KINETIC COLLECTIVE EXCITATIONS IN LIQUIDS: HEAT WAVES

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We present a theoretical study of non-hydrodynamic propagating processes, which correspond to heat waves in liquids. It is shown, that heat waves can propagate in liquids only on a finite spatial scale and do not appear in the long-wavelength region. An expression for a propagation gap for heat waves is derived within a five-variable generalized hydrodynamic treatment. Molecular dynamics simulations were performed for four thermodynamic states of a one-component Lennard-Jones fluid in order to estimate dependence of the propagation gap on temperature.

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1. INTRODUCTION

Collective dynamics in media with topological disorder, and liquids in particular, is one of challenging and not yet solved problems of modern statistical physics. Analytical solutions for collective dynamics can be obtained only in some limits. For the case of small wavenumbers k and frequencies ω, when the description of dynamics is limited by solely most slow processes on large spatial scales, the problem reduces to solving of a system of hydrodynamic equations with dynamical variables, which describe fluctuations of conserved quantities. For the case of pure single-component liquids such a hydrodynamic problem was considered by Landau and Placzek [1] more than 70 years ago, however correct analytical expressions for dynamical structure factor, as well as for a set of hydrodynamic time correlation functions within the precision of first three sum rules were obtained only in the 70-th [2]. The analytical expression for dynamical structure factor of single-component fluids $S(k,\omega)$ within the hydrodynamic approach is represented as a sum of three contributions: central Rayleigh peak comes from the relaxation process of thermal diffusivity, and two side Brillouin peaks, centered at the frequencies $\pm\omega_B(k)$, which reflect propagating in opposite directions acoustic excitations with wavenumber k and frequency ω_B. Although hydrodynamic approach treats the fluids as a continuum, it and its empiric generalized version, known as damped harmonic oscillator (DHO), are frequently used for analysis of experimental data on light, neutron or X-ray scattering in fluids [3]. In fact this leads to a postulate, that beyond the hydrodynamic region exist only one type of collective excitations and just a single relaxation process. Within the DHO analysis of experimental data the wavenumber dependence of excitation frequency, damping coefficient and lifetime of relaxation process are treated as fitting parameters that cannot shed light on the origin of the relaxation process beyond the hydrodynamic region as well as correct mechanisms of damping of collective excitations.

Essential advance in methods of computer simulations of liquid dynamics during the last decade has defined a new direction in theoretical studies of collective processes in liquids: calculation of various time correlation functions in a wide region of wavenumbers and their analysis by generalized hydrodynamic theory. Theoretical approaches within the generalized hydrodynamics are focused on solving the generalized Langevin equation (GLE), which is a master equation for time correlation functions [4]. A consistent treatment of slow and short-time fluctuations in the system permits to represent the GLE in a matrix form, which can be subsequently solved in terms of eigenmodes existing in the studied fluid on different spatial and time scales. Such an approach to solving the GLE is known as an approach of generalized collective modes (GCM) [5, 6]. In this paper we will use the GCM approach for a study of non-hydrodynamic collective excitations of thermal origin, which are the heat waves in liquids. These excitations cannot exist on large spatial scales, because in comparison with hydrodynamic sound excitations there is so called propagation gap in long-wavelength region [7]. Such a type of excitations with finite lifetime in the hydrodynamic limit belongs to kinetic collective excitations. Here we will study how the coupling to viscous processes affects the propagation gap within the five-variable approach of GCM, as well as analyze the molecular dynamics (MD) results in order to estimate temperature dependence of the propagation gap for heat waves.

The remaining paper is organized as follows: in the next Section we will discuss the first results for heat waves obtained within the GCM approach. Section 3 contains details of molecular dynamics simulations performed for several thermodynamic points of Lennard-Jones fluid and as well as results of the five-variable GCM analysis of non-hydrodynamic processes in these fluids. Conclusions of this study are collected in Section 4.

2. APPROACH OF GENERALIZED COLLECTIVE MODES

The GCM approach consists in solving of GLE in terms of dynamical eigenmodes, which contribute in different way to dynamics of fluids on different spatial and time scales. Using a chosen basis set of N dynamical variables one obtains a generalized (NxN) hydrodynamic matrix

$$T^{(N)} = F(k,t=0)\tilde{F}^{-1}(k,z=0)\,, \tag{1}$$

where $F(k,t)$ is a (NxN) matrix of time correlation functions between basis variables, and $\tilde{F}(k,z)$ is a (NxN) matrix of their Laplace transforms. Complex-conjugated pairs of eigenvalues of the generalized hydrodynamic matrix correspond to propagating excitations in the system, while purely real eigevalues reflect the relaxation processes.

A simple separated treatment of slow and short-time thermal processes was performed within a two-variable dynamical model [7] with the basis set of dynamical variables

$$\mathbf{A}^{(2h)} = \{h(k,t), \dot{h}(k,t)\}\,, \tag{2}$$

which are the hydrodynamic variable of heat density and its first time derivative. Hydrodynamic variable and its first time derivative are orthogonal variables, i.e. they describe processes of different time scale. The eigenmodes of the dynamical model (2) were obtained as

$$z_h^{\pm}(k) = \sigma_h(k) \pm \left[\sigma_h^2(k) - \frac{k^2 G^h(k)}{\rho}\right]^{\frac{1}{2}}, \tag{3}$$

where

$$\sigma_h(k) = \frac{c_V(k) G^h(k)}{2m\lambda(k)}\,, \tag{4}$$

and $c_V(k)$, $G^h(k)$, and $\lambda(k)$ are generalized k-dependent specific heat at constant volume, thermal rigidity modulus and thermal conductivity, respectively. The eigenmodes (3) become a pair of complex-conjugated eigenvalues

$$z_h^{\pm}(k) = \sigma_h(k) \pm i\omega_h(k)\,, \tag{5}$$

where $\sigma_h(k)$ is a damping of thermal propagating excitations and $\omega_h(k)$ denotes the dispersion law, for wavenumbers larger than some boundary value

$$k_h^{(2)} = \frac{nc_V}{2\lambda}\sqrt{\frac{G^h}{\rho}}, \tag{6}$$

which gives in fact a width of propagating gap for heat waves. However, the two-variable model (2) does not take into account coupling to density fluctuations, and therefore must be improved. Our task is to obtain an expression for propagation gap of heat waves within a more general five-variable dynamical model and analyze it temperature dependence using molecular dynamics computer simulations.

3. RESULTS AND DISCUSSION

We have performed molecular dynamics simulations for four thermodynamic points of Lennard-Jones fluid with constant density n*=0.845 shown in Fig. 1.

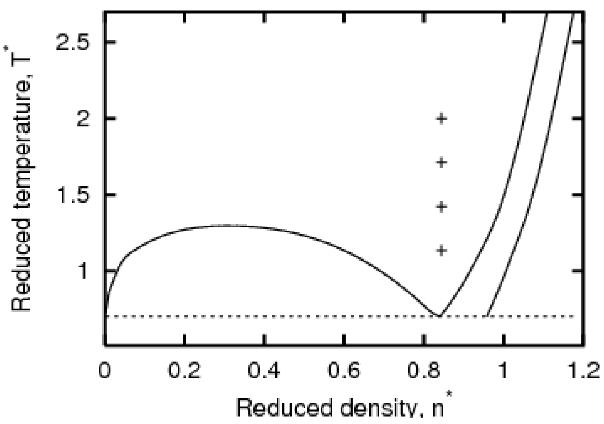

Fig. 1. *Four thermodynamic points (symbols) on the phase diagram of Lennard-Jones fluid used in this study of generalized collective eigenmodes*

All the static and time correlation functions needed for construction of generalized hydrodynamic matrices were calculated directly in MD simulations via statistical averages. The theoretical GCM analysis of MD data was performed within a generalized five-variable dynamical model with the following basis set [8]

$$\mathbf{A}^{(5)}(k,t) = \left\{n(k,t), J^L(k,t), \dot{J}^L(k,t), h(k,t), \dot{h}(k,t)\right\},$$
$$A^j(k,t) = \frac{1}{\sqrt{N}}\sum_{i=1}^{N} A_i^j(t) e^{i\mathbf{k}\mathbf{r}_i(t)}\,. \tag{7}$$

One can analytically solve the five-variable dynamical model in long-wavelength region within the precision of k^2. Among the five eigenvalues the lowest three ones exactly correspond to regular hydrodynamic modes: a relaxing mode of thermal diffusivity and a pair of acoustic propagating modes

$$d_1(k) = D_T k^2\,, \qquad z_s^{\pm}(k) = \Gamma k^2 \pm ic_s k\,, \tag{8}$$

where D_T, Γ and c_s are thermal diffusivity, sound attenuation coefficient and adiabatic speed of sound. Two additional non-hydrodynamic modes are purely real and correspond to kinetic relaxing processes. One of these two kinetic relaxing modes, namely,

$$d_2(k) = d_2^0 - D_L k^2 + (\gamma - 1)\Delta k^2\,, \tag{9}$$

reflects processes connected with structural relaxation, while another kinetic relaxing mode

$$d_3(k) = d_3^0 - \gamma D_T k^2 - (\gamma - 1)\Delta k^2\,, \tag{10}$$

is of thermal origin. In Eqs. (9) and (10) the following shortcuts were introduced

$$d_2^0 = \frac{c_\infty^2 - c_s^2}{D_L}, d_3^0 = \frac{c_V}{m\lambda}\left(G^h - \frac{\gamma - 1}{\kappa_T}\right), \tag{11}$$

and

$$\Delta = \frac{d_2^0 d_3^0}{d_3^0 - d_2^0}\frac{D_T}{D_L c_s^2}(D_T - D_L)^2\,, \tag{12}$$

where D_L, c_∞, γ and κ_T are kinematic viscosity, high-frequency speed of sound, ratio of specific heats and isothermal compressibility. In Fig. 2 we show how the analytical solutions in long-wavelength limit correspond to numerical eigenmodes obtained in the whole region of wavenumbers.

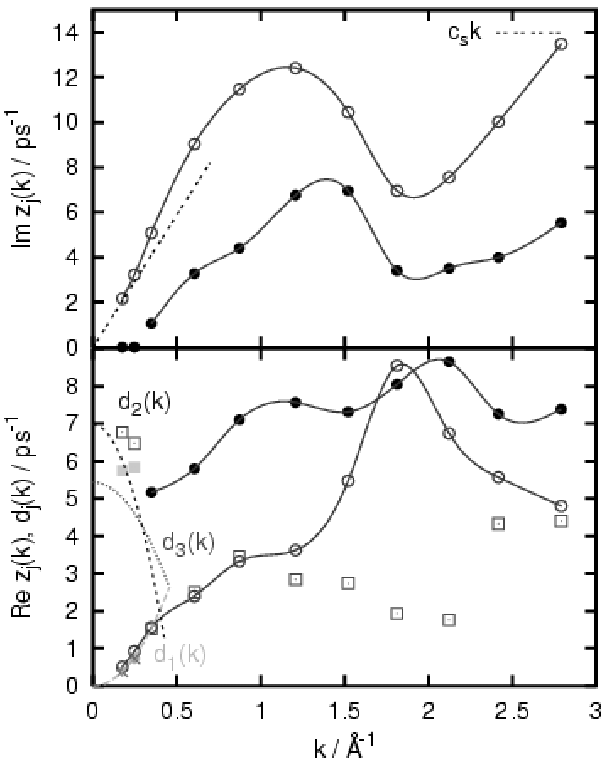

Fig. 2. *Generalized modes for T*=1.71, obtained within the five-variable generalized hydrodynamic treatment of collective dynamics. Upper frame – imaginary parts (dispersion) of generalized acoustic excitations (shown by open circles connected by solid line) and heat waves (closed circles with solid line); lower frame – real parts (damping) of collective excitations shown by line-connected symbols and inversed lifetimes of relaxation processes $d_i(k)$. Dashed lines are the analytical results for corresponding modes*

First feature is a good agreement between analytical and numerical results on hydrodynamic modes, for which linear asymptote in dispersion law and quadratic in wavenumbers dependence of damping is observed. Second, the cross-point of two analytical results for relaxing modes of thermal origin $d_1(k)$ and $d_3(k)$ is quite close to the propagation gap boundary that permits us to use such a condition for the theoretical estimation of the propagation gap. Hence, within the five-variable dynamical model the width of the propagation gap for heat waves reads:

$$k_h^{(5)} = \sqrt{\frac{d_3^0}{(\gamma+1)D_T + (\gamma-1)\Delta}}. \qquad (13)$$

In case of decoupled heat and viscous fluctuations one would obtain an expression similar to the one obtained within the two-variable dynamical model of heat fluctuations. One can predict, that since the coupling between thermal and viscous processes shifts the thermal kinetic mode to the higher lifetimes, corresponding to smaller d_3^0, there should be a tendency to reduction of the propagation gap for heat waves because of such coupling. Since the ratio of specific heats and other thermodynamic quantities depend on temperature (and viscosity) in a non-trivial way we have studied numerically the dependence of the propagation gap for heat waves within the generalized five-variable dynamical model. These results are shown in Fig. 3 and one can make a conclusion, that by approaching the melting point (shown by a solid vertical line in Fig. 3) the propagation gap of heat waves essentially reduces, that makes the dispersion law of heat waves in liquids looking like the zero-sound dispersion suggested in Ref. [9] for the case of liquid cesium and rubidium.

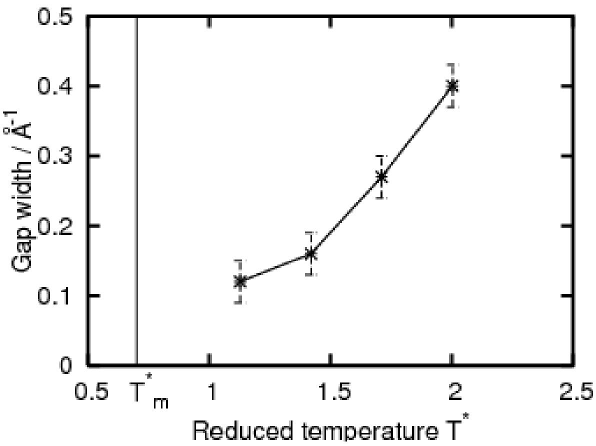

Fig. 3. *Dependence of the propagation gap width (symbols with errorbars) for heat waves on temperature for four studied thermodynamic points of Lennard-Jones fluids. Solid vertical line corresponds to the melting temperature at fixed density*

4. CONCLUSIONS

We have studied an effect of viscosity on heat waves dispersion in Lennard-Jones fluids within a five-variable treatment of the approach of generalized collective modes. Our results point out that higher viscosity and coupling between thermal and viscous processes favor more long-wavelength heat waves in fluids. It was shown from analysis of MD simulations and subsequent GCM analysis, that the propagation gap for heat waves increases versus temperature.

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КИНЕТИЧЕСКИЕ КОЛЛЕКТИВНЫЕ ВОЗБУЖДЕНИЯ В ЖИДКОСТЯХ: ТЕПЛОВЫЕ ВОЛНЫ

Т.М. Брык, И.М. Мрыглод

Представлено теоретическое исследование негидродинамических пропагаторных процессов, которые соответствуют тепловым волнам в жидкостях. Показано, что тепловые волны могут распространяться в жидкостях только на конечных пространственных масштабах и исчезают в длинноволновой области. В рамках пятипеременного подхода обобщенной гидродинамики получено выражение для пропагаторной щели для тепловых волн. С целью определения зависимости пропагаторной щели от температуры выполнено компьютерное моделирование методом молекулярной динамики для четырех термодинамических состояний однокомпонентной Ленард-Джонсовской жидкости.

КІНЕТИЧНІ КОЛЕКТИВНІ ЗБУДЖЕННЯ В РІДИНАХ: ТЕПЛОВІ ХВИЛІ

Т.М. Брик, І.М. Мриглод

Представлено теоретичне дослідження негідродинамічних пропагаторних процесів, що відповідають тепловим хвилям у рідинах. Показано, що теплові хвилі можуть поширюватись у рідинах лише на скінчених просторових масштабах і зникають у довгохвильовій області. В рамках п’ятизмінного підходу узагальненої гідродинаміки отримано вираз для пропагаторної щілини для теплових хвиль. З метою визначення залежності пропагаторної щілини від температури виконано комп’ютерне моделювання методом молекулярної динаміки для чотирьох термодинамічних станів однокомпонентної Ленард-Джонсівської рідини.