Comment on ”Direct evidence for strong crossover of collective excitations and fast sound in the supercritical state”

T. Bryk$^{1,2}$, I. Mryglod$^1$

$^1$Institute for Condensed Matter Physics of the National Academy of Sciences of Ukraine, 1 Svientsitskii Street, UA-79011 Lviv, Ukraine

$^2$Institute of Applied Mathematics and Fundamental Sciences, Lviv Polytechnic National University, UA-79013 Lviv, Ukraine

(Dated: October 27, 2015)

Abstract

We comment on three incorrect claims in the paper by Fomin et al (arXiv:1507.06094) concerning the generalized hydrodynamic methodology and positive sound dispersion in fluids.
In a recent paper the authors reported results on dispersion of collective excitations in simple Lennard-Jones fluids obtained numerically from molecular dynamics simulations. Fomin et al have made several incorrect statements on a methodology of generalized hydrodynamics known as the approach of generalized collective modes (GCM) as well as they claimed they explained "the phenomenon of fast sound originating from transverse modes". We comment on the following three issues.

(i). The GCM methodology, historically originated from the papers by D.Kivelson and T.Keyes and E.G.D.Cohen with coworkers, is based on an extension of the hydrodynamic set of equations by additional balance equations for non-conserved quantities. The choice for the extended non-conserved dynamic variables via the time derivatives of the hydrodynamic ones was very obvious because of the "orthogonality" condition for equal-time static averages

\[ \langle A(-k) | \dot{A}(k) \rangle \equiv 0 \]

in equilibrium. Here the overdot means the time derivative of the dynamic variable \( A(k, t) \), where \( k \) is wave number. The extended set of \( N_v \) dynamic variables allows to write down the obtained system of equations in a matrix form of the generalized Langevin equation for the \( N_v \times N_v \) matrix of Laplace-transformed time correlation functions

\[
\tilde{F}(k, z) = \left[ zI - i\Omega(k) + \tilde{M}(k, z) \right]^{-1} F(k, t = 0),
\]

where the \( N_v \times N_v \) matrices \( I, \Omega(k), \tilde{M}(k, z) \) are the unity matrix, frequency matrix and matrix of memory functions, respectively, that proves the GCM approach being essentially the memory-function formalism. This system of \( N_v \) equations can be strictly derived by the method of non-equilibrium statistical operator.

In Markovian approximation the \( N_v \times N_v \) generalized hydrodynamic matrix reads

\[
T(k) = -i\Omega(k) + \tilde{M}(k, z = 0) \equiv F(k, t = 0) \left[ \tilde{F}(k, z = 0) \right]^{-1} .
\]

and allows to control the Markov approximation for the highest-order memory function by the order of the time derivatives in the extended dynamic variables, see. A basis set of \( s + 1 \) dynamic variables which contains a sequence of the time derivatives of hydrodynamic variable \( A(k, t) \) up to the \( s \)-th order when applied for theoretical description of a time correlation function \( F_{AA}(k, t) \) is formally equivalent to the \( s + 1 \) step in Mori’s continued fraction expansion for its Laplace-transform \( \tilde{F}_{AA}(k, z) \) with all the corresponding sum
rules satisfied. It is easily to check by straightforward algebra using the eigenvalues of
the generalized hydrodynamic matrix $T(k)$, that the sum rules (frequency moments) are
exactly satisfied for the first $s + 1$ frequency moments of $\tilde{F}_{AA}(k, z)$ if the basis set of GCM
methodology contains a sequence of time derivatives of hydrodynamic variable $A(k, t)$ up to
the $s$-th order.

Hence, it is not clear how Fomin et al came to a claim (quotation from [1]) "First, the
number of relevant variables in this approach is guessed [27]. Not based on a fundamental
principle the method is ad hoc and is not generally applicable". This gives evidence that
the authors of [1] do not understand the role of extended (non-hydrodynamic) dynamic
variables and how they are chosen. In paper [11] (referenced as [27] in [1]) a sequence of
time derivatives of hydrodynamic variables was taken up to the third order providing the
precision for description of the density-density time correlation functions within the highest
by date fourth-order memory function, that allowed to check the Markovian approximation
and convergence of the results with increasing order of memory functions.

In another quotation from [1] the authors claim that the GCM approach "is internally
inconsistent and violates the sum rules because the odd moments are non-zero in the method
employing exponentials for the correlators". Fomin et al refer for this claim to a paper [12],
in which the velocity autocorrelation function is analyzed. It seems Fomin et al do not
see the difference between the autocorrelation function of a non-conserved quantity (single-
particle velocity, or stress [13] etc) which decays with long tail $\sim t^{-3/2}$ and hydrodynamic
time correlation functions of conserved quantities, like density-density ones which pretty
well are described by exponentials (see [14] for detailed analysis). Concerning the sum
rules fulfilled - the GCM approach provides even higher number of the sum rules than the
regular memory function approach (viscoelastic model with two relaxation times), because
it provides simultaneously at least first three frequency sum rules for the energy-energy
correlations and first four frequency rules for the density-energy correlations. As it was
mentioned above the hierarchy of memory functions provided by the time derivatives of
hydrodynamic variables makes the GCM approach very flexible in fulfillment of the exact
sum rules up to any desired order. Namely a requirement to obtain the desired level of
fulfilled sum rules for the analytical GCM representation of the time correlation function
of interest (like density-density or energy-energy ones) leads to the unambiguous choice of
extended dynamic variables.
(ii). It seems there is not only a lack of understanding of the generalized hydrodynamic methodology by Fomin et al. In [1] it was claimed that the GCM methodology numerically leads to wrong results. The authors of [1] compared their estimated dispersion curves from peak positions of the longitudinal current spectral function for supercritical Ar at reduced temperature $T^* = 1.71$ and four densities with the GCM results taken as it is claimed from Ref.[15] - see Figs.1a,b. Based on these figures it was concluded in [1] that ”the dispersion curves derived in the GCM method stay nearly the same at different densities, the result not expected on physical grounds”. In Fig 1c we reproduce the dispersion curves for the four densities of supercritical Ar at $T^* = 1.71$ published in [15] and the readers can easily compare the data and estimate how the dispersions depend on density. It is not clear why the authors of [1] try to publish obvious fake ascribed as the GCM results.

(iii). Fomin et al claimed that they have explained the positive sound dispersion in liquids as "originating from transverse modes in the supercritical state below the Frenkel line". The PSD in fluids consists in bending up the dispersion of longitudinal collective excitations from the linear hydrodynamic dispersion law $\omega_{\text{hyd}}(k) = c_s k$ towards higher frequencies because of the viscoelastic effects. Here the adiabatic speed of sound $c_s$ is defined via macroscopic quantities as

$$c_s = \sqrt{\frac{\gamma}{\rho \chi_T}} = \sqrt{\frac{B_s}{\rho}},$$

where $\chi_T$ is isothermal compressibility, $\gamma$ - the ratio of specific heats, $B_s$ is the adiabatic
bulk modulus, and $\rho$ is mass density. The viscoelasticity of fluids is the consequence of two different regimes in dynamics of fluids which are governed by different stress tensors: the viscous one on macroscopic scale and the elastic one on atomic-resolution scale. The viscous stress tensor depends only on the velocity field in fluid, while the elastic stress tensor is defined by microscopic forces acting between atomistic particles \[5, 6, 16\]. In order to discriminate between the viscous and elastic regimes the elastic moduli are marked in a standard way as the high-frequency ones: the high-frequency bulk $B_\infty$ and shear $G_\infty$ moduli \[5, 6\]. Corresponding high-frequency speed of sound, which would have the idealized non-damped long-wavelength propagating longitudinal modes in elastic regime, is

$$c_\infty = \sqrt{\frac{B_\infty + 4/3G_\infty}{\rho}},$$  \hspace{1cm} (4)

and both speeds of sound, $c_s$ and $c_\infty$ are well defined in the whole range of densities of fluid, as it is shown in Fig.2 on example of supercritical Ar at 363 K. It is possible to define also in analogy the high-frequency speed of propagation of idealized non-damped long-wavelength transverse modes

$$c_\infty^T = \sqrt{\frac{G_\infty}{\rho}},$$ \hspace{1cm} (5)

that does not make much sense because the real long-wavelength transverse acoustic modes in fluids cannot propagate and the linear dispersion for long-wavelength transverse excitations with propagation speed $c_\infty^T$ is not valid for fluids. This is the clear difference between the idealized non-damped (sometimes called as ”bare”) propagating modes and collective excitations observed in real scattering experiments or computer simulations.

In \[1\] the authors used the expression for the high-frequency longitudinal speed of sound (4) as well as the adiabatic one with dropped indices,

$$v_L^2 = \frac{B + 4/3G}{\rho},$$

and

$$v_{hyd}^2 = \frac{B}{\rho},$$

respectively, and treating $B$ as the same quantity they substituted in the high-frequency longitudinal speed of sound in fact the bulk modulus of the viscous regime, that is totally incorrect. It is concluded then that the high-frequency speed of sound is the adiabatic one enhanced by the coupling to transverse propagating modes, in their notations being \[1\]:

$$v_L^2 = v_{hyd}^2 + 4/3v_T^2,$$
FIG. 2: Adiabatic and high-frequency speeds of sound for supercritical Ar at T=363K in a wide range of densities, obtained in molecular dynamics simulations [17]. The methodology of calculations of $c_s$ and $c_\infty$ was the same as described in [15].

that is totally a consequence of wrong manipulation in their expression with the adiabatic and high-frequency bulk moduli. Note, that the quantity ($c_\infty^2 - c_s^2$) appears in different generalized hydrodynamic approaches [6, 15, 18] and is well defined for the whole range of fluid densities (see Fig.2) however nobody associated it with the transverse excitations.

In summary, we have shown that the claim on the positive sound dispersion in fluids "originating from transverse modes in the supercritical state below the Frenkel line" does not have any theoretical basis and was derived from the misused expression for the high-frequency speed of sound. The comments by authors of [1] on the generalized hydrodynamics and in particular on the approach of GCM give evidence of the lack of understanding what the GCM approach is. Moreover, in [1] some dispersion curves were stated as the GCM results taken from Ref. [15] which do not depend on density of fluid - we consider this as the obvious fake. This can be easily detected by comparison with real GCM results for dispersion of collective excitations in supercritical Ar at different densities reported in [15] (see Fig.2).

[1] Yu.D. Fomin, V.N. Ryzhov, E.N. Tsiok, V.V. Brazhkin, K. Trachenko, e-print arXiv:1507.06094 (2015); published 22-07-2015; http://arxiv.org/abs/1507.06094
[2] T. Keyes, D. Kivelson, J. Chem. Phys. 54, 1786 (1971).
[3] D. Kivelson, T. Keyes, J. Chem. Phys. 57, 4599 (1972).

[4] I.M. deSchepper, E.G.D. Cohen, C. Bruin, J.C. van Rijs, W. Montfrooij, and L.A. de Graaf, Phys. Rev. A 38, 271 (1988).

[5] J.-P. Hansen, I.R. McDonald, *Theory of Simple Liquids* (London: Academic) (1986).

[6] J.-P. Boon, S. Yip, *Molecular Hydrodynamics* (New-York: McGraw-Hill) (1980).

[7] I.M. Mryglod, Condens. Matter Phys. 1 753 (1998).

[8] I.M. Mryglod, I.P. Omelyan, M.V. Tokarchuk, Mol. Phys. 84 235 (1995).

[9] I.M. Mryglod, I.P. Omelyan, Mol. Phys. 92 913 (1997).

[10] H. Mori, Progr. Theor. Phys. 57, 767 (1965).

[11] T. Bryk, I. Mryglod, Phys. Rev. E 63, 051202 (2001).

[12] M.H. Lee, Phys. Rev. Lett. 51, 1227 (1983).

[13] D.J. Evans, J. Stat. Phys. 22, 81 (1980).

[14] F. Barocchi, E. Guarini, U. Bafile, Phys. Rev. E 90, 032106 (2014).

[15] T. Bryk, I. Mryglod, T. Scopigno, G. Ruocco, F. Gorelli, M. Santoro, J. Chem. Phys. 133, 024502 (2010).

[16] J.R.D. Copley, S.W. Lovesey, Rep. Progr. Phys., 38, 461 (1975).

[17] F.A. Gorelli, T. Bryk, M. Krisch, G. Ruocco, M. Santoro, T. Scopigno, Sci. Rep. 3, 1203 (2013).

[18] T. Scopigno, U. Balucani, G. Ruocco, F. Sette, J. Phys.: Condens. Matter, 12, 8009 (2000).