of the width for the excitation modes are overestimated by about twice. The damping of collective modes will be discussed in detail in the subsequent paper [11].

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