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Heat Waves in Liquid Metals and Semimetals

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Теплові хвилі в рідких металах та напівметалах

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Анотація. Пропонується мікроскопічний підхід до дослідження теплових колективних збуджень в простих рідинах. Спектри колективних збуджень металічних рідин Pb і Cs, та напівметалічного Bi отримані в рамках методу узагальнених колективних мод. Показано, що в рідині можуть існувати дві (високо- і низькочастотні) вітки теплових хвиль.

Heat Waves in Liquid Metals and Semimetals

T.Bryk, I.Mryglod

Abstract. A microscopic approach to investigation of heat collective excitations in pure liquids is developed. Spectra of collective excitations of metallic liquids Pb and Cs, and semimetallic Bi are obtained within the generalized collective mode method. It is found, that there can exist two (high- and low-frequency) branches of heat waves in liquid.

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1. Introduction

Heat waves are for long time the subject of active study in continuum mechanics [1], which is based on phenomenological differential equations. Heat waves are also known as the ‘second sound’ excitations in solids [2] and two-liquid model of He [3]. However, we could not find any reference on a study on microscopic nature of heat waves in ordinary liquids. In the case of liquids the hydrodynamic set of equations derives only two mechanisms of heat transmission in a liquid: via thermodiffusion and by means of propagating sound waves. Since propagating heat waves cannot be obtained within hydrodynamic treatment, they belong to so-called *kinetic* collective excitations, which have a finite time of life and are located in the spectrum beyond the hydrodynamic region. Hydrodynamic equations, which reflect local conservation laws, describe the most long-time processes in liquid. However, the short-time kinetics for some liquid systems cannot be neglected, because it contributes into dynamic structure factors. The ‘fast sound’ and optic-like modes in binary liquids with disparate masses are the examples of kinetic modes, which cannot be obtained within the standard hydrodynamic treatment. The theoretical approach, which enables to investigate kinetic collective excitations, was proposed in [4] and developed into parameter-free method of generalized collective modes (GCM) in [5]. This method treats in addition to three hydrodynamic variables (the density $n(k, t)$, density of longitudinal current $J_l(k, t)$ and density of energy $e(k, t)$) also their time derivatives, which are supposed to describe short-time processes in liquids. The recent results on ‘fast sound’ in $\text{He}_{65}\text{Ne}_{35}$ [6] and optic-like excitations in binary Lennard-Jones liquids and metallic alloys [7] showed the reliability of the GCM method for investigation of kinetic modes.

It is not known *a priori* the type of dispersion for heat waves in ordinary liquids. The most interesting question can be formulated as follows: where the branch of heat waves is located in the spectrum of collective excitations relatively to the acoustic branch? The answer is quite impossible to obtain within the regular approach to the study of heat waves based on the phenomenological differential equations [1]. Therefore, the microscopic approach to this problem is of great interest.

In this Letter we report an analysis of spectra of liquid metals and a semimetal, which enables to identify heat waves in the system. To our knowledge this is the first report, when starting from molecular dynamics simulations and the generalized Langevin equation for time correlation functions one obtains the dispersion and damping of kinetic heat waves

in liquids. We investigated three liquids: metals Cs ($n = 0.0083\text{\AA}^{-3}$, $T = 308\text{K}$) and Pb ($n = 0.03094\text{\AA}^{-3}$, $T = 623\text{K}$), and a semimetal Bi ($n = 0.0289\text{\AA}^{-3}$, $T = 578\text{K}$). Interatomic potentials were taken from [8–10], respectively.

2. Spectra of collective excitations

In this study we apply for solving the generalized Langevin equation the following basis set of dynamical variables:

$$\mathbf{A}^{(9)}(k, t) = \left\{ n(k, t), J_l(k, t), e(k, t), \dot{J}_l(k, t), \dot{e}(k, t), \ddot{J}_l(k, t), \ddot{e}(k, t), \ddot{J}_l(k, t), \ddot{e}(k, t) \right\}, \quad (1)$$

where the three operators $n(k, t)$, $J_l(k, t)$, and $e(k, t)$ are the hydrodynamic variables. In (1) the dots denote the order of time derivatives of relevant operator, which are used for treatment of short-time processes. The basis set (1) is used to generate the 9×9 eigenvalue problem for the generalized hydrodynamic matrix $\mathbf{T}(k)$ (see [4,5]). Nine eigenvalues $z_\alpha(k)$ form the spectrum of collective relaxing and propagating modes of liquids studied.

In Figures 1,2 and 3 we show dispersion (imaginary parts of complex eigenvalues) of propagating modes for Pb, Cs and Bi, respectively. There are three pairs of complex conjugated numbers (propagating modes) and three purely real ones (relaxing modes) among the nine eigenvalues obtained for these three liquids in small- k region. In the case of liquid metals Pb and Cs there emerges another low-frequency branch of propagating excitations at $\approx 0.3\text{\AA}^{-1}$ and $\approx 2.0\text{\AA}^{-1}$, respectively. It is quite easy to identify the branch with almost linear dispersion in small- k region (shown by asterisks in Figures 1-3) as the generalized acoustic excitations.

To find the origin of each branch in the spectra of collective excitations, we will apply the same treatment of time-dependent processes by separated subsets of dynamical variables, as we did for the case of transverse propagating modes in binary liquids [7]. We will divide the set of nine dynamical variables (1) into two subsets, which correspond to thermal and viscoelastic properties of pure liquids. To expect the small coupling effects between different processes, we will use the dynamical variable of heat density

$$h(k, t) = e(k, t) - \frac{f_{ne}}{f_{nn}} n(k, t), \quad (2)$$

which is orthogonal, in contrast to the energy density $e(k, t)$, to the dynamical variable of density $n(k, t)$ in the sense of thermodynamic theory of fluctuations. In (2) $f_{ne}(k)$ and $f_{nn}(k)$ are the ‘energy-density’ and ‘density-density’ static correlation functions, respectively. The four-variable subset

$$\mathbf{A}^{(4h)}(k, t) = \left\{ h(k, t), \dot{h}(k, t), \ddot{h}(k, t), \bar{h}(k, t) \right\}, \quad (3)$$

can be used for separated treatment of thermal processes. It allows to generate the 4×4 eigenvalue problem for the generalized thermodynamic matrix $\mathbf{T}(k)$ and to compare four eigenvalues obtained with the nine-variable spectra. Another five-variable subset of dynamical variables

$$\mathbf{A}^{(5)}(k, t) = \left\{ n(k, t), J_l(k, t), \dot{J}_l(k, t), \ddot{J}_l(k, t), \bar{J}_l(k, t) \right\}, \quad (4)$$

is often called as ‘viscoelastic approximation’, when the coupling with thermal processes is neglected. Two subsets $\mathbf{A}^{(4h)}$ and $\mathbf{A}^{(5)}$ form together the nine-variable ‘coupled’ set of dynamical variables, which can be obtained from 1 by a simple linear transformation. In Figures 1, 2 and 3 we show the imaginary parts of eigenvalues obtained by treatment of separated subsets $\mathbf{A}^{(4h)}$ and $\mathbf{A}^{(5)}$ by dashed and solid lines, respectively. One can immediately estimate, that in the case of liquid metals Pb and Cs two branches correspond to propagating heat excitations. The low-frequency branch has a propagation gap in small- k region. In the case of liquid semimetallic Bi we did not find the low-frequency heat waves. At least, in the region $k < 3\text{\AA}^{-1}$ they are absent. Inside the propagation gap one obtains two relaxing modes instead of two complex conjugated eigenvalues. The lower relaxing mode is the generalized thermodiffusive eigenvalue. This is in complete agreement with predictions of hydrodynamic treatment: there cannot exist in hydrodynamic region (small wavenumbers and frequencies) eigenvalues other than thermodiffusive mode and acoustic waves.

The high-frequency branch of heat waves emerges due to treatment of very short-time thermal processes, mainly due to taking into account dynamical variables $\dot{h}(k, t)$ and $\bar{h}(k, t)$. One can estimate from the difference between results for the four- and nine-variable treatments, shown by dashed line and cross symbols in Figures 1-3, respectively, that in the case of liquid Pb the coupling between thermal and viscoelastic processes is stronger than for Cs or Bi. This is consistent with estimated values of ratio of specific heats γ , which are 1.22, 1.10 and 1.12 for Pb, Cs and Bi, respectively.

3. Analytical treatment of low-frequency heat waves

When one can neglect the coupling between heat- and viscoelastic processes (approximation, when the ratio of specific heats is supposed to be $\gamma \approx 1$), the treatment of heat waves is in complete analogy with the case of shear waves. To perform theoretical estimates for heat excitations we will consider a two-variable approximation neglecting the coupling of thermal processes with density and current fluctuations. In this case, a single-variable treatment immediately would derive an exponential form of time correlation function [11]

$$F_{hh}^{(1)}(k, t)/F_{hh}^{(1)}(k, 0) = e^{-\frac{\lambda}{nC_V}k^2 t}, \quad (5)$$

where λ is the coefficient of thermal conductivity, n is the numerical density and C_V is the specific heat at constant volume. In fact, the MD-derived functions $F_{hh}(k, t)$ contain oscillations, which are due to contributions of acoustic-like excitations. However, at $k \rightarrow 0$ the time correlation functions ‘heat density – heat density’ tend to an single-exponential form modulated by weak oscillations with a normalized contribution $\approx (1 - 1/\gamma)$.

One can write down the expression for the generalized hydrodynamic matrix $\mathbf{T}(k)$ [5] evaluated by means of two-variable basis set $\mathbf{A}^{(2h)} = \{h(k, t), \dot{h}(k, t)\}$, which is the simplest nontrivial case for the treatment of heat fluctuations:

$$\mathbf{T}(k) = \begin{pmatrix} 0 & -1 \\ \bar{\omega}_{2,h}\bar{\omega}_{2,h}\tau_h & \end{pmatrix}, \quad (6)$$

where the k -dependent Maxwell-like time of relaxation $\tau_h(k)$ is evaluated from (5) using the definition of correlation times within the GCM approach [5]:

$$\tau_h(k) = \frac{1}{F_{hh}(k, t=0)} \int_0^\infty F_{hh}(k, t) dt. \quad (7)$$

In (6) $\bar{\omega}_{2,h}(k)$ is the second-order frequency moment of the ‘heat density–heat density’ spectral function:

$$\bar{\omega}_{2,h}(k) = \frac{\langle \dot{h}(k)\dot{h}(-k) \rangle}{\langle h(k)h(-k) \rangle}.$$

In Figure 4 one can see, that the functions $\bar{\omega}_{2,h}(k)/k^2$ tend to finite nonzero values in small- k region for the three liquids under study. We

will use this fact to rewrite the second-order frequency moment $\bar{\omega}_{2,h}(k)$ as follows:

$$\bar{\omega}_{2,h}(k) = \frac{k^2 G^h(k)}{\rho}. \quad (8)$$

In an analogy with the case of transverse dynamics we introduced in Eq. (8) a quantity $G^h(k)$, which has the same dimension as rigidity modulus $G(k)$. Thus, we can call the quantity $G^h(k)$ as a k -dependent heat-rigidity modulus. Obviously, that $G^h(k)$ tends to a constant in hydrodynamic limit. The formal analogy in treatment between heat- and shear-processes is known in continuum mechanics [1].

One can immediately obtain the two-mode spectrum of heat excitations as eigenvalues of the generalized hydrodynamic matrix (6):

$$z_h^\pm(k) = \frac{\bar{\omega}_{2,h}(k)\tau_h(k)}{2} \pm \left[\frac{\bar{\omega}_{2,h}^2(k)\tau_h^2(k)}{4} - \bar{\omega}_{2,h}(k) \right]^{\frac{1}{2}},$$

or using (8) and expression for $\tau_h(k)$ obtained from (5):

$$z_h^\pm(k) = \frac{\delta(k)}{2} \pm \left[\frac{\delta^2(k)}{4} - \frac{k^2 G^h(k)}{\rho} \right]^{\frac{1}{2}}. \quad (9)$$

The function

$$\delta(k) = \frac{C_v G^h(k)}{m\lambda}.$$

tends in longwave limit $\delta(k)$ to a constant. One can see, that the Eq. (9) has two different kinds of solutions. In the case, when

$$\frac{\delta(k)\tau_h(k)}{4} < 1 \quad (10)$$

one obtains two complex conjugated eigenvalues

$$z_h^\pm = \pm i\omega_h(k) + \sigma_h(k),$$

which correspond to propagating in opposite directions heat waves with frequency $\omega_h(k)$ and damping $\sigma_h(k)$. The condition for existence of heat waves in the system (10) defines a limiting k -value, which is, in fact, the width of propagating gap for low-frequency heat-waves:

$$k_H \simeq \frac{C_v}{2\lambda} \sqrt{\frac{nG^h}{m}}. \quad (11)$$

Since the left side of condition (10) contains $\tau_h(k) \sim k^{-2}$, it will always not be valid for small k -values. Inside the propagation gap, for $k < k_H$,

Eq. (10) derives two purely real eigenvalues, which in longwave limit behave as:

$$z_h^+(k) = z_h^{2R}(k) = \frac{C_v G^h}{m\lambda} - \frac{\lambda}{nC_v} k^2, \quad z_t^-(k) = z_t^{1R}(k) = \frac{\lambda}{nC_v} k^2.$$

One can see, that the lowest real eigenvalue $z_t^-(k)$ is just the thermodiffusive hydrodynamic eigenvalue for the case, when the coupling with viscoelastic processes is neglected (see [11]).

Within our two-variable treatment of heat fluctuations, one can improve the analytical hydrodynamic expression for time correlation functions (5). The basis set $\mathbf{A}^{2,h}$ allows to derive the time correlation function $F_{hh}(k, t)$ within the precision of the second order frequency moment:

$$\frac{F_{hh}^{(2)}(k, t)}{F_{hh}^{(2)}(k, 0)} = -\frac{z_h^-(k)}{z_h^+(k) - z_h^-(k)} e^{-z_h^+(k)t} + \frac{z_h^+(k)}{z_h^+(k) - z_h^-(k)} e^{-z_h^-(k)t}. \quad (12)$$

It is possible to perform a self-consistent loop, taking for evaluation of correlation time $\tau_h(k)$ expression (12), what would allow to get some corrections to expressions obtained above. However, the general picture will remain the same: there always exists a propagation gap for low-frequency heat waves in a liquid. Its width depends on the values of thermal conductivity, specific heat at constant volume and heat-rigidity modulus.

4. Conclusions

The main results of this study are the following:

(i) We were able to identify in the spectra of propagating collective excitations of liquid metals and semimetals branches, which corresponded heat waves. For metallic Cs and Pb there exist two (high- and low-frequency) branches of heat waves, that is in perfect agreement with results obtained within the continuum mechanics. This explains "fast waves carrying small amounts of heat and slower speeds carrying larger amounts of heat" [1];

(ii) There exists a propagation gap for low-frequency heat waves in liquids in the region of small wavenumbers, that is in agreement with hydrodynamic treatment. Inside the propagation gap instead of two complex conjugated eigenvalues one obtains two relaxing modes, the lower of which is the generalized thermodiffusive eigenvalue;

(iii) A simple analytical two-variable treatment within the GCM approach allows to explain propagation gap for low-frequency heat waves and to obtain the condition for their existence.

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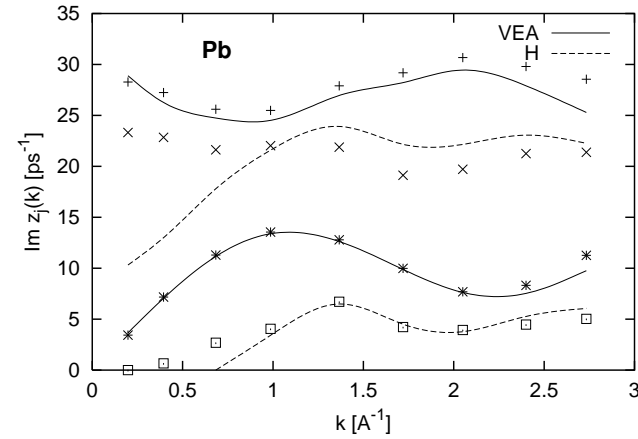


Figure 1. Dispersion of propagating collective excitations in liquid Pb. Imaginary parts of eigenvalues, obtained by nine-variable basis set $\mathbf{A}^{(9)}(k, t)$ are shown by different symbols. Results for separated subsets $\mathbf{A}^{(5)}(k, t)$ and $\mathbf{A}^{(4h)}(k, t)$ are shown by spline interpolated solid and dashed lines, respectively.

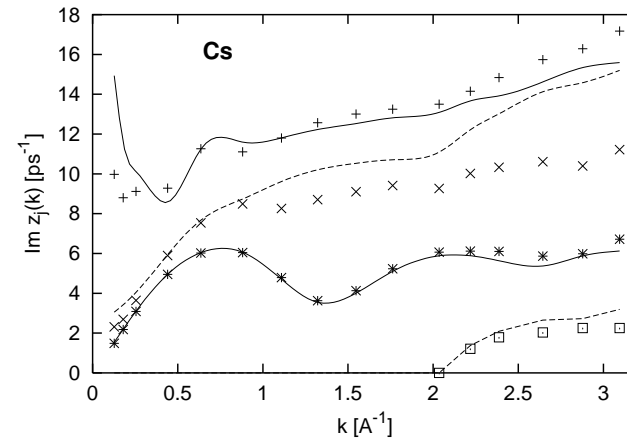


Figure 2. Dispersion of propagating collective excitations in liquid Cs. All settings are the same as in Figure 1.

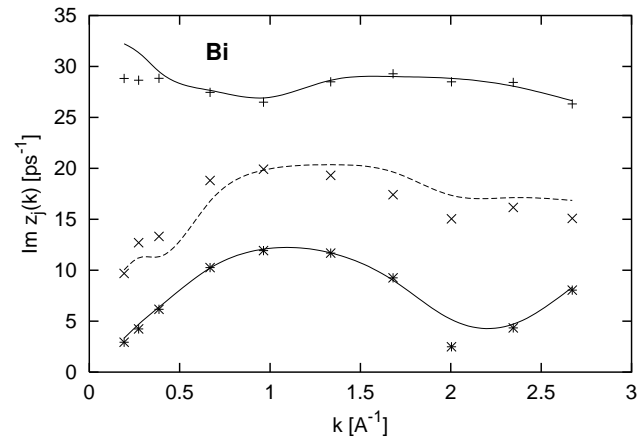


Figure 3. Dispersion of propagating collective excitations in liquid Bi. All settings are the same as in Figure 1.

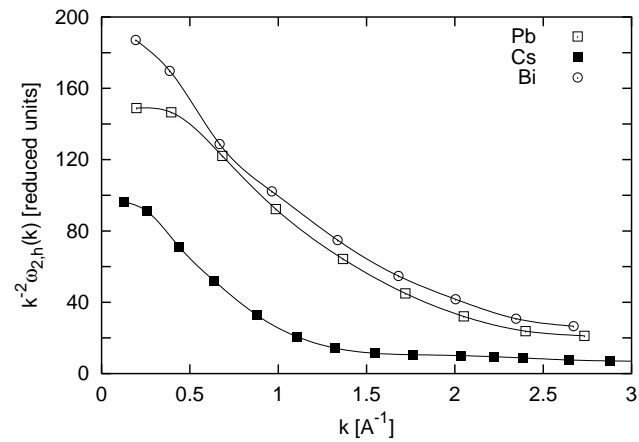


Figure 4. Second frequency moment of the 'heat-heat' spectral function, divided by k^2 . This quantity is connected with generalized heat-rigidity modulus $G^h(k)$ via Eq. (8).

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