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Original Article

High-frequency Collective Ionic Dynamics in Liquid Metals

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Abstract: The coexistence of the transverse and fast sounds of liquid metals in the terahertz range near the melting point is explained. These sound modes are phonon polaritons arisen from the interaction between the transverse collective ionic oscillations, known as phonons, and the electromagnetic wave radiated by the ions in vibration at high enough frequencies, for instance, in liquid Zn, Cu, and Fe. Applying the phonon-polariton dispersion relations, several critical dynamic parameters of these liquid metals such as the structural relaxation times, speeds of the fast and transverse sound modes, dielectric constant at THz frequency are extracted, allowing to further understand dynamic behaviors of liquid metals at the atomic level. Phonon-polariton theory can be used for the study of the dynamics in the terahertz frequency range of similar liquid metals.

Keywords: Fast sound, collective ionic dynamics, liquid metals, phonon polaritons.

1. Introduction

Longitudinal collective modes or common sound waves in liquid metals have been quite well understood. Yet, the contribution of these modes to the energy and heat capacity is inconsiderable. It demonstrated that the energy of metallic liquids as well as nonmetallic liquids is mostly governed by two types of collective excitations at terahertz frequencies [1-4]. The first mode is transverse collective oscillations whose speed is smaller, a bit, than the speed of the common sound waves. The other mode is the high-frequency collective excitations whose speed is more than twice the speed of the transverse excitations, sometime called the fast sound. Investigating the collective ionic oscillations can reveal information on microscopic dynamic behaviors [5-6] of liquid metals such as the diffusion of ions, ion-ion interaction, and the thermodynamic properties.

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In recent years, many experimental works [7-10] based on inelastic X-ray and inelastic neutron scatterings have been executed to study the collective ion dynamics at terahertz frequencies of liquid metals. The complicated dynamical behaviors at high frequencies are also investigated by molecular dynamic simulations [6, 11, 12]. There are great efforts in modelling the liquid properties. Due to the coexistence of strong ion-ion interaction and the strong diffusions of ions, it is difficult to develop a unified theory of liquid metals. Considering liquids as systems in a mixed dynamical state [1-4, 13] combining behaviors of both solid and gas phases is an effective theoretical approach to probe their dynamics at high frequencies. Despite continuous progress in the development of theoretical schemes, it remains many unanswered questions towards the understanding of the collective ionic dynamics, for example, the origin of the two collective ionic excitation modes in liquid metals.

This work focuses on understanding the origin of the fast sound and the transverse sound in liquid metals near the melting point using the phonon-polariton theory, which has ever been applied for the description of the dispersion of the fast and the transverse sound modes in liquid water at ambient temperature [13]. We proposed that there are transverse excitations or phonons at a high enough frequency propagating in liquid metals like that in solids. The interaction between phonon and electromagnetic wave radiated by the vibration of ions leads to the coexistence of two phonon-polariton modes, corresponding to the transverse and fast sound waves. The dispersion of the two modes is analyzed in detail. Comparing to experimental data, several critical dynamic parameters as well as the dynamic properties at high frequencies of liquid Zn, Cu, Fe are extracted.

2. Phonons in Liquid Metals

The short-range order liquids can provide structure similarly to amorphous solids [6-9]. The local structure of liquid metals such as gallium or zinc was observed to be analogous to their crystal structure, with the existence of ionic dimers. Moreover, liquid water and liquid metals at temperatures near to the melting point were known to well support the propagation of both longitudinal and transverse collective density oscillations, like solids [1]. It means that liquid still conserves itself several dynamic behaviors at solid phase. Therefore, theoretical model based on a phonon theory has been used to investigate the properties in thermodynamics of liquids [2, 3, 14].

Phonons are known as quantization of collective excitations of systems with periodic and elastic structure of atoms and molecules. They play a critical role in many of the physical properties of condensed matters, such as thermal conductivity and electrical conductivity. Differing from solid systems, the matter particles in liquids can oscillate around their temporary equilibrium positions and diffuse because they are governed by both near and far interactions between each other [1, 13-15]. The average time between diffusive hopping or reorientation events is symbolized by τ which is referred to as the structural relaxation time, about ps. Frenkel proposed [16] that if the frequency Ω of collective density oscillations is low, i.e.,$\Omega\tau < 1$the local rearrangements of the particles are considerable due to the hopping diffusion and reorientation of ions or atoms. The system is a flowing liquid, and hence does not support the emergence of transverse excitations or phonons. In this state, only a longitudinal sound wave can travel. However, at times shorter than the relaxation time, no particle rearrangements take place in the system like in crystal regime. It means that when the frequency of collective density oscillations is high enough, $\Omega\tau \geq 1$, the propagation of not only longitudinal but also transverse collective ionic oscillations is supported. Thus, the transverse collective vibrations (phonons) could be emerged in metallic liquids and propagate along the local dimers confined in icosahedral or cage until they scatter. The existence of phonons in liquid water at ambient temperatures has ever been confirmed [3, 14]. Indeed, the terms "collective modes" and "phonons" have been used interchangeably as investigating liquid thermodynamics at high frequencies [1].

3. Phonon Polaritons in Liquid Metals

Liquid metals consist of positive ions, free electrons, and atoms. The vibration of positive ions could produce an electromagnetic wave of THz frequency whose wavelength is approximately μm. Because it is much larger than the inter-ionic distance (about nm [6, 9]), the electromagnetic wave radiated by positive ions can travel in the liquid system. The interaction between energy excitations (photon or neutron) with low energy and positive ions could result in only the longitudinal collective ionic mode at frequency $\Omega < \omega_F$ The electromagnetic wave radiated by the ions in vibration can't combine with the longitudinal mode. Hence, the collective density oscillation with frequency smaller than Frenkel frequency is the common longitudinal sound wave. However, the interaction between excitations with high enough energy and positive ions can lead to the emergence of both the transverse collective mode with frequency ω_T and the longitudinal mode with frequency ω_L higher than ω_F . The coupling between the transverse collective vibrations and the local electromagnetic field radiated by the ionic oscillation gives rise phonon polaritons.

Suppose that simple harmonic vibrations with frequency ω_T are isotropic and uniformly distributed in the entire space. For a plane wave with the wave vector *Q*, the response of the liquid system to the radiation field with frequency Ω satisfies the Gauss equation

$$Q^2(\Omega) = \frac{\Omega^2}{c^2}\varepsilon(\Omega), \tag{1}$$

in which c is the speed of photon and $\varepsilon(\Omega)$ is the dielectric function. The dielectric function is defined by

$$\varepsilon(\Omega) = \varepsilon_\infty \frac{\omega_L^2 - \Omega^2}{\omega_T^2 - \Omega^2}. \tag{2}$$

Note that ε_∞ is the electric response of liquid metal at terahertz frequency. The frequencies $\Omega_\pm$ of phonon polaritons, which are extracted from Eqs. (1) and (2), in liquid metals are described by two relations [17]:

$$\Omega_\pm^2(Q) = \frac{1}{2}\left\{\frac{c^2}{\varepsilon_\infty}Q^2 + \omega_L^2 \pm \left[(\frac{c^2}{\varepsilon_\infty}Q^2 + \omega_L^2)^2 - 4\omega_T^2 Q^2\right]^2\right\}. \tag{3}$$

The dispersion of these two modes is shown by two solid curves in Figure 1. The phonon-polariton mode at higher frequency is in purple and the phonon-polariton mode at lower frequency is in black.

As the wave vector *Q* is large, the lower-frequency mode $\Omega_- \to \omega_T$ and the higher-frequency mode depends linearly on the wave vector *Q* (shown by the dotted lines in Figure 1)

$$\Omega_+ = v_f Q, \tag{4}$$

in which $v_f = c/\sqrt{\varepsilon_\infty}$ is the velocity of the fast sound mode. The longitudinal mode observed in experimental work is the phonon polaritons with higher frequencies and in the large-*Q* limit [9,10]. In the low-*Q* limit, the higher-frequency mode Ω_+ reaches to ω_L while the lower-frequency mode is a linear function of *Q* (shown by the dashed lines in Figure 1)

$$\Omega_- = v_l Q. \qquad (5)$$

The traverse mode observed in experimental work is the phonon polaritons with lower frequencies and in the low-*Q* limit. The data of both longitudinal and the traverse sound modes of several liquid metals are measured [9-10] as shown in Figure 1. We found that Eq. (3) can describe quite well the dispersion of both two modes.

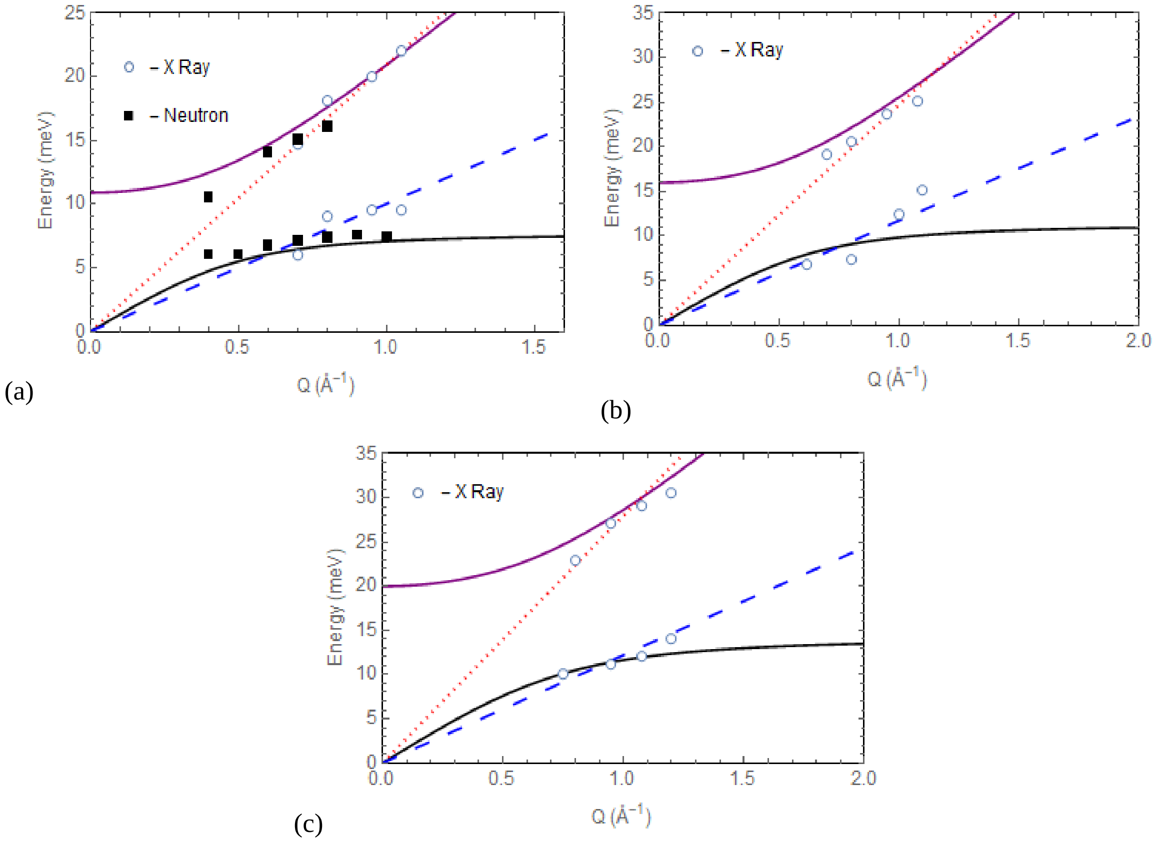

Figure 1. Dispersion of phonon polaritons with two modes for liquid Zn (a), Cu (b) and Fe (c) are presented by two solid curves (purple – the mode with frequency Ω_+ and black – the mode with frequency) Ω_-. Squared symbols illustrate elastic neutron scattering data in [10] and open circles are data of elastic X-ray scattering in [9].

4. Dynamic Parameters of Liquid Metals at High Frequencies

Several critical dynamic parameters of liquid metals can be calculated by using phonon-polariton theory. In this section, we extract some dynamic parameters of liquids Zn, Cu, and Fe.

Combining the two expressions in Eq. (3) with the experimental data reported in [9,10], the dynamic parameters in Eq. (3) for liquid metals can be given. For liquid Zn, it is extracted $\hbar\omega_T = 7.5$ meV, $\hbar\omega_L = 10.9$ meV, $v_f = 21,2$ meV.Å^{-1} (about 3300 m.s^{-1}) and $v_l = 10,1$ meV.Å^{-1} (about 1550 m.s^{-1}). For liquid Cu, $\hbar\omega_T = 10.4$ meV, $\hbar\omega_L = 16.1$ meV, $v_f = 24.8$ meV.Å^{-1} and $v_f = 11.5$ meV.Å^{-1}. We calculated $\hbar\omega_T = 13.4$ meV, $\hbar\omega_L = 19.8$ meV, $v_f = 28.1$ meV.Å^{-1}, and $v_f = 12.2$ meV.Å^{-1} for liquid Fe. In three cases, the ratio $v_f / v_s \approx 2$ is automatically obtained and the extracted values of v_f and v_l are relatively close to those reported in literatures [9, 10].

Frenkel frequency of liquid metals can be estimated by the phonon-polariton model. It is about 1.7 THz for Zn, 2.6 THz for Cu, and 3.1 THz for Fe. Because the frequency of the transverse collective oscillations is classified in the following order zinc < copper < iron, the Frenkel frequency is also classified in the same order. It means that the structural relaxation time τ is ordered as zinc > copper > iron, consistent well with the results reported in [9].

Both the high- and low-frequency collective modes could travel in liquid metals if the propagation length is larger than the inter-ionic spacing. The propagation length of the fast sound mode is given by $d = v_f / \Omega_+$. Here, Debye frequency ω_D is to be the highest frequency of the upper phonon-polariton mode (corresponding to wave vector Q_D) whose propagation length equals the average inter-ionic space. Here, Q_D is considered to be the gap value of the wave vector which was mentioned in [18]. We predict that the frequency range of the two phonon-polariton modes in liquid metals are from ω_F to ω_D, corresponding to the wave vector range from 0.5 Å^{-1} to 1.2 Å^{-1}. According to the experimental data, the Debye frequencies of liquid Zn, Cu, and Fe are estimated about 4.38, 6.01, and 7.25 TH, respectively.

Dielectric function is an important parameter which reflects the strength of storage of energy of the materials due to the polar effect of the material to the electric field. When an external field is applied, there is the electric polarization of atoms and ions due to the interaction between electron cloud as well as ions in the metals and the electric field. The relationship $\varepsilon_\infty = c^2 / v_f^2$ in the phonon-polariton model has ever been applied for calculating the dielectric function of liquid water at terahertz frequencies, which is consistent well with experimental data. Analogously, this relation can be used to calculate the dielectric constant of liquid metals in the range from 3.62 THz to 7.25 THz, whose is the frequency of the fast sound. It is estimated that the dielectric function of liquid Zn, Cu, and Fe near the melting point are 8.74, 5.6, and 4.4, quite close to their dielectric function at the solid phase [19]. Indeed, for crystalline metals, the atoms and ions locate at fixed positions. At high frequencies, neither the reorientation nor the self-diffusion of ions and atoms could be seen, i.e., the system behaves in the solid regime. Therefore, the response to electric field of the liquid metals is similar to that of solid metals.

5. Conclusions

In this work, the origin of two types of collective ionic excitations travelling in liquid metals near the melting point is revealed. We suggested that the transverse collective vibrations of ions above Frenkel frequency in liquid metals are referred as phonons propagating along ionic dimers. The interaction between the phonon and local electromagnetic wave radiated from the vibration of ions leads to the emergence of two modes of phonon polaritons. The phonon polariton at higher frequency is traveled with fast speed whereas the phonon polariton at lower frequency is propagated with lower speed, corresponding to fast sound and transverse sound observed in liquid metals. The phonon-polariton theory describes quite well the dispersion of both the two modes in liquid Zn, Cu, and Fe. Several important dynamic parameters of liquid metals such as Frenkel frequencies, relaxation times, and dielectric function at terahertz frequency can be extracted by comparing the model to experimental data, in good agreement with the results reported in literature. We pointed out the frequency and the wave-vector ranges of these two modes based on the phonon-polariton theory. The phonon-polariton theory can be used for further understanding the microscopic dynamics at terahertz frequencies of similar metallic liquids.

Nowadays, liquid metals have been actively studying, because they are known as advanced functional materials for novel applications which exploit the material flexibility coupled to the high electrical conductivity such as notably transient devices, soft robotics, biomedical sensing, and health monitoring [20]. The impact of liquids Hg and Ga as adaptive sensors and Ga-based alloys as biomaterials [21] is receiving a great attention. The knowledge of the dynamics of liquid metals at high frequencies is useful for well understanding the thermodynamic behaviors of liquid systems as well the dynamics at high frequencies of similar liquid metals observed in experimental works.

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