

Comment on “Collective dynamics in liquid lithium, sodium, and aluminum”

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In a recent paper, Singh and Tankeshwar (ST) [Phys. Rev. E **67**, 012201 (2003)] proposed a new interpretation of the collective dynamics in liquid metals and, in particular, of the relaxation mechanisms ruling density fluctuations propagation. At variance with both the predictions of the current literature and the results of recent inelastic x-ray scattering experiments, ST associate the quasielastic component of the $S(Q, \omega)$ to the thermal relaxation, as it holds in ordinary adiabatic hydrodynamics valid for nonconductive liquids and in the $Q \rightarrow 0$ limit. We show here that this interpretation leads to a nonphysical behavior of different thermodynamic and transport parameters.

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Recently, Singh and Tankeshwar (ST) reported a new version of the finite wave-vector, Q , extension of the generalized hydrodynamics (the so-called “molecular hydrodynamics”) applied to the dynamics of simple liquid metals [1]. The goal of the ST paper is twofold. On the one hand, the authors propose an analytic expression for the density-density correlation function, $F(Q, t)$, which is based on the existence of two relaxation channels, and they test it through its Fourier transform against the dynamic structure factor recently measured by inelastic x-ray scattering (IXS) on several liquid metals. On the other hand, the authors assign a specific meaning to these two relaxation processes: the slower process is traced back to the thermal relaxation, while the faster one is ascribed to viscous effects. More specifically, at variance with the results of previous studies performed on the same IXS data used by ST [2–4], they assign the quasielastic component of the IXS spectra to the thermal relaxation.

The aim of this Comment is to point out how, although the analytical spectral shape proposed by the authors turns out to reproduce the experimental spectra at a reasonable level of accuracy, the interpretation behind it is inadequate to describe the microdynamics of simple metals. In particular, assigning the whole quasielastic IXS spectrum to the thermal relaxation, the value and the Q dependence of the derived fitting parameters are not consistent with independent determination of the transport (viscosity, thermal conductivity) and thermodynamic (specific-heat) properties and disagree with what is expected in general.

The dynamic structure factor of simple liquids, in the $Q \rightarrow 0$ limit, is constituted by three lines: a quasielastic, Lorentzian component centered at zero frequency, and a doublet (Brillouin peaks) symmetrically shifted at finite energy [5]. In this limit, the energy position of the side lines, their broadening, and the broadening of the central line are successfully described within the well-known simple hydrodynamic approach. In particular, the frequency of the Brillouin mode is $\omega_B = c_0 Q$, where c_0 is the adiabatic sound velocity, while its linewidth (half width at half maximum) is ruled by thermal (Γ_{th}) and viscous (Γ_{η}) damping as

$$\Gamma = \Gamma_{\eta} + \Gamma_{\text{th}},$$

$$\Gamma_{\eta} = \frac{Q^2}{2\rho} \left[\frac{4}{3} \eta_s + \eta_B \right],$$

$$\Gamma_{\text{th}} = \frac{Q^2}{2\rho} [(\gamma - 1)\lambda/C_p], \quad (1)$$

where λ , γ , and C_p are the thermal conductivity, specific-heat ratio, and constant pressure heat capacity, while η_s and η_B are the shear and bulk viscosity, respectively. The width of the quasielastic mode, instead, is $1/\tau_{\text{th}} = D_T Q^2$, i.e., it is ruled by the thermal diffusion only.

In Ref. [1], ST extend this approach to the finite wave-vector domain probed by IXS, and they apply it to a specific subclass of simple liquids, namely liquid metals. To this purpose, ST replace the Lorentzian shape stemming from simple hydrodynamics with a hyperbolic secant shape, leaving unchanged the origin of the individual contributions.

The extension to finite wave vectors, however, in the special case of highly conductive systems, requires careful evaluation of the physics behind the model for two main reasons. First, as pointed out in the celebrated textbook by Faber [6], in a liquid metal, owing to the high thermal conductivity, on pushing the wave vector to values comparable to the inverse mean interparticle distance (as in the present case) the quantity $D_T Q^2$ soon becomes larger than the Brillouin frequency ω_B . Consequently, as predicted (Ref. [6]), the thermal peak broadens, ultimately overlapping with the Brillouin lines, the sound propagation turns from adiabatic to isothermal, and independent thermal fluctuations become impossible. A second reason is that, on the snapshot time scale probed by IXS (THz), the diffusive atomic motion characteristic of the liquid state looks frozen, and therefore part of the viscous contribution ruling the Brillouin width at low Q is transferred to the elastic line. Both of these reasons have been disregarded by ST.

A formal way to quantify the scenario qualitatively depicted above is to introduce the memory-function formalism. Within this framework, the normalized density autocorrelation function $\phi(Q, t) = F(Q, t)/S(Q)$ obeys the Langevin equation

$$\ddot{\phi}(Q,t) + \omega_0^2(Q)\phi(Q,t) + \int_0^t M(Q,t-t')\dot{\phi}(Q,t')dt' = 0, \quad (2)$$

where $\omega_0^2(Q) = -\ddot{\phi}(Q,0) = K_B T Q^2 / m S(Q)$ is related to the generalized isothermal sound velocity $c_i(Q) = \omega_0(Q)/Q$ and $M(Q,t)$ is the second-order memory function which, in the hydrodynamic limit, reads

$$M(Q,t) = 2D_V Q^2 \delta(t) + (\gamma - 1)\omega_0^2(Q)e^{-D_T Q^2 t} \quad (3)$$

with $D_V = (\frac{4}{3}\eta_s + \eta_B)/\rho$ the longitudinal viscosity and γ the specific-heat ratio. It is easy to show from Eqs. (2) and (3), indeed, that if the condition $\omega_B \gg D_T Q^2$ holds, the dynamic structure factor (i.e., the Fourier transform of F) reduces to the sum of a (thermal) central Lorentzian contribution and a damped harmonic-oscillator spectrum of characteristic frequency $\omega_B \approx \sqrt{\gamma}\omega_0$ (which is the sum of two symmetrically shifted Lorentzians in the limit $\Gamma \ll \omega_0$). As $\gamma = (c_0/c_i)^2$, one ultimately gets the hydrodynamic result, i.e., an adiabatic regime.

The finite Q wave-vector generalization stems from dropping the hypothesis of the instantaneous (Markovian) nature of the viscous term. In particular, one can introduce a finite time scale (τ) for the decay of the first term in Eq. (3) and, according to the $\omega_0\tau$ value, the viscous relaxation can affect both the quasielastic and the inelastic peaks. Actually, the situation is even more involved. In earlier MD studies of liquid metals, it was soon realized that the viscous dynamics in the microscopic regime (i.e., at a wavelength comparable with the inverse mean interparticle separation) proceeds through two distinct processes, characterized by two well-separated time scales (τ_α and τ_μ) [7]. This idea has been substantiated recently by a number of IXS investigations, where the presence and the role of the two relaxation mechanisms have been identified and widely discussed [2–4,8,9]. In particular, it has been pointed out that the slower (α) relaxation time satisfies the condition $\omega_B(Q)\tau_\alpha(Q) \gg 1$, i.e., some part of the viscous flow is frozen. As a consequence, at the wave vectors typical of the IXS experiments ($Q = 1-20 \text{ nm}^{-1}$), the quasielastic spectrum acquires a component arising from this frozen structural relaxation. Moreover, owing to the high thermal conductivity, in liquid metals the condition $\omega_B\tau_{th} \approx (c_0/D_T Q) < 1$ holds above wave vectors of the order of 0.1 nm^{-1} [15]. In this limit, the sound propagation is isothermal and not adiabatic, which means that the thermal relaxation is too broad to give a noticeable quasielastic component, while it renormalizes the sound velocity from the hydrodynamic value c_0 to the isothermal value c_i , as clearly discussed in Ref. [8] and pointed out in previous literature [16].

Summing up, the quasielastic peak in the $S(Q,\omega)$ is expected to arise from the frozen structural relaxation and not from the thermal process. Its linewidth is therefore associated to τ_α^{-1} and not to $D_T Q^2$.

A decisive support to the origin that we propose for the quasielastic peak can be gained by the wave vector and temperature dependence of the spectrum. The signature of a vis-

cous origin of the central peak is, indeed, (i) a substantial Q independence (τ_α is almost Q -independent) and (ii) a strong temperature dependence of its width (the structural relaxation follows the Arrhenius or an even faster behavior [10]). On the contrary, a central peak of thermal origin must show (i) a strong Q dependence (width $\propto Q^2$ until the structure factor is flat) and (ii) a very weak temperature dependence (traced back to the mild temperature dependence of the thermal conductivity). While the temperature dependence of the central peak is difficult to determine experimentally, because of the difficulty of supercooling liquid metals [some hints could come from the molecular-dynamics (MD) simulation, see below], the Q dependence of the central peak is rather clear: its experimental width (as determined by IXS spectra) is a quantity that can be roughly determined by a ruler, or better by a fitting procedure, and turns out to be almost constant in the examined Q range. If one interpreted (following ST) this width as due to the thermal relaxation process, it would be equal to $D_T Q^2$ and, as a consequence, the generalized thermal diffusivity would obviously become strongly Q -dependent [$D_T(Q) \propto Q^{-2}$], ultimately dropping by a factor ≈ 400 from the hydrodynamic limit to the examined Q range. This behavior is difficult to understand on a physical basis, and is very different from that observed in other liquids. Indeed, although we are not aware of any explicit $D_T(Q)$ estimates for liquid metals, detailed calculations for other liquids (water [11]) show a decrease of only a factor 10 on going from $Q=0$ and the Q value of the the maximum of the static structure factor. The too strong Q dependence of $D_T(Q)$ derived by ST speaks against the assignment of the central peak to the thermal process. Turning our attention now to the temperature dependence of the central peak width, a recent MD work on undercooled liquid lithium showed that this width is actually strongly temperature-dependent. More importantly, the derived relaxation time τ_α closely follows the behavior of the mass diffusion coefficient (as expected, for example, from the predictions of the mode-coupling theory for the structural relaxation time [12]), increasing by more than a factor 10 in the spanned temperature range [13]. Such a strong temperature dependence is not expected for the thermal diffusivity, indicating once more the nonthermal origin of the central peak.

A further consequence of the assignment of the central peak to the thermal relaxation process is the anomalous Q dependence, obtained by ST, of the parameter describing the ratio of the elastic to inelastic scattering intensity. In the authors' notation, this is the quantity $a(Q)$ entering in their Eq. (4), which is related to the generalized specific-heat ratio $\gamma(Q)$ via the expression $\gamma = 1/(1-a)$. In Fig. 1, we report $\gamma(Q)$ as obtained by ST compared to previous numerical calculation for the case of liquid lithium [14]. The values from the ST analysis clearly overestimate the calculated ones, although these latter have been obtained through simulations which well reproduce the experimental spectra.

Finally, the hydrodynamic expression [Eq. (1)] which ST utilize to estimate the sound attenuation (and to judge the reliability of their model) is valid only for ordinary (nonconducting) liquids in the $Q \rightarrow 0$ limit. It accounts, indeed, for the first-order nonvanishing attenuation contribution from

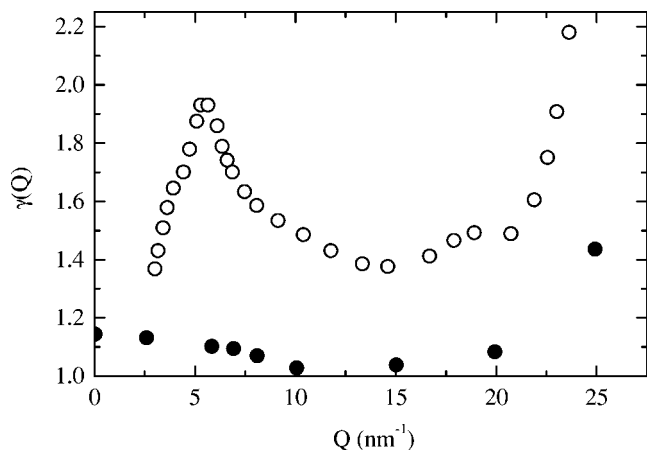


FIG. 1. Comparison between the generalized specific-heat ratio $\gamma=c_p/c_v$ as obtained by the ST model (○) and by direct numerical calculation (●).

the thermal diffusive mode, and it relates the attenuation to the whole longitudinal viscosity. As pointed out in Ref. [8], the small attenuation contribution from the thermal process in the IXS wave-vector range has, in liquid metals, the different expression

$$\Gamma_{th} = (\gamma - 1)c_t^2/D_T, \tag{4}$$

where c_t is the isothermal sound speed. More important, at the probed wave vectors, only the microscopic, relaxed, part of the viscosity is involved in the sound damping Γ_{η} as the

structural relaxation contribution is frozen on the probed time scale (in liquid lithium this latter contribution from the microscopic part is one-half of the whole viscous term [8]).

In conclusion, in our opinion the model proposed by Singh and Tankeswar has the merit to indicate a possible heuristic analytical time (and frequency) dependence of the intermediate scattering function (dynamic structure factor) appropriate to catch some features of the dynamics in the THz frequency region. Indeed, for instance, the functional form proposed by ST has all the spectral moments finite, while the memory function approach, leading to spectral shapes that are described by fractions of polynoms, has only a finite number of converging spectral moments. The ST analysis, however, seems to be rather weak in the physical interpretation of the relaxation processes that drive the collective dynamics. Neither of the two parameters τ_1 and τ_2 has a clear meaning and can be directly associated to any relaxation mechanism, as it happens, for example, within a memory-function framework. As a consequence of the incorrect identification of the role of the thermal process, the parameter τ_1 has no connection with any thermal property (being in fact mainly related to the structural relaxation time τ_α), the generalized specific-heat ratio obtained from the fitting shows marked discrepancies with the expected behavior, and the viscosity cannot be estimated through Eq. (11) in Ref. [1].

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 [15] This estimate is valid in the case of interest, i.e., in a wave-vector region not too close to the main peak of the structure factor, where structural effects are expected to occur, so that one can reasonably assume $\omega(Q) \approx cQ$ and $D_T(Q) \approx D_T(Q \rightarrow 0)$.
 [16] For example, in Ref. [6] the discrepancy observed in liquid lead between the sound velocity measured with ultrasound (adiabatic) and with inelastic neutron scattering has been tentatively assigned to the isothermal nature of the sound propagation at the probed wave vectors.