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# Comment on "Collective modes and gapped momentum states in liquid Ga: Experiment, theory, and simulation"

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We show that the theoretical expressions presented in Khusnutdinoff *et al.* [Phys. Rev. B **101**, 214312 (2020)] for the longitudinal current spectral function $C^L(k,\omega)$ and the dispersion of collective excitations are not correct. Indeed, they are not compatible with the continuum limit and $C^L(k,\omega\to 0)$ contradicts the continuity equation.

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## I. INTRODUCTION

In a recent paper [1], the authors formulated their "overarching goal of this research programme ...to reach the stage where, despite the complexity of their theoretical description, liquids emerge as systems amenable to theoretical understanding at the level comparable to gases and solids." Looking at Figs. 4 and 5 of Ref. [1], one can really make sure that the authors of Ref. [1] reached their ambitious goal in perfect agreement between the proposed theory and computer simulations. In their paper, the authors proposed theoretical expressions for the longitudinal current spectral function $C^L(k,\omega)$, with $k$ and $\omega$ being the wave number and frequency, and for the dispersion of longitudinal collective excitations $\omega_c^L(k)$. Their expressions for $C^L(k,\omega)$ [Eq. (18)] and $\omega_c^L(k)$ [Eq. (20)], as one can judge from their Figs. 4 and 5, recover with high precision the molecular dynamics (MD) data in a wide range of wave numbers and temperatures. The $C^L(k,\omega)$ in their theoretical scheme was obtained from a simple continued fraction shown in their Eq. (11). Although the standard approach for a description of collective dynamics in liquids is to represent the Laplace-transformed density-density time correlation function as a continued fraction [2,3], in Ref. [1] the authors derived the continued fraction for the longitudinal current-current correlations. Applying different closures for the chain of memory functions as in Refs. [4–6], one can obtain a formal solution for $C^L(k,\omega)$ within a precision of several of its frequency moments.

However, such an approach of Ref. [1] is not really consistent with hydrodynamics [4,7], which is a collection of local conservation laws. Any liquid system on spatial scales much larger than the mean interatomic distance must behave similarly from the point of view of slow collective modes derived by fluctuations of conserved quantities. In Ref. [1] the proposed theoretical approach is developed from a single conserved dynamic variable, a longitudinal component of total momentum $J^L(k,t)$, which is the slowest dynamic variable in the presented approach. It is well known from textbooks [4,7] as well as from other multivariable approaches [8–10] which dynamic variables are responsible for a description of the viscoelastic transition in the dispersion of collective excitations [11,12]. The theoretical approach [1] does not contain a coupling of longitudinal current fluctuations with fluctuations of other conserved quantities, namely density $n(k,t)$ and energy $e(k,t)$. The energy (or heat) density fluctuations reflect specifically for liquid fluctuations of local temperature [13], and long-wavelength heat relaxation processes are responsible for the central Rayleigh peak of the dynamic structure factor $S(k,\omega)$ for one-component liquids at sufficiently small wave numbers $k$. Outside the hydrodynamic regime the short-wavelength density fluctuations $n(k,t)$ reflect the processes connected with structural relaxation, and instead of heat relaxation, form the leading contribution to the central peak of $S(k,\omega)$ [12,14,15]. The presence of heat and density relaxation, therefore, are essential ingredients for a correct description of the spectra, including the propagating density fluctuation regions, which are the main target of Ref. [1].

The poor theoretical approach presented in Ref. [1], missing the coupling with slow processes that are the most important for liquids, is an oversimplified theory. It is therefore difficult to understand why it is able to reproduce to a very good degree of accuracy the molecular dynamics (MD) data for $C^L(k,\omega)$ in some region of wave numbers as it is shown in their Fig. 4 [1]. Moreover, we were motivated to understand why their expressions were able to recover the adiabatic speed of sound in the long-wavelength region of their Fig. 5. Our question was as follows: Is it possible within the proposed fit-free theoretical scheme to obtain in the long-wavelength limit the propagating modes with an adiabatic speed of sound $c_s$? The multivariable approaches based on the set of dynamic variables $\{J^L(k,t), \dot{J}^L(k,t), \ldots\}$ usually can produce in the long-wavelength limit the propagating modes only in the elastic regime, with the propagation speed being the high-frequency one $c_\infty$ slightly renormalized due to the coupling to faster kinetic modes. No viscoelastic effects such as positive sound dispersion can be expected in this theory.

Motivated by the surprisingly good agreement shown in their Fig. 4 we will check the expressions [Eqs. (17)–(20)] of Ref. [1] and the behavior of their "relaxation parameters"

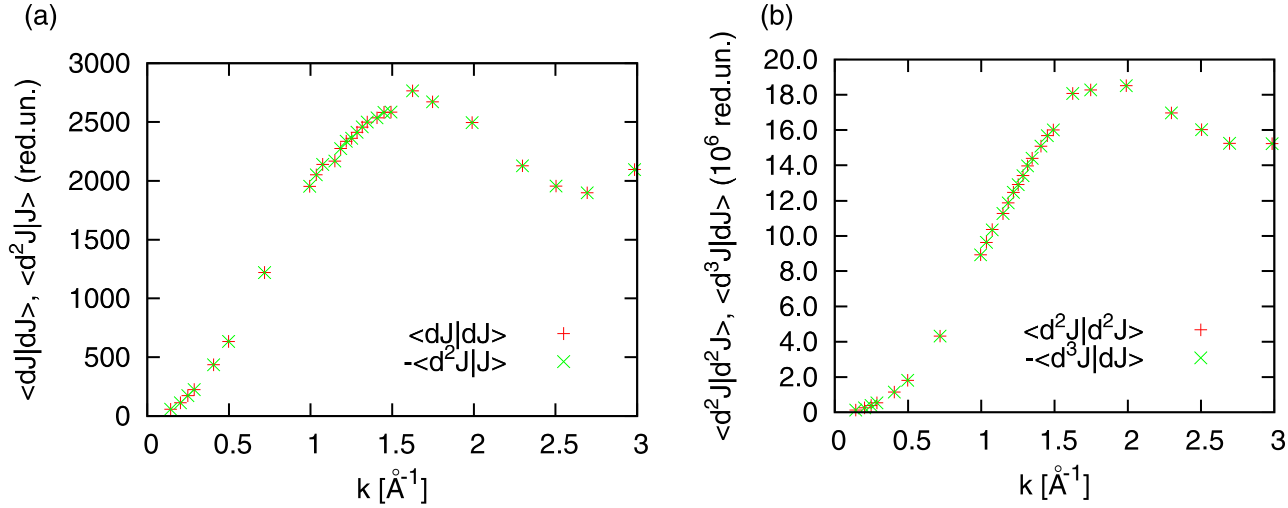

FIG. 1. Check of the properties of time derivatives of the longitudinal current for static correlators (a) $\langle \dot{J}_L(-k)\dot{J}_L(k)\rangle \equiv -\langle \ddot{J}_L(-k)J_L(k)\rangle$ and (b) $\langle \ddot{J}_L(-k)\ddot{J}_L(k)\rangle \equiv -\langle \dddot{J}_L\,(-k)\dot{J}_L(k)\rangle$ for a supercritical Ne at $T = 295$ K and density $1600\ \mathrm{kg/m^3}$.

$\Delta_i(k)$ in the $k \to 0$ limit using a simple Lennard-Jones fluid, because of its simplicity in order to have analytical spatial derivatives of the interparticle potential needed for calculations of $\Delta_i(k)$ and their Eqs. (17)–(20). In the next section we provide details of our MD simulations and calculations of corresponding correlators. Then we will present our results and discuss them in comparison with Eqs. (17)–(20) of Ref. [1]. The last section contains the conclusion of this study.

## II. DETAILS OF MD SIMULATIONS

We performed molecular dynamics simulations for supercritical Ne at $T = 295$ K and density $1600\,\mathrm{kg/m^3}$ using its Lennard-Jones potentials, the same as in our previous study [16]. A model system of 4000 particles was simulated in a microcanonical ensemble with perfect energy conservation over the whole production run of 300 000 time steps. The time step was 0.5 fs. Our main task was in sampling the space-Fourier components of all hydrodynamic variables, i.e., of density $n(k,t)$, mass current $\mathbf{J}(k,t)$, and energy $e(k,t)$, as well as of their time derivatives, in particular, of the mass current up to the third order $\dddot{\mathbf{J}}\,(k,t)$. We sampled all the possible wave vectors corresponding to the same absolute value, and used all of them in a spherical average of the corresponding correlators. The smallest wave number sampled in this MD study was 0.143 598 Å$^{-1}$.

In order to check the reliability of the sampled time derivatives of the longitudinal mass current and of our calculated static correlators, we made use of the exact relations, which follow from a property of the time derivatives of time correlation functions [4],

$$\langle \dot{J}_L(-k)\dot{J}_L(k)\rangle \equiv -\langle \ddot{J}_L(-k)J_L(k)\rangle,$$
$$\langle \ddot{J}_L(-k)\ddot{J}_L(k)\rangle \equiv -\langle \dddot{J}_L\,(-k)\dot{J}_L(k)\rangle.$$

One can see in Fig. 1 that a perfect equivalence (a difference of less than 0.2% for any $k$ point) is evidence of the correct direct sampling of $J_L(k,t)$, $\dot{J}_L(k,t)$ $\ddot{J}_L(k,t)$, and $\dddot{J}_L\,(k,t)$ in MD simulations. These dynamic variables are needed for calculations of quantities $\Delta_i(k)$, $i = 1, 2, 3$ in the expressions for $C^L(k,\omega)$ and $\omega_c^L(k)$ in Ref. [1]. Throughout this Comment we will use reduced units of energy $k_BT = 1$, mass $m = 1$, and time $\tau_\sigma = 1.997\,446$ ps.

## III. RESULTS AND DISCUSSION

As we mentioned above, the perfect agreement between the fit-free theory proposed in Ref. [1] and MD results for $C^L(k,\omega)$ in their Fig. 4 looks too good to be true. Indeed, a simplest check of their Eq. (18) in the $\omega \to 0$ limit results in the nonzero value of $C^L(k,\omega = 0)$,

$$C^L(k,\omega=0) = \frac{1}{\pi}\frac{\Delta_1(k)\Delta_2(k)\Delta_3(k)^{3/2}}{B_0(k)} \equiv \frac{1}{\pi}\frac{\Delta_2(k)}{\Delta_1(k)\Delta_3(k)^{1/2}}, \tag{1}$$

while any viscoelastic theory must result in $C^L(k,\omega = 0) \equiv 0$ as a consequence of the continuity equation. We cannot explain how the authors of Ref. [1] obtained in their Fig. 4 the $C^L(k,\omega \to 0) \propto \omega^2$ behavior from their fit-free theory [their Eq. (18)].

We calculated from their Eqs. (16) and (17) the "relaxation parameters" $\Delta_i(k)$, $i = 1, 2, 3$ and double checked the relations

$$\Delta_1(k) + \Delta_2(k) = \frac{\langle \ddot{J}(-k)\ddot{J}(k)\rangle}{\langle \dot{J}(-k)\dot{J}(k)\rangle},$$

where the right-hand side tends to a constant in the long-wavelength limit and is simply the ratio of $k$ dependences shown in Figs. 1(a) and 1(b), and

$$\Delta_3(k) = \left[\langle \dddot{J}\,(-k)\,\dddot{J}\,(k)\rangle - \frac{\langle \ddot{J}_L(-k)\ddot{J}_L(k)\rangle^2}{\langle \dot{J}_L(-k)\dot{J}_L(k)\rangle}\right] \Bigg/ \left[\langle \ddot{J}_L(-k)\ddot{J}_L(k)\rangle - \frac{\langle \dot{J}_L(-k)\dot{J}_L(k)\rangle^2}{\langle J_L(-k)J_L(k)\rangle}\right].$$

In Fig. 2 we show the $k$ dependence of the relaxation parameters [1], and one can see the parameters $\Delta_2(k)$ and $\Delta_3(k)$

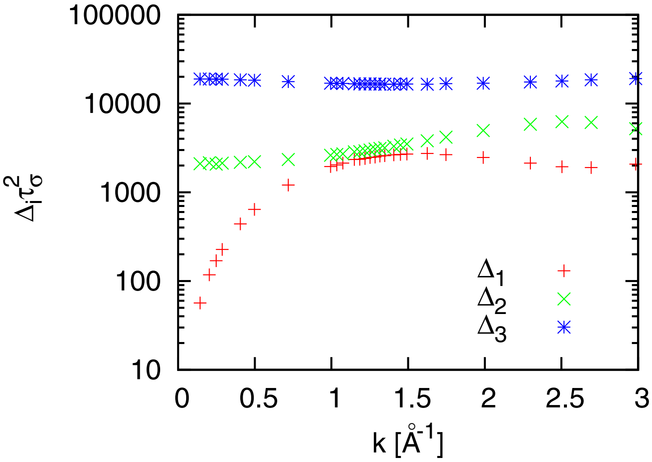

FIG. 2. Dependence of the "relaxation parameters" $\Delta_i$, $i = 1, 2, 3$ [Eq. (16) of Ref. [1]] on wave numbers for supercritical Ne at $T = 295$ K and density 1600 kg/m$^3$.

tending in the long-wavelength limit to nonzero values while

$$\Delta_1(k) \equiv \frac{\langle \dot{J}_L(-k)\dot{J}_L(k)\rangle}{\langle J_L(-k)J_L(k)\rangle}$$

behaves in the $k \to 0$ limit as $\propto c_\infty^2 k^2$, with $c_\infty$ being the high-frequency speed of sound.

Now we can estimate how large is the deviation of $C^L(k, \omega = 0)$ from the correct zero value. Since the $\Delta_1(k)$ goes to zero in the long-wavelength limit and $\Delta_2(k \to 0)$ and $\Delta_3(k \to 0)$ tend to finite nonzero values, the resulting $C^L(k, \omega = 0)$ taken from Eq. (18) of Ref. [1] should diverge for $k \to 0$. Indeed, in Fig. 3 one can observe the strong increase of $C^L(k, \omega = 0) \propto k^{-2}$ in Ref. [1], which means a wrong theoretical result compared with the exact relation $C^L(k, \omega \to 0) = 0$.

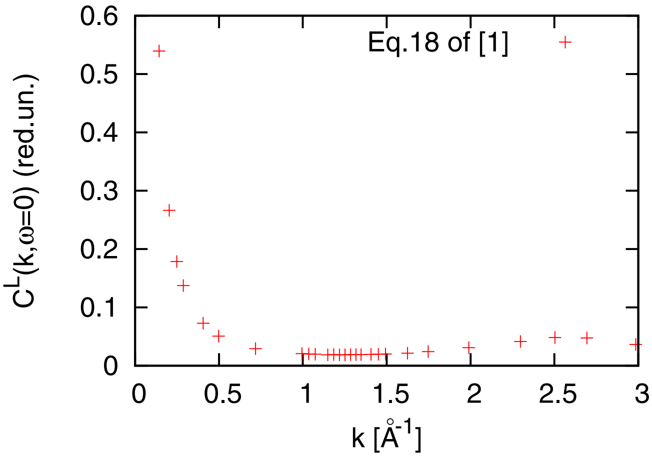

FIG. 3. Dependence of the zero-frequency value $C^L(k, \omega = 0)$ [Eq. (18) of Ref. [1]] on wave numbers for supercritical Ne at $T = 295$ K and density 1600 kg/m$^3$.

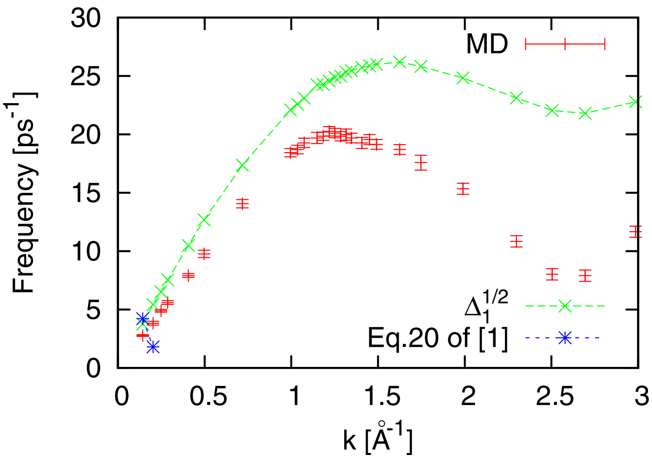

FIG. 4. Peak positions of the longitudinal current spectral function $C^L(k, \omega)$, obtained from MD simulation (plus symbols with error bars). The dispersion of the nondamped high-frequency acousticlike modes with a long-wavelength asymptote (2) is shown by the line-connected cross symbols. Equation (20) of Ref. [1] (line-connected star symbols) contains a positive expression under the square root only for the two lowest $k$ points, and for larger $k$ values no real $\omega_c^L(k)$ exist.

Now we will analyze the expression for the dispersion of collective excitations [1]. Since only the relaxation parameter $\Delta_1(k)$ tends to zero as $k^2$ in the long-wavelength limit, and higher relaxation parameters $\Delta_{2,3}(k)$ tend to constants in that limit, one can easily estimate that their Eq. (20) for $\omega_c^L(k)$ tends to a constant for $k \to 0$,

$$\omega_c^L(k \to 0) = \frac{\Delta_2(0)}{\sqrt{2[\Delta_3(0) - \Delta_2(0)]}},$$

while the correct dispersion law had to recover in that limit the hydrodynamic dispersion law $\omega(k \to 0) = c_s k$. In Fig. 4 we show the dispersion of collective acoustic modes estimated from the peak positions of MD-derived $C^L(k, \omega)$ (plus symbols with error bars) and compare it with the dispersion of "bare" (nondamped) high-frequency modes which in the long-wavelength limit have a linear dispersion with the high-frequency (elastic) speed of sound $c_\infty$,

$$\omega_\infty(k \to 0) = \left[\frac{\langle \dot{J}_L(-k)\dot{J}_L(k)\rangle}{\langle J_L(-k)J_L(k)\rangle}\right]^{1/2}\Bigg|_{k\to 0} \to c_\infty k. \tag{2}$$

The coupling to the faster dynamic modes (connected with higher time derivatives of the longitudinal current) can only slightly renormalize down the theoretical dispersion law, however, it will never result in the hydrodynamic speed of sound $c_s$ and positive sound dispersion [11]. Within the theoretical approach proposed in Ref. [1] it is impossible to obtain propagating modes with an adiabatic speed of sound, because in order to obtain it one has to include coupling with density and energy (or heat) density fluctuations in the theoretical scheme. And, as it was expected from the wrong behavior of $C^L(k, \omega)$ discussed above, the proposed expression for the dispersion of longitudinal collective excitations is wrong too. In Fig. 4 only for the two lowest $k$ values did we obtain a positive expression under the square root in their Eq. (20). For higher wave numbers the expression under the square root became negative, i.e., no propagating modes for those wave numbers. It is not clear how in Fig. 5 of Ref. [1] the authors were able to reproduce perfectly the MD data by using their

Eq. (20) and even reach the adiabatic speed of sound in the long-wavelength region, that is impossible to do in their theoretical approach. Even conceptually, their theoretical approach does not contain coupling to fluctuations of conserved quantities, density $n(k,t)$, and energy density $e(k,t)$, and Eq. (20) cannot result in a long-wavelength limit in a linear dispersion with the adiabatic speed of sound. In their run for the "overarching goal of this research programme" the authors forgot about the existing methodologies of calculations and theories of collective excitations in liquids, which correctly satisfy the exact relations and a large number of sum rules.

## IV. CONCLUSION

The theoretical scheme proposed in Ref. [1] for the description of longitudinal collective excitations in simple liquids is not consistent with hydrodynamics, because only one hydrodynamic variable, the longitudinal current, was used in that scheme, which raised questions about whether the expressions obtained in Ref. [1] for the longitudinal current spectral function $C^L(k,\omega)$ and for the dispersion of collective excitations are correct. We performed molecular dynamics simulations on a simple supercritical Ne at 295 K and density 1600 $\mathrm{kg/m^3}$ with the purpose of numerically checking these expressions.

We showed that the expression proposed in Ref. [1] for $C^L(k,\omega)$ does not have the correct low-frequency limit $C^L(k,\omega\to 0)$ and even diverges in the long-wavelength limit, which is wrong, while according to the continuity equation it must be $C^L(k,\omega=0)\equiv 0$. We cannot explain why their Fig. 4 shows perfect agreement of their theoretical $C^L(k,\omega)$ with MD data.

Within the theoretical scheme proposed in Ref. [1] it is impossible to recover the hydrodynamic dispersion law in the $k\to 0$ limit and macroscopic adiabatic speed of sound, because the coupling of the longitudinal current with other fluctuations of conserved quantities is absent in that scheme. We checked the expression proposed in Ref. [1] for the dispersion of collective excitations and found that with increasing wave numbers the expression under the square root in their Eq. (20) becomes negative, i.e., wrong result. We cannot explain why their Fig. 5 shows perfect agreement between their theoretical expression and the MD-obtained dispersion of collective excitation, and even recovers the hydrodynamic linear dispersion law with $c_s$. We would suggest for the authors of Ref. [1] to show their similar checks for the correlators $\langle \ddot{J}_L(-k)J_L(k)\rangle$ and $\langle \dddot{J}_L\,(-k)\dot{J}_L(k)\rangle$ as we presented in Fig. 1, as well as to reveal the $k$ dependence of their $\Delta_i(k)$. This will definitely allow us to find out why the low-frequency limit of $C^L(k,\omega)$, their Eq. (18), and the long-wavelength limit of $\omega_c^L(k)$, their Eq. (20), do not correspond to the data in their Figs. 4 and 5, respectively.

## ACKNOWLEDGMENT

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