

Landau-Placzek ratio for heat density dynamics and its application to heat capacity of liquids

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Exact relation for contributions to heat capacity of liquids is obtained from hydrodynamic theory. It is shown from analysis of the long-wavelength limit of heat density autocorrelation functions that the heat capacity of simple liquids is represented as a sum of two contributions due to “phonon-like” collective excitations and heat relaxation. The ratio of both contributions being the analogy of Landau-Placzek ratio for heat processes depends on the specific heats ratio. The theory of heat density autocorrelation functions in liquids is verified by computer simulations. Molecular dynamics simulations for six liquids having the ratio of specific heats γ in the range 1.1–2.3, were used for evaluation of the heat density autocorrelation functions and predicted Landau-Placzek ratio for heat processes. The dependence of contributions from collective excitations and heat relaxation process to specific heat on γ is shown to be in excellent agreement with the theory. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4774406>]

I. INTRODUCTION

Collective dynamics in liquids essentially differs from the dynamic processes in solids because of the absence of fixed local energy minimum positions for atoms. The atomic particles in liquid state take part in different relaxation processes connected with diffusion, heat transfer and structural rearrangement. On macroscopic length scales all the relaxation processes in liquids are constrained by local conservation laws, that actually form the set of hydrodynamic equations. Any liquid system must obey these general laws of local conservation of number of particles, total momentum, and energy. The local conservation laws lead to hydrodynamic mechanism of sound propagation when collective excitations emerge due to coupling of density and momentum density fluctuations having the linear dispersion law with adiabatic speed of sound. On a shorter length scale comparable with mean interatomic distance, the elastic properties of liquid become important in the mechanism of sound propagation (like in solids) and this is actually the essence of the well-known viscoelastic transition in sound dispersion when the apparent speed of sound changes from the macroscopic (adiabatic) value c_s to the high-frequency (elastic) speed of sound c_∞ .^{1,2} The region of wave numbers $k \sim k_{ve}$ where the viscoelastic transition takes place, in general, depends on the thermodynamic state:³ for systems close to melting points characteristic wavenumber k_{ve} is much smaller than for liquids with small viscosity and high diffusion. In any case for the dynamics of liquids, one cannot underestimate the role of hydrodynamic and non-hydrodynamic relaxation processes.

Recently a “phonon theory” of liquid thermodynamics was suggested⁴ that was based on solid-like treatment of liquid dynamics.^{5,6} It follows from the results of Ref. 4 that the

heat capacity at constant volume is completely defined by the phonon-like modes in liquids.

Strictly speaking there are no well-defined phonon-like modes in liquids, because even on macroscopic scale the collective excitations have damping as described by the hydrodynamic theory.^{7,8} Outside the hydrodynamic regime the damping of collective excitations strongly increases due to coupling to different relaxation processes, marking an essential difference from the solid state case.²³ This raised a question whether the hydrodynamic relaxation processes that play an important role in liquid dynamics should contribute to the heat capacity of liquids.

II. THEORY

It is well known that any liquid must obey local conservation laws that are represented in form of hydrodynamic equations. For the case of simple one-component liquids these are: continuity equation, Navier-Stokes equation, and Fourier law of heat transport.⁸ Hydrodynamic equations can be solved in terms of collective modes. For the case of longitudinal dynamics two collective modes define the shape of particle density and heat density autocorrelation functions. According to hydrodynamic theory of simple liquids the heat density autocorrelation function is represented as follows:⁹

$$F_{hh}(k, t) = A_{hh}e^{-D_T k^2 t} + [B_{hh} \cos c_s k t + D_{hh}(k) \sin c_s k t]e^{-\Gamma k^2 t}, \quad (1)$$

where the first term comes from the heat relaxation, and D_T is thermal diffusivity. The two terms in square brackets come from acoustic collective excitations with hydrodynamic linear in k dispersion law $\omega = c_s k$ and damping Γk^2 with Γ being the sound damping coefficient. The weight

coefficient $D_{hh}(k)$ is linear in k and this term can be ignored in the $k \rightarrow 0$ limit. The coefficients A_{hh} and B_{hh} , being constants in the $k \rightarrow 0$ limit, are not independent – their ratio is equal to

$$A_{hh}/B_{hh} \equiv I_{hh}^{centr}/2I_{hh}^{side} \equiv (\gamma - 1)^{-1}, \quad (2)$$

where I_R^{hh} and I_B^{hh} are the integral intensities of the central and side peaks of heat dynamic structure factor $S_{hh}(k, t)$. In other words, this is an analogy of the Landau-Placzek ratio, only for the heat dynamic structure factor $S_{hh}(k, \omega)$. For the case of heat dynamics the ratio of integral intensities (2) is the inverse of the standard Landau-Placzek ratio $(\gamma - 1)$.

The connection between dynamics and thermodynamics can be obtained in static limit¹⁰

$$F_{hh}(k, t = 0) \equiv \langle \omega_{hh}^0 \rangle = C_V(k)k_B T^2, \quad (3)$$

where $C_V(k)$ is the wavenumber dependent generalized heat capacity at constant volume, k_B is Boltzmann constant, T is temperature, and

$$\langle \omega_{hh}^0 \rangle(k) = \frac{1}{2\pi} \int_{-\infty}^{\infty} S_{hh}(k, \omega) d\omega$$

is the zeroth moment of heat dynamic structure factor. In the limit $k \rightarrow 0$, the generalized wavenumber dependent specific heat $C_V(k)$ tends to its macroscopic value C_V .

Hence, according to (1) and (3), the hydrodynamics gives evidence that in liquids the specific heat at constant volume has two contributions: one coming from the heat relaxation process and another one from collective excitations

$$C_V = (A_{hh} + B_{hh})/k_B T^2 \equiv C_V^{rel} + C_V^{sound}, \quad (4)$$

and the most important is that the ratio of the two contributions for the case of pure liquids depends only on the ratio of specific heats γ ,

$$C_V^{sound}/C_V^{rel} \equiv \gamma - 1. \quad (5)$$

It follows immediately, that for systems with γ close to unity, like in liquid metals, the C_V is almost completely defined by the relaxation component. For regular Lennard-Jones liquids that have the ratio of specific heats close to 2 there will be comparable contributions to C_V from collective excitations and heat relaxation.

III. MOLECULAR DYNAMICS (MD) RESULTS

In order to study heat density time correlation functions in systems with different values of the ratio of specific heats γ , that according to Eqs. (4) and (5) defines the mutual strength of contributions to C_V in liquids, we performed MD simulations for two liquid metals Li and Fe, and liquid Ar at several densities. The idea was to cover a wide range of γ and trace down the changes in the contributions to C_V making comparison with hydrodynamic theory.

We performed MD simulations for two liquid metals (Li at $T = 1000$ K and Fe at $T = 1843$ K) and four states of supercritical Argon along the isothermal line $T = 280$ K. Liquid lithium was simulated with 3300 particles interacting via an effective two-body potential obtained from the second order perturbation theory in weak electron-ion pseudopotential with cut-off radius 19.47 Å. Simulations of liquid Fe were

performed with the embedded-atom type potential proposed in Ref. 11 and 3000 particles. The temperature and density as well as the simulation setup was identical as in Ref. 12, where good agreement with inelastic X-ray scattering (IXS) experimental data by Hosokawa *et al.*¹³ were reported. For all four states of supercritical Argon we used systems of 3000 particles interacting via *ab initio* Woon¹⁴ potentials. This type of potential permitted to obtain very nice agreement with the NIST data¹⁵ and was actively used in simulations of supercritical Ar.¹⁶ The six simulated here systems permitted to study heat density autocorrelation functions in the range of γ from 1.1 to 2.3.

In each simulation every sixth configuration was used for sampling of dynamic variables. Dynamic variables of particle density, momentum density, and energy density as well as their time derivatives needed for generalized collective modes (GCM) analysis were sampled for 30 different wave numbers directly in MD simulations. The averages of static and time correlation functions over all possible directions of different wave vectors with the same magnitude were performed. The smallest available from these simulations wave numbers k_{min} were in the range 0.185 Å⁻¹ (liquid Fe) to 0.098 Å⁻¹ for the most low-density Ar state. These small values of k_{min} allow us to study behaviour of the heat density autocorrelation functions at the boundary of hydrodynamic regime.

The heat density autocorrelation functions were calculated directly from MD-sampled dynamic variables of particle density and energy density as

$$F_{hh}(k, t) = \langle h(k, t)h^*(k, t = 0) \rangle, \quad (6)$$

where the brackets mean ensemble average and the spatial-Fourier components of heat density $h(k, t)$ were expressed via spatial-Fourier components of particle density

$$n(k, t) = \frac{1}{\sqrt{N}} \sum_{i=1}^N e^{-i\mathbf{k}\mathbf{r}_i(t)},$$

and energy density

$$e(k, t) = \frac{1}{\sqrt{N}} \sum_{i=1}^N \varepsilon_i(t) e^{-i\mathbf{k}\mathbf{r}_i(t)},$$

by the definition¹⁷

$$h(k, t) = e(k, t) - \frac{f_{ne}}{f_{nn}} n(k, t). \quad (7)$$

In the expressions above N is the number of particles, $\mathbf{r}_i(t)$ and $\varepsilon_i(t)$ are the position and single-particle energy of the i th particle, $f_{ne}(k) = \langle n(k)e(-k) \rangle$ and $f_{nn}(k) = \langle n(k)n(-k) \rangle$ are the static correlators density-energy and density-density, respectively. Hence, the time evolution of the heat density $h(k, t)$ can be easily calculated from MD data.

In Figs. 1–3, the calculated from MD simulations heat density autocorrelation functions are shown at the smallest available wave numbers in the simulations of our six model systems. Note, that at origin the normalized by $(k_B T)^2$ heat-heat static correlator according to (3) are equal to the wave-number dependent specific heat $C_V(k)$ that in the long-wavelength limit tends to its macroscopic value C_V . As it is

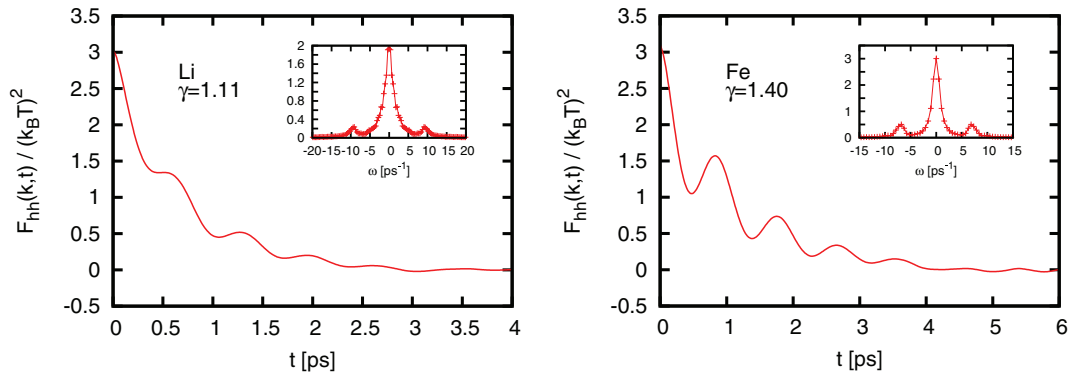


FIG. 1. Heat density autocorrelation functions $F_{hh}(k, t)$ and corresponding dynamic structure factors for liquid Li and Fe for the smallest available in simulations wave numbers. The insets show corresponding heat dynamic structure factors $S_{hh}(k_{min}, \omega)$ in units of picoseconds.

seen in Fig. 1 for liquid metals, the specific heats $C_V(k)$ obtained from $F_{hh}(k, t=0)$ are very close to $3k_B$, and smaller values of C_V in the range 2.5–1.6 are observed for decreasing densities of supercritical Ar.

Figures 1–3 clearly show that increasing of the ratio of specific heats γ (the smallest γ for our six simulated systems is for Li and the largest one for low-density Ar as it is shown in corresponding figures) causes larger contributions from oscillating processes that are coming from propagating collective excitations. For the case of Li the sound excitations barely affect the shape of $F_{hh}(k, t)$, while the systems with increasing γ get more pronounced oscillations of $F_{hh}(k, t)$.

Corresponding heat dynamic structure factors $S_{hh}(k, \omega)$ are shown in insets of each figure. It is seen that the intensity of the central/side peak of $S_{hh}(k, \omega)$ is the largest/smallest among the studied here systems for the case of Li (Fig. 1) and the smallest/largest for the case of low-density Argon with large γ (Fig. 3). In fact the situation with the mutual intensities of central and side peaks of the heat dynamic structure factors is opposite to what is observed for the regular dynamic structure factors $S(k, \omega)$.

The next step in analysis of the heat density autocorrelation functions $F_{hh}(k, t)$ was to separate contributions to their time dependence coming from the two hydrodynamic processes: heat relaxation and collective excitations – according to hydrodynamic expression (6), and hence permitting to estimate two contributions to C_V (4). Since the smallest wave

numbers available in MD simulations usually are beyond or on the boundary of hydrodynamic regime, one has to apply for analysis of $F_{hh}(k, t)$ a generalized hydrodynamic scheme that in the limit $k \rightarrow 0$ coincides with hydrodynamic description. In this sense, the most reliable generalized hydrodynamic scheme for description of propagating and relaxing modes in liquids is the approach of GCM^{18,19} that permits very consistent calculations of contributions coming from hydrodynamic and non-hydrodynamic collective modes.²⁰ The details of GCM analysis can be found elsewhere. The GCM analysis of collective dynamics in the six studied liquids was performed within a thermo-viscoelastic dynamic model for pure liquids³ that yields a five-term form of the heat density autocorrelation functions outside the hydrodynamic regime

$$F_{hh}(k, t) = \sum_{\alpha=1}^3 A_{hh}^{\alpha}(k) e^{-d_{\alpha}(k)t} + [B_{hh}(k) \cos(\omega(k)t) + D_{hh}(k) \sin(\omega(k)t)] e^{-\sigma(k)t} \quad (8)$$

with real k -dependent amplitudes of mode contributions: from relaxation processes $A_{hh}^{\alpha}(k)$, symmetric $B_{hh}(k)$ and asymmetric $D_{hh}(k)$ contributions from acoustic collective excitation. This expression is the direct extension of the hydrodynamic form (1) on the case of existing non-hydrodynamic relaxing modes. In (8), the $\omega(k)$ and $\sigma(k)$ correspond to dispersion and damping of collective excitations, and $d_{\alpha}(k)$ to the eigenvalues

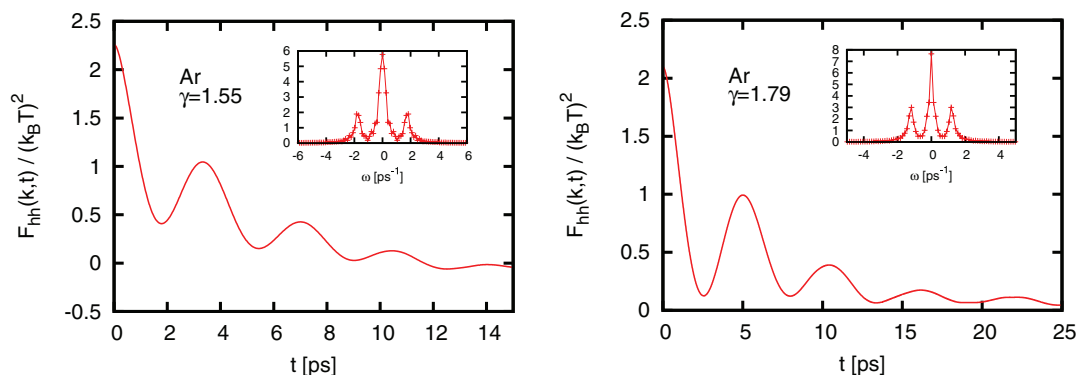


FIG. 2. Heat density autocorrelation functions $F_{hh}(k, t)$ and corresponding dynamic structure factors for dense liquid Ar for the smallest available in simulations wave numbers. The insets show corresponding heat dynamic structure factors $S_{hh}(k_{min}, \omega)$ in units of picoseconds.

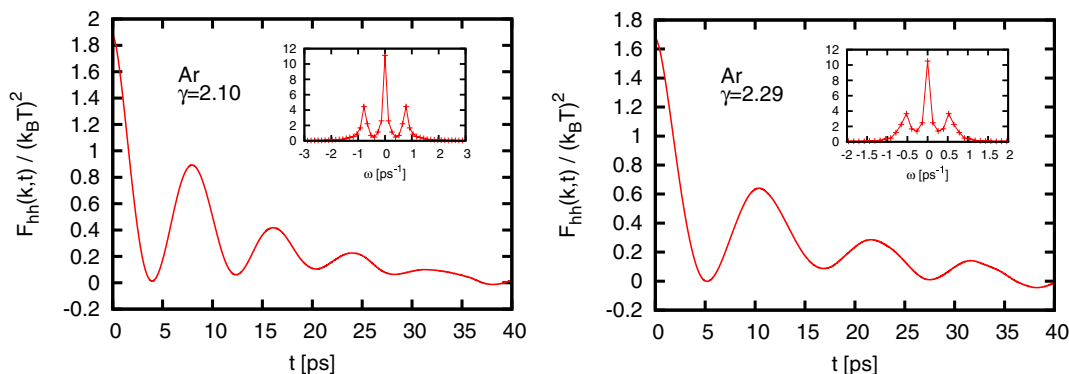


FIG. 3. Heat density autocorrelation functions $F_{hh}(k, t)$ and corresponding dynamic structure factors for low-density liquid Ar for the smallest available in simulations wave numbers. The insets show corresponding heat dynamic structure factors $S_{hh}(k_{min}, \omega)$ in units of picoseconds.

of relaxing modes. In the hydrodynamic regime, the lowest real eigenvalue $d_1(k)$ is exactly proportional to the square of wave number $D_T k^2$ with D_T being thermal diffusivity, while dispersion and damping of collective excitations are $\omega(k) = c_s k$ and $\sigma(k) = \Gamma k^2$. The non-hydrodynamic relaxing modes $d_2(k)$ and $d_3(k)$, which correspond to structural relaxation and heat current relaxation, respectively, tend in the $k \rightarrow 0$ limit to non-zero values,³ and their weight coefficients $A_{hh}^{2,3}(k)$ decay faster as k^2 , making the generalized form of $F_{hh}(k, t)$ identical to hydrodynamic expression (1) in the long-wavelength limit. The ratio of two wave-number dependent amplitudes of contributions tends in the long-wavelength limit to the ratio (5) of contributions to heat capacity

$$\lim_{k \rightarrow 0} B_{hh}(k)/A_{hh}(k) = C_V^{sound}/C_V^{rel} \equiv \gamma - 1. \quad (9)$$

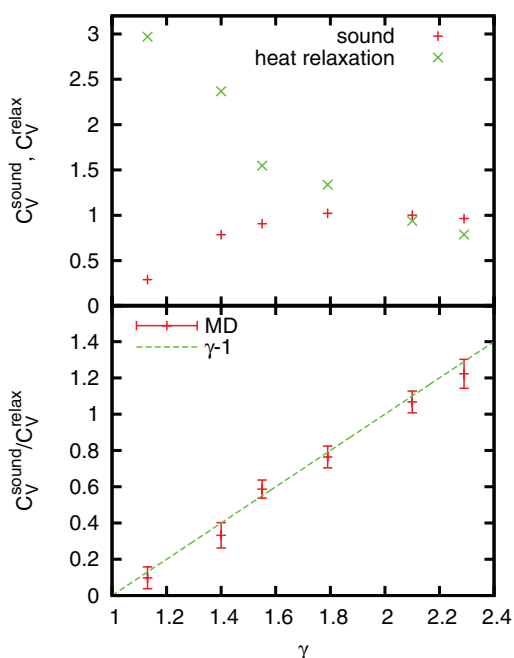


FIG. 4. (Top panel) Contributions to the heat capacity C_V coming from collective excitations and heat relaxation process. (Bottom panel) Estimated from MD simulations ratio of contributions C_V^{sound}/C_V^{rel} for six studied systems in comparison with the hydrodynamic asymptote $\gamma - 1$, Eq. (5).

We obtained the collective modes and corresponding weight coefficients for the six studied liquids, and for the smallest available in simulations wave numbers we show in Fig. 4 the normalized according to (4) contributions from heat relaxation mode $A_{hh}(k_{min})$ and acoustic excitations $B_{hh}(k_{min})$, and their ratio (5). Note, that since we analyze the mode contributions to $F_{hh}(k, t)$ at some non-zero value of the wave number $k = k_{min}$, a small effect coming from the other non-hydrodynamic relaxing processes like structural relaxation $d_2(k)$ or relaxation of heat current $d_3(k)$ takes place in estimation of the ratio (9). The asymmetric contribution with a coefficient $D_{hh}(k)$ in (1) does not contribute to the static quantities such as $C_V(k)$ because its integral in calculations of the zeroth moment $\langle \omega_{hh}^0 \rangle(k)$ is equal to zero. In general, for larger simulated systems the wave numbers k_{min} will get closer to the hydrodynamic regime and hence the effect from other non-hydrodynamic relaxing modes in calculations of the ratio (9) will vanish.

The contribution to C_V from the relaxing mode in the top frame of Fig. 4 decreases with the increase of the ratio of specific heats γ in agreement with our observation of the change in the shape of MD-derived functions $F_{hh}(k, t)$, while the tendency for the contribution coming from collective excitations is opposite. For systems with the small value of the ratio of specific heats (liquid metals), the specific heat C_V contains only small contribution from collective excitations, while the main contribution to C_V comes from heat relaxation process. Liquids with $\gamma \approx 2$ have comparable contributions from both leading hydrodynamic processes. The bottom frame in Fig. 4 shows the ratio of both contributions comparing to the exact hydrodynamic results. It is seen that our estimated contributions to C_V are in agreement with theoretical prediction (5).

IV. CONCLUSIONS

We have shown by analysis of the analytic expression of the hydrodynamic heat density autocorrelation functions, that heat capacity of liquids contains two contributions: one coming from collective “phonon-like” excitations and another one from the heat relaxation process. The ratio of this contributions depends for simple liquids on the ratio of specific heats γ and in fact is the analogy of the famous Landau-Placzek ratio for heat dynamic structure factors $S_{hh}(k, \omega)$.

We have demonstrated by a combination of MD simulations and the GCM approach that the calculated contributions from heat relaxation and collective excitations are in very good agreement with the predictions of hydrodynamic theory for the case of six realistic liquids studied here within the range of γ 1.1–2.3.

We stress that the obtained analytical result for contributions to the specific heat of simple liquids is the exact result – there were no approximations applied, and hydrodynamic approach being in fact a set of local conservation laws must be correct for any liquid.

A note should be added about the application of this hydrodynamic approach to complex many-component and molecular systems. The system of hydrodynamic equations for many-component and molecular liquids is larger than for the case of simple liquids: additional equations due to the conservation of local concentrations of species and total momentum of rotational motions would lead to additional exponential terms in hydrodynamic expression for the heat density autocorrelation functions (see Eq. (1)). Corresponding Landau-Placzek ratio for complex liquids will differ from the case of simple liquids (see Refs. 21 and 22), however the same methodology as proposed here can be applied to observe different modes in $F_{hh}(k, t)$ and calculate the corresponding contributions to specific heat C_V .

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