

Atomic Collective Excitations in Liquid Lead

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The atomic dynamics of liquid lead at the temperature $T = 600$ K has been simulated on the basis of the embedded atom model potential (the “embedded” atom model making it possible to effectively take into account the many-particle interactions) in order to study the mechanisms of formation of the atomic collective excitations. Spectra of the dynamic structure factor $S(k, \omega)$ and the spectral densities of the time correlation functions of the longitudinal $\tilde{C}_L(k, \omega)$ and transverse $\tilde{C}_T(k, \omega)$ currents have been calculated for the wavenumber region $0.11 \text{ \AA}^{-1} \leq k \leq 2.01 \text{ \AA}^{-1}$. It has been established that the dynamics of density fluctuations is characterized by two dispersion “acoustic-like” branches of the longitudinal and transverse polarization.

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1. INTRODUCTION

Establishing the mechanism of propagation of the collective excitations associated with the motion of atoms/molecules in liquids is one of the important problems of condensed matter physics [1–4]. It is known that the collective dynamics of particles in liquid metals is characterized by a series of specific features [5]. In particular, the frequency spectrum of the dynamic structure factor $S(k, \omega)$ containing information about the dynamics of the density fluctuations has a pronounced three-peak structure, which is observed in experiments on neutron and inelastic X-ray scattering in liquid metals [1, 5]. The analysis of the dispersion curves characterizing the dependence $\omega_c(k)$ of the position of the high-frequency peak on the wavenumber revealed the presence of the so-called “positive dispersion” of the speed of sound [1, 3, 5]. Another important feature found in the experiments on neutron and X-ray spectroscopy in liquids is the fact that the three-peak shape $S(k, \omega)$ is not reproduced by a combination of three Lorentzian functions (over the frequency ω at the fixed k value) [6]. These and other features characterizing the collective atomic (molecular) dynamics in liquids stimulate additional experiments [7–9] and the development of the corresponding theoretical interpretations [5].

The first experimental results on the neutron inelastic scattering in liquid lead were obtained in the middle of the 1950s by the research groups headed by Egelstaff and Brockhouse. A detailed discussion of these results can be found in [1, 5, 7–14]. The presence of the high-frequency collective excitations in the spectra $S(k, \omega)$ of liquid lead was indicated there. Later on the basis of the experimental data obtained independently by two research groups [15, 16], it was supposed that there are two inelastic peaks in $S(k, \omega)$

forming two pronounced dispersion curves, the physical nature of which was presumably associated with the longitudinal and transverse *acoustics-like* excitations. However, the subsequent experiments could not give any confirmation of this hypothesis [17–21]. The features observed in the low-frequency region of the spectra $S(k, \omega)$ were associated with the effects of multiple scattering [7–9].

The molecular dynamics computer simulations make it possible to establish the physical factors responsible for the collective correlated dynamics of particles in liquids [22, 23]. Similar numerical studies were performed for water [22, 23], liquid gallium [24–26], tin [27], silica [9], germanium oxide [28], and different metal alloys and compounds [29–31]. At the same time, the first results on the simulation of the atomic dynamics of liquid lead near the melting temperature ($T = 613$ K) showed the presence of a single dispersion branch [32, 33] manifested in the spectra $S(k, \omega)$ that was confirmed in the subsequent molecular-dynamics calculations [34–36]. Thus, a clear understanding of the physical mechanisms of the propagation of the atomic collective excitations in liquids is absent to date, even for the case of simple one-component systems [9].

2. SIMULATION DETAILS

The system considered in this work consisted of $N = 13\,500$ atoms in a cubic cell with periodic boundary conditions. The particles interacted via the embedded atom model potential adapted for lead [37]. In this model, the corrections taking into account the influence of the environment are introduced in addition to the pair interatomic interactions [38, 39]. The potential energy for metals described by the embedded

atom model potentials can be written in the general form as

$$\mathcal{U}(r) = \sum_{i < j} \varphi(r_{ij}) + \sum_i \Phi(\rho_i). \quad (1)$$

Here, $\varphi(r_{ij})$ is the pair potential of the interatomic interaction, and $\Phi(\rho_i)$ is the “embedded” function characterizing effectively the many-particle interactions in terms of the electron density of the i th atom ρ_i . The simulation was performed in the canonical (NVT) ensemble. To maintain the system in the state of thermodynamic equilibrium, we used a Nosé–Hoover thermostat with the interaction parameter $\tau = 100.0$ ps. The equations of motion of atoms were integrated on the basis of the velocity Verlet algorithm with the time step $dt = 10^{-15}$ s [40]. Liquid lead was prepared by melting a crystal with the fcc structure and making the temperature of the system $T = 3000$ K with the subsequent cooling to the temperature $T = 600$ K. The cooling rate was $\gamma = 10^{10}$ K/s. To transfer the system to the state of the thermodynamic equilibrium, 10^6 time steps were performed. The time characteristics were calculated over the time scale $t = 1.2$ ns.¹

3. EXPERIMENTAL RESULTS

The dynamic structure factor $S(k, \omega)$ is related to the coherent scattering function

$$F(k, t) = \frac{\langle \delta\rho_k^*(0)\delta\rho_k(t) \rangle}{\langle |\delta\rho_k(0)|^2 \rangle} \quad (2)$$

as follows:

$$S(k, \omega) = \frac{S(k)}{\pi} \int_0^\infty F(k, t) e^{i\omega t} dt, \quad (3)$$

where $S(k) = \langle |\delta\rho_k(0)|^2 \rangle$ is the static structure factor [41], the quantity

$$\delta\rho_k(t) = \frac{1}{\sqrt{N}} \sum_{j=1}^N e^{-i(\mathbf{k}, \mathbf{r}_j(t))} \quad (4)$$

determines the density fluctuations in the spatial region with the size of $2\pi/|\mathbf{k}|$, $|\mathbf{k}|$ is the wavenumber, and $\mathbf{r}_j(t)$ is the radius vector characterizing the position of the j th particle at the time t . Thus, the dynamic structure factor contains information about the density redistribution over a certain spatial scale along the direction given by the wave vector \mathbf{k} . On the other hand, the propagation of the collective excitations in

the multiparticle system can be characterized by the current variables

$$j_L(k, t) = \frac{1}{\sqrt{N}} \sum_l^N [\mathbf{e}_k, \mathfrak{g}_l(t)] e^{-i(\mathbf{k}, \mathbf{r}_l(t))}, \quad (5)$$

$$j_T(k, t) = \frac{1}{\sqrt{N}} \sum_l^N [\mathbf{e}_k, \mathfrak{g}_l(t)] e^{-i(\mathbf{k}, \mathbf{r}_l(t))}. \quad (6)$$

Here, $j_L(k, t)$ determines the value of the longitudinal current, i.e., the motion of particles along the direction \mathbf{k} . The quantity $j_T(k, t)$ characterizes the transverse current, i.e., the motion (vibrations) of the particles in the plane orthogonal to the direction \mathbf{k} . The time correlation functions of these (current) variables [42]

$$C_\alpha(k, t) = \frac{\langle j_\alpha^*(k, 0) j_\alpha(k, t) \rangle}{\langle j_\alpha^*(k, 0) j_\alpha(k, 0) \rangle}, \quad \alpha \in \{L, T\}, \quad (7)$$

will determine the features of the propagation of the waves owing to the redistribution of the number density of particles with the longitudinal ($\alpha \equiv L$) and transverse ($\alpha \equiv T$) polarizations. Analogous to expression (3), we determine the spectral densities:

$$\begin{aligned} \tilde{C}_\alpha(k, \omega) &= \frac{1}{\pi} \int_0^\infty C_\alpha(k, t) e^{i\omega t} dt \\ &= \frac{1}{t_M} \left| \int_0^{t_M} j_\alpha(k, t) e^{i\omega t} dt \right|^2, \end{aligned} \quad (8)$$

$\alpha \in \{L, T\},$

where t_M is the observation time scale. The last equality in Eq. (8) follows from the Wiener–Khinchin theorem [43]. The spectral features in $\tilde{C}_L(k, \omega)$ and $\tilde{C}_T(k, \omega)$ determine the characteristic frequencies of the vibrational processes of the longitudinal and transverse polarizations, respectively, and the positions of the high-frequency peaks in these spectra at different wavenumbers, i.e., the dispersion dependences $\omega_c^{(L)}(k)$ and $\omega_c^{(T)}(k)$.

It should also be noted that the high-frequency features of the spectra of the dynamic structure factor will be more vividly manifested in the spectral density of time correlation functions of the longitudinal current $\tilde{C}_L(k, \omega)$. This follows directly from the expression [44]

$$\frac{k_B T k^2}{m} C_L(k, t) = -\frac{d^2 F(k, t)}{dt^2}. \quad (9)$$

¹ The frequency characteristics are given in units of $\omega_E =$

$\sqrt{\frac{4\pi n}{3m} \int_0^\infty g(r) \nabla^2 \mathcal{U}(r) r^2 dr}$, which estimates the so-called Einstein frequency.

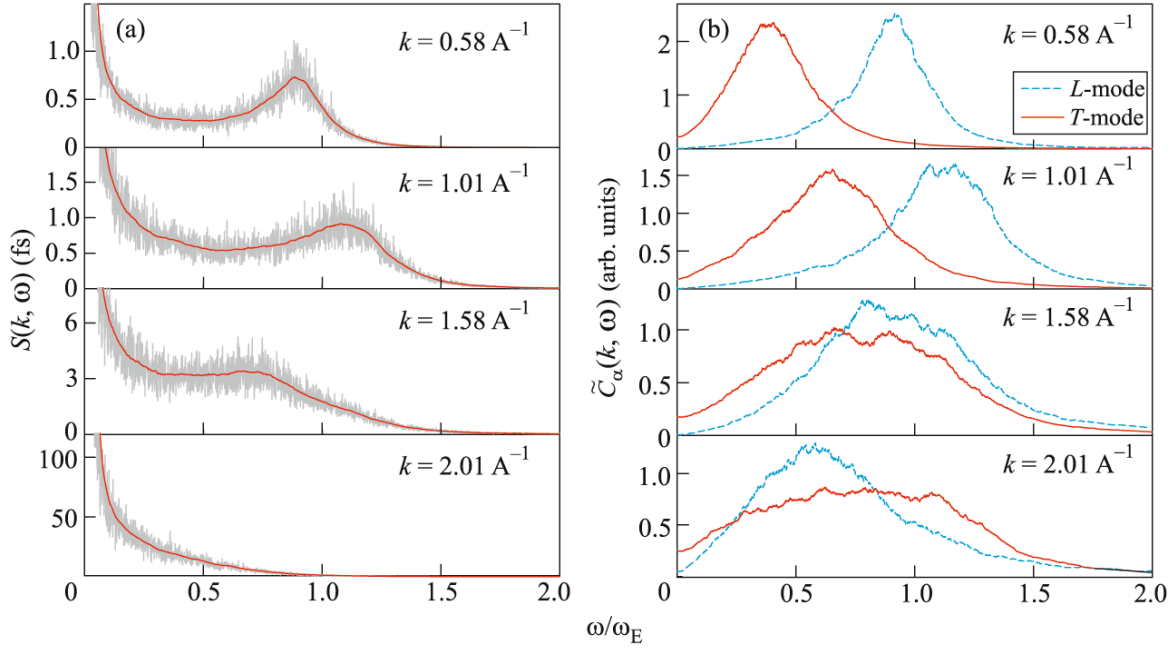


Fig. 1. (Color online) (a) Dynamic structure factor for liquid lead at the temperature $T = 600$ K for the wavenumbers $0.58 \text{ \AA}^{-1} \leq k \leq 2.01 \text{ \AA}^{-1}$. (b) Spectrum of the density of the time correlation functions of the (L) longitudinal and (T) transverse currents.

Therefore,

$$\frac{k_B T}{m} \tilde{C}_L(k, \omega) = \frac{\omega^2}{k^2} S(k, \omega). \quad (10)$$

Expression (10) determines the relation between the dispersion curve determined via the positions of the peaks in $S(k, \omega)$ at different k values and the dispersion curve $\omega_c^{(L)}(k)$.

Figure 1 shows the spectra of the dynamic structure factor $S(k, \omega)$ and the spectral density of the time correlation functions of the longitudinal and transverse currents of liquid lead at different wavenumbers ($0.58 \text{ \AA}^{-1} \leq k \leq 2.01 \text{ \AA}^{-1}$). These spectral characteristics were calculated on the basis of the results of the molecular dynamics simulation. The dynamic structure factor $S(k, \omega)$ was determined from Eqs. (2) and (3). The quantities $\tilde{C}_L(k, \omega)$ and $\tilde{C}_T(k, \omega)$ were calculated via expression (8). The correspondence between the high-frequency peaks in $S(k, \omega)$ and $\tilde{C}_L(k, \omega)$ is vividly traced. The presence of the pronounced inelastic component indicates the vibrational processes of the longitudinal polarization (L mode). The corresponding characteristic frequency $\omega_c^{(L)}(k)$ increases with k in the interval from $k \rightarrow 0$ to $k \approx k_m/2 = 1.1 \text{ \AA}^{-1}$, where k_m is the position of the main maximum in the static structure factor $S(k)$ [31]. The high-frequency peak is also observed in the spectral density of the transverse current (see

Fig. 1a), the shape and position of which differ considerably from those of the high-frequency peak in $\tilde{C}_L(k, \omega)$.

Figure 2 shows the dispersion curves $\omega_c^{(L)}(k)$ and $\omega_c^{(T)}(k)$ obtained from the analysis of the corresponding spectral densities. Both curves are characterized by the linear increase in the region of low wavenumbers and reach the maximum at $k \approx k_m/2$. Such a character of the dispersion law corresponds to the “acoustic-like” vibrational processes [13, 45]. The slopes of the interpolation lines in the region of the extremely low wavenumbers (the hydrodynamic limit) will characterize the corresponding velocities of the propagation of the “acoustic-like” vibrations of the longitudinal and transverse polarizations. The velocities obtained were $\vartheta_L = 1816 \pm 5.4$ m/s and $\vartheta_T = 874 \pm 3.3$ m/s. The results shown in Fig. 2 indicate the absence of the “optic-like” branch in the dispersion law for liquid lead in contrast to the hydrogen-containing liquids, where such features in the dispersion law were revealed [46]. The presence of the lower branch in the dispersion law in Fig. 2, which was also observed in experiments on inelastic scattering [15, 16] in the vicinity of the wavenumbers $k \approx k_m/2$, can be considered as a reflex of the acoustic-like vibrations of the transverse polarization. The appearance of the latter in the experimental spectra $S(k, \omega)$ is due to the quasielastic properties of the medium at the microscopic spatial scales.

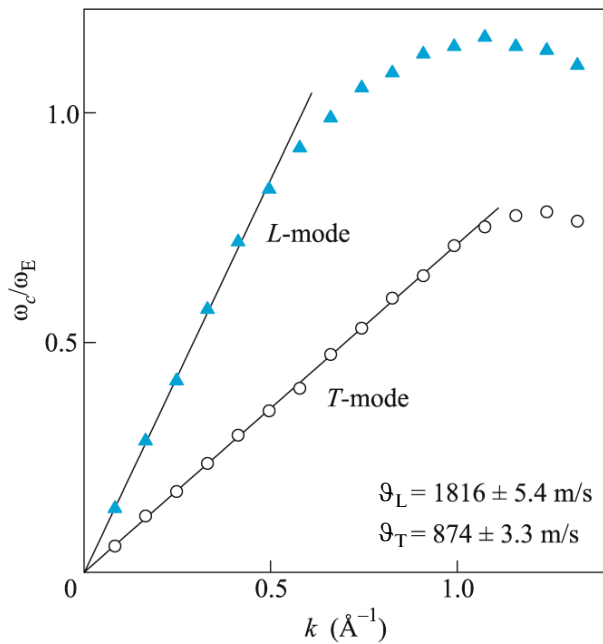


Fig. 2. (Color online) Dispersion relations of the collective excitations $\omega_c^{(\alpha)}(k)$ of the longitudinal ($\alpha \equiv L$) and transverse ($\alpha \equiv T$) polarizations. The slopes of the interpolation lines to the dispersion dependences in the region of the low wavenumbers determine the corresponding speeds of sound $v_L = 1816 \pm 5.4$ m/s and $v_T = 874 \pm 3.3$ m/s.

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