PROPAGATING DENSITY FLUCTUATIONS
IN HYDRODYNAMICS AND BEYOND

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Abstract. Density fluctuations in simple liquids are analysed in the context of three different and widely used formalisms, whose equivalence in the hydrodynamic limit is shown. We, furthermore, address the issue of the dispersion of the propagating modes outside the hydrodynamics, by comparing three different definitions of the generalized sound velocity. The first definition is standard in statistical mechanics. It relates the sound velocity to the imaginary part of the complex conjugate poles of the so-called intermediate scattering function. Other definitions, frequently used in the literature, identify the characteristic frequencies of the inelastic excitations with the maxima of the inelastic features of the dynamic structure factor, or with the maxima of the current function. The behaviour of these three quantities in the hydrodynamic limit is discussed. Deviations from hydrodynamic dispersion law are also considered with particular emphasis given to the analysis of different sound propagation regimes related to different density fluctuations decay channels.

1. Introduction

Propagating density fluctuations can be measured in different regions of the $Q - \omega$ (wave number – frequency) plane by Brillouin Light Scattering (BLS), Inelastic X-ray Scattering (IXS) and Inelastic Neutron Scattering (INS) which span the range of wave numbers from hydrodynamic (BLS) to short-wavelength region (INS/IXS). Traditionally, the experimentalists identify the characteristic frequency of the density-fluctuations modes with the maxima of the dynamic structure factor, $S(Q, \omega)$, or, alternatively, with the maxima of the longitudinal current, $J(Q, \omega)$. The maxima of the two functions $S(Q, \omega)$ and $J(Q, \omega)$ coincide in the hydrodynamic region, but, they can, however, differ outside the small Q region, as follows from the relation

$$J(Q, \omega) = \frac{\omega^2}{Q^2} S(Q, \omega). \tag{1}$$

On the theoretical side, the standard definition of collective excitations in statistical mechanics is via the poles of the Green functions or of the dynamic response functions. It has not yet been, however, established the exact correspondence between the analytical

definition of the collective excitations and the direct observation of the peak in $S(Q, \omega)$ or $J(Q, \omega)$ used by the experimentalists. One of the first studies in this direction was performed by Bafile *et al.* (2006).

Before to analyze both the theoretical and empirical definitions of the speed of sound, we will discuss three different theoretical frameworks aimed to describe density fluctuations in a monoatomic fluid. Particular emphasis is deserved to their ability in modelling the Rayleigh-Brillouin spectra.

The manuscript is organized as in the following. Section 2 describes how density fluctuations can be characterized in the hydrodynamic region by providing the solution of the phenomenological equations of macroscopic fluid mechanics (linearized hydrodynamics). Characteristic parameters defining the fluid mechanics equations are the thermodynamic quantities and the macroscopic transport coefficients. Standard treatment is exploited. The expression of the dynamic structure factor related to density fluctuations is given in this framework. Section 3 introduces two well-known and largely exploited approaches aimed to generalizing the hydrodynamics results to the region of higher wavevectors and frequencies, *i.e.*, the Memory function and the Generalized Collective Modes (GCM) frameworks. The second order memory function accounts for all the relaxation mechanisms affecting longitudinal acoustic dynamics. The characteristic parameters are the amplitudes and the characteristic times of the different decaying contributions entering the memory function. Characteristic parameters of the GCM are instead the initial values and the time integrals of the time correlation functions (which can be eventually obtained by Molecular Dynamics simulations). As an original result of the present manuscript the two approaches are compared between them, showing their equivalence in the hydrodynamic limit where the results obtained in both the frameworks converge to the correct hydrodynamics results. Section 4 analyses the expressions related to three different definition of speed of sound, currently exploited in literature with particular emphasis to the transition between different sound propagation regimes.

2. Linearized hydrodynamics

The nature of *macroscopic* sound propagation in fluids is very different from the case of solids, where atoms are restricted to small oscillations around stable potential energy minima. In liquid state instead one has to treat density fluctuations which are constrained by local conservation laws (Landau and Lifshitz 1987). Hence, the existence of macroscopic density fluctuations in simple fluids is governed by three general local conservation laws: conservation of number of particles, total momentum and energy (Landau and Lifshitz 1987; Hansen and McDonald 1990; Boon and Yip 1991; Pecora 2013). This means that once a macroscopic density fluctuation emerged in fluid, it cannot dissipate locally but starts propagating due to local conservation laws, that is the essence of the hydrodynamic mechanis of sound propagation in fluids. The basic variables of fluid mechanics are the densities of conserved quantities: number density $\rho(\mathbf{r}, t)$, momentum density $\mathbf{J}(\mathbf{r}, t)$ and energy density $e(\mathbf{r}, t)$, given as functions of the space coordinate ($\mathbf{r}$) and time (t). The five balance equations for these quantities in terms of the flux densities associated to each

variable read as

$$\dot{\rho}(\mathbf{r},t) + \nabla \cdot \mathbf{J}(\mathbf{r},t) = 0; \tag{2}$$

$$\dot{\mathbf{J}}(\mathbf{r},t) + \nabla \cdot \hat{\sigma}(\mathbf{r},t) = 0; \tag{3}$$

$$\dot{e}(\mathbf{r},t) + \nabla \cdot \mathbf{J^e}(\mathbf{r},t) = 0, \tag{4}$$

where $\hat{\sigma}(\mathbf{r},t)$ is the momentum flux, or stress tensor, and $\mathbf{J^e}(\mathbf{r},t)$ is the energy flux. We would like only to mention here, that for the case of n-component liquid mixtures the number of conserved quantities, and corresponding balance equations, will be $5 + (n-1)$, because of additional conservation of $n-1$ local concentrations in liquid mixtures.

We will not repeat the standard procedure of obtaining the closed set of balance equations by making use of the expression for the stress tensor and of thermodynamic relations between macroscopic fluctuations of pressure, density and temperature (Landau and Lifshitz 1987; Hansen and McDonald 1990; Boon and Yip 1991). We only stress the convenience to use temperature density instead of energy density, which ultimately results in a complete set of equations (five equations) with respect to the variables $\rho, T, \mathbf{J}$. These equations are simplified by retaining only terms of leading order in the deviations of all the independent variables from their average (linearization) and taking the double Fourier-Laplace transform in space and time,

$$\tilde{\mathbf{A}}_{\mathbf{q}}(z) = \int_0^{\infty} dt e^{-zt} \int_{-\infty}^{+\infty} e^{i\mathbf{Q}\cdot\mathbf{r}} \delta\mathbf{A}(\mathbf{r},t) \tag{5}$$

($\mathbf{A} = \rho$, $\mathbf{J}$, $\mathbf{T}$). One last step follows, consisting in the separation of the longitudinal and transverse part of $\tilde{\mathbf{J}}_q(z)$ with respect to the direction defined by the momentum $\mathbf{Q}$, by convention directed along the z-axis. The matrix of coefficients of the linear system of equations obtained in the Fourier-Laplace domain, is known as *hydrodynamic matrix* (Boon and Yip 1991). The hydrodynamic matrix, $\mathscr{T}$, is block-diagonal, the transverse current fluctuations being completely decoupled from the fluctuations of other variables. The analysis can be thus focused on the remaining three variables: density, temperature and longitudinal current (J^l) (Boon and Yip 1991). The system of linear equations for these variables in the Fourier-Laplace space can be written as

$$\begin{pmatrix} z & iQ & 0 \\ \gamma^{-1}c_S^2 iQ & [z+\nu Q^2] & \gamma^{-1}\alpha c_S^2 iQ \\ 0 & \alpha^{-1}(\gamma-1)iQ & [z+\gamma D_T Q^2] \end{pmatrix} \begin{pmatrix} \tilde{\rho}_{\mathbf{q}}(z) \\ \tilde{J}^l_{\mathbf{q}}(z) \\ \tilde{T}_{\mathbf{q}}(z) \end{pmatrix} = \begin{pmatrix} \rho_{\mathbf{q}} \\ J^l_{\mathbf{q}} \\ T_{\mathbf{q}} \end{pmatrix}, \tag{6}$$

where c_s, D_T, ν are adiabatic speed of sound, thermal diffusivity and longitudinal kinematic viscosity, and $\gamma = C_P/C_V$, α are ratio of specific heats and thermal expansion coefficient, respectively. No approximation, but linearization, has been done in writing Eq. (6). It is clear from (6) that the fluctuations of ρ, J^l and $\mathbf{T}$ are coupled together, we can thus refer to *longitudinal modes* referring to the decay mechanisms of fluctuations in these three variables.

We define the vector $\mathbf{F}(Q,t) = \big(\rho(\mathbf{Q},t), J^l(\mathbf{Q},t), T(\mathbf{Q},t)\big)$ and its conjugate in time-Laplace transform $\tilde{\mathbf{F}}(\mathbf{Q},z)$. The i-th component of $\tilde{\mathbf{F}}(\mathbf{Q},z)$ is found to be:

$$\tilde{F}_i(Q,z) = [det\,\mathscr{T}(Q,z)]^{-1} \sum_j P_{ij}(Q,z) F_j(Q,t=0) \tag{7}$$

The algebraic functions $P_{ij}(Q,z)$ are the elements of minors of $\mathscr{T}(Q,z)$. The matrix of correlation functions can be computed as

$$\langle \tilde{F}_i(Q,z)F_1^*(Q)\rangle = [det\,\mathscr{T}(Q,z)]^{-1}\sum_j P_{ij}(Q,z)\langle F_j(Q)F_1^*(Q)\rangle,\qquad (8)$$

where $\langle ...\rangle$ is the ensemble average over the initial values of the variables. The intermediate scattering function for ρ fluctuations, $\tilde{F}(Q,z)$, is given by

$$\frac{\langle \rho_{\mathbf{q}}(z)\rho_{\mathbf{q}}^*\rangle}{\langle \rho_{\mathbf{q}}\rho_{\mathbf{q}}^*\rangle} = \frac{\tilde{F}(Q,z)}{S(Q)} = \frac{z^2+Az+B}{z^3+Az^2+Cz+D},\qquad (9)$$

where

$$\begin{aligned}
A &= \gamma D_T Q^2 + \nu Q^2\\
B &= \gamma D_T \nu Q^4 + \tfrac{\gamma-1}{\gamma}c_S^2 Q^2\\
C &= \gamma D_T \nu Q^4 + c_S^2 Q^2\\
D &= D_T c_S^2 Q^2
\end{aligned}\qquad (10)$$

The dynamic structure factor, $S(Q,\omega)$, can be found according to the relationship (Boon and Yip 1991)

$$S(Q,\omega) = \frac{1}{\pi}ReF(Q,z=i\omega).\qquad (11)$$

It can be expressed as a function of the poles of the intermediate scattering function, requiring that we find the roots of the denominator of Eq. (9) when it is set to zero (dispersion equation). This will be discussed in Sec. **4**. We report here the standard approximated expression for $S(Q,\omega)$. Usually, in treating the hydrodynamic limit it is adopted an approximate expression for the roots of the dispersion equation in order to skip algebraic complexity (Boon and Yip 1991). They are valid when $D_T Q/c_S$ and $\nu Q/c_S$ are small. The poles of $\tilde{F}(Q,z)$, z_0 and $z_{\pm}$, at the first order in such small quantities (or to order Q^2) are (Boon and Yip 1991)

$$\begin{aligned}
z_0 &= -D_T Q^2\\
z_{\pm} &= \pm ic_S Q - \tfrac{1}{2}\left[\nu+(\gamma-1)D_T\right]
\end{aligned}\qquad (12)$$

The dynamic structure factor becomes (Boon and Yip 1991)

$$\begin{aligned}
S(Q,\omega) &= \frac{NK_B T}{2\pi V}\frac{k_T}{\gamma}\left[\frac{2(\gamma-1)D_T Q^2}{\omega^2+D_T^2 Q^4} + \frac{\Gamma Q^2}{(\omega+c_S Q)^2+\Gamma^2 Q^4} + \frac{\Gamma Q^2}{(\omega-c_S Q)^2+\Gamma^2 Q^4}+\right.\\
&\left.+\ [\Gamma+D_T(\gamma-1)]\frac{Q}{c_S}\left(\frac{\omega+c_S Q}{(\omega+c_S Q)^2+\Gamma^2 Q^4} - \frac{\omega-c_S Q}{(\omega-c_S Q)^2+\Gamma^2 Q^4}\right)\right]
\end{aligned}\qquad (13)$$

being $\Gamma = \frac{1}{2}\left(\nu+D_T(\gamma-1)\right)$ and $k_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ the isothermal compressibility. Eq. (13) is the sum of a zero frequency centered Lorentz function, associated to the elastic response of the system to an external perturbation, plus two Lorentz functions centered at $\omega = \pm c_S Q$, providing a representation for the inelastic response of the system. They are characterized by a full width at half maximum (FWHM) ΓQ^2, the so-called damping coefficient, to which they contribute both viscous processes and thermal diffusion (this contribution is small if $\gamma \sim 1$).

It is important to recall that these hydrodynamic results reflect macroscopic treatment of dynamics of fluids (no atomistic structure, no microscopic forces acting between particles). However, any simple liquid must obey these expressions in the long-wavelength limit, because they are the direct consequence of the fundamental local conservation laws. Another important point concerns the *adiabatic* speed of sound and the role of thermal processes in macroscopic dynamics of fluids. Since the sound propagation (pressure waves) is faster process than the thermal diffusivity (diffusion of local temperature) the adiabatic propagation means that pressurized/rarefied regions in the pressure wave will have different local temperature, that immediately gives rise to thermal relaxation, see real eigenvalue in Eq. (12) , in order to equalize the temperature difference. That is why always in the long-wavelength region the adiabatic speed propagation comes together with thermal relaxation, responsible for the central peak of $S(Q, \omega)$ in Eq. (13) .

3. Beyond hydrodynamics

3.1. Memory function approach. The theoretical framework developed by Zwanzig (1960) and Mori (1965) (see also Hansen and McDonald 1990; Boon and Yip 1991; Zwanzig 2001), based on the introduction of a so-called memory function, constitutes the starting point for an extension of hydrodynamic results to finite value of wavevector. The time-evolution of the autocorrelation function of a generic dynamic variable is given by an integro-differential equation whose kernel is the memory function. It describes all the relevant processes contributing to the decay of the autocorrelation function. Details can be found in the papers by Hansen and McDonald (1990), Boon and Yip (1991), and Balucani and Zoppi (1995). It is shown on the following that, when applied to hydrodynamics regime, the memory-function formalism permits to retrieve the correct hydrodynamics results.

Given a dynamic variable $A(t)$, its equation of motion in the phase-space reads as

$$\frac{dA(t)}{dt} = \{A, \mathscr{H}\}_{\mathrm{P}} \doteq i\mathscr{L}A, \tag{14}$$

where $\mathscr{H}$ is the hamiltonian of the system, $\{\cdot\}_{\mathrm{P}}$ denotes the Poisson brackets, $A = A(0)$ and $\mathscr{L}$, implicitly defined by Eq. (14) , is the *Liouville operator*. In the space defined by all the dynamic variables it is defined an inner product and thus a projection operator $\mathscr{P}$. The action of $\mathscr{P}$ on the variable $B(t)$ is

$$\mathscr{P}B(t) \doteq \frac{\langle B(t)A^* \rangle}{\langle AA^* \rangle}A, \tag{15}$$

where $\langle B(t)A^* \rangle$ is the time correlation function between $B(t)$ and A defining their inner product. The projector on the subspace orthogonal to A is $\mathscr{Q} = 1 - \mathscr{P}$. Exploiting the projection operators, it is possible to decompose the equation of motion in two equations describing respectively the time-evolution of the components of $A(t)$, parallel and orthogonal to A (Hansen and McDonald 1990; Balucani and Zoppi 1995). The first one, outlined below, rules the time-evolution of the self-correlation function of A, see Eq. (15). If $C(t) = \langle A(t)A^* \rangle$, it is (Boon and Yip 1991)

$$\dot{C}(t) - i\Omega C(t) + \int_0^t M(t - t')C(t')dt' = 0, \tag{16}$$

with $M(t) = \frac{\langle R(t)R^* \rangle}{\langle AA^* \rangle}$; $R(t) = e^{i(\mathscr{QL})t}\mathscr{Q}\dot{A}$ is the so called random force, a dynamical variable itself, representing the time-evolution of the orthogonal component of $\dot{A}$. Its time correlation function is the memory function, $M(t)$. The quantity Ω, with the dimensions of a frequency, is defined as $\Omega = <A\dot{A}^*><AA^*>^{-1}$. In the present case it is equal to zero due to the properties of time correlation functions.

In the following we keep as dynamical variable the number density, whose time and space fluctuations determine the dynamic structure factor, see Eqs. 9 and 11. The relevant relaxation processes, determining the decay of hydrodynamic longitudinal fluctuations, can conveniently be expressed by introducing a second-order memory function, $M^{(2)}(Q,t)$, as shown in the following. We will refer to the previously introduced memory function, Eq. (16) as the *first order memory function* $M^{(1)}(Q,t)$. From Eq. (16) it follows that $M^{(1)}(Q,t)$ enters the following balance equation for the density autocorrelation function (Hansen and McDonald 1990; Boon and Yip 1991)

$$\dot{F}(Q,t) + \int_0^t M^{(1)}(Q,t-t')F(Q,t')dt' = 0 \qquad (17)$$

The problem of solving Eq. (17) reduces to the task of deriving an analytical expression for $M^{(1)}(Q,t)$, which is practically impossible to obtain from the definition of the memory function (Hansen and McDonald 1990; Boon and Yip 1991) in term of the random force. However, once noticed that $M^{(1)}(Q,t)$ is itself an autocorrelation function, one can use another balance equation for $M^{(1)}(Q,t)$ and introduce a second order memory function (Boon and Yip 1991)

$$\dot{M}^{(1)}(Q,t) + \int_0^t M^{(2)}(Q,t-t')M^{(1)}(Q,t')dt' = 0 \qquad (18)$$

The procedure can be generalized up to an arbitrary order n, leading to a series of chained equations all of the same form. To our task, however, a second order expansion revealed to be sufficient. Equations (17) and (18) form a system of two coupled equations. Under Laplace transforming of Eqs. (17) and (18) it is finally obtained

$$\tilde{F}(Q,z) = \frac{F(Q,0)}{z + \frac{\tilde{M}^1(Q,0)}{z+\tilde{M}^{(2)}(Q,z)}} = \frac{S(Q)}{z + \frac{\omega_0^2}{z+\tilde{M}^{(2)}(Q,z)}}, \qquad (19)$$

where $\omega_0^2 \doteq M^{(1)}(Q,t=0)$ is the normalized second frequency moment of $S(Q,\omega)$ and $S(Q) = F(Q,t=0)$ is the static structure factor. It can be as well easily verified that Eq. (19) in the direct time space corresponds to the second order integro-differential equation,

$$\ddot{F}(Q,t) + \omega_0^2(Q)F(Q,t) + \int_0^t M^{(2)}(Q,t-t')\dot{F}(Q,t')dt' = 0. \qquad (20)$$

Considering further orders, $\tilde{F}(Q,z)$ can be expressed by a continued fraction expansion, with coefficients depending on the initial values of the memory functions up to any desired order (Hansen and McDonald 1990; Boon and Yip 1991; Balucani and Zoppi 1995), *i.e.*, taking into account higher frequency moments of $S(Q,\omega)$, in time domain to a systematic improvement of the short-time behaviour of the density-density time correlation function.

Note, that already the fourth frequency moment of $S(Q,\omega)$, directly related to the initial value of the second order memory function, takes into account microscopic forces acting between particles, *i.e.*, extension of the treatment of density fluctuations beyond hydrodynamics.

One can ask why it is useful to introduce a second order memory function and truncate the continued fraction representation instead of expressing $\tilde{F}(Q,z)$ in terms of higher order memory functions. An answer to this question lies in the form of the second order memory function associated to the correct hydrodynamic solution for the density autocorrelation function. We will look in the following for an expression of the so-called "hydrodynamic" second order memory function, *i.e.*, the one which inserted in Eq. (20) gives the hydrodynamic intermediate scattering function, Eq. (9). Such a function has a simple expression as well as a direct physical interpretation and it allows an extension of hydrodynamics to high Q values. By equating Eqs. (19) and (9) we find

$$
\begin{aligned}
\frac{\tilde{F}(Q,z)}{S(Q)} &= \left\{ z + \frac{\omega_0^2}{z + \tilde{M}^2(Q,z)} \right\}^{-1} = \left\{ \frac{z + \tilde{M}^{(2)}(Q,z)}{z^2 + z\tilde{M}^2(Q,z) + \omega_0^2} \right\} \\
&= \frac{z^2 + (\gamma D_T Q^2 + \nu Q^2)z + (\gamma D_T \nu Q^4 + \frac{\gamma-1}{\gamma} c_S^2 Q^2)}{z^3 + (\gamma D_T Q^2 + \nu Q^2)z^2 + (D_T \nu Q^4 + c_S^2 Q^2)z + (D_T c_S^2 Q^4)}
\end{aligned}
\tag{21}
$$

leading to the following "hydrodynamic" second order memory function (Bafile *et al.* 2006)

$$
\tilde{M}^{(2)}(Q,z) = \nu Q^2 + \frac{c_S^2(\gamma-1)}{\gamma} \frac{Q^2}{z + \gamma D_T Q^2}.
\tag{22}
$$

In the time domain Eq. (22) reads as

$$
M^{(2)}(Q,t) = 2\nu Q^2 \delta(t) + \frac{c_S^2}{\gamma} Q^2 (\gamma-1) e^{-\gamma D_T Q^2 t}.
\tag{23}
$$

This expression is valid for low Q. Its physical interpretation is straightforward: the second order memory function displays two relevant processes ruling the decay of the density autocorrelation function, one, acting on a timescale of order $\tau_{th} = \frac{1}{\gamma D_T Q^2}$, represents the decay channel of thermal fluctuations, and another acting on timescales shorter than those probed in the hydrodynamic region, due to viscous relaxation (Balucani *et al.* 1993; Cunsolo *et al.* 2001; Ruocco and Sette 2001; Bencivenga *et al.* 2007; Gorelli *et al.* 2009; Cunsolo 2015). Equation (23) can be easily generalized by introducing more appropriate decay channels in the form of instantaneous or exponentially decaying contributions (Levesque *et al.* 1973; Li *et al.* 1992; Scopigno *et al.* 2000b,c, 2002; Monaco *et al.* 2004; Scopigno *et al.* 2005; Gorelli *et al.* 2006; Schirmacher and Sinn 2008; Bafile *et al.* 2009; Cunsolo 2016).

3.2. Generalized Collective Modes (GCM) approach. The GCM approach is closely related to the memory function methodology, also having its roots in the Generalized Langevin Equation (GLE). Its advantage is that it treats not a single autocorrelation function $F(Q,t)$ beyond hydrodynamics, but a set of all time correlation functions between conserved

and introduced extended dynamic variables via the solution of the GLE in matrix form (Mryglod *et al.* 1995). Instead of making a continued fraction expansion for each variable-related memory function, however, a Markovian approximation is adopted, which permits to describe the elements of the memory matrix as instantaneous functions of time. Such an approximation results in a solvable equation, so in this case the correlation functions of each dynamical variables of the set can be written down. The formulation based on GLE appeared to be in perfect agreement with similar approach derived from kinetic theory by Schepper *et al.* (1988). The GCM approach leads to a concept of non-hydrodynamic modes (Bryk 2011), which do not survive on macroscopic scales, however on mesoscopic and molecular scales they strongly contribute to the time correlation functions and corresponding spectral functions.

The essence of the GCM approach is in obtaining the n eigenmode solutions of the $n \times n$ generalized hydrodynamic matrix $\mathbf{T}(\mathbf{Q})$, which is the generalization of the hydrodynamic matrix (6) to the case of coupled fluctuations of hydrodynamic ($n_{hyd} = 3$ for longitudinal dynamics) and $n - n_{hyd}$ non-hydrodynamic quantities. The simplest non-hydrodynamic quantities are longitudinal component of stress tensor and energy (or heat) density flux, because they are equal to the first time derivatives of the corresponding fluctuations of conserved quantities in (2) and therefore they are orthogonal dynamic variables to the hydrodynamic current and energy ones. The idea to extend the hydrodynamic set of equations by adding to them balance equations for the orthogonal non-hydrodynamic quantities appeared to be very fruitful for understanding the dynamic processes outside the hydrodynamic region in various simple and many-component liquids (Bryk *et al.* 1997; Cazzato *et al.* 2008; Bryk and Mryglod 2009; Bryk and Ruocco 2011; Bryk and Klevets 2012, 2013; Bryk and Ruocco 2013; Bryk *et al.* 2014; Bryk and Wax 2016).

In the following we define a link between the GCM and the second order memory function approach in the hydrodynamics region. This will furthermore permit to show how hydrodynamics results are correctly reproduced by the GCM approach. We'll treat only the simple case of a monatomic fluid. We start by discussing a many-variables extension of the GLE formalism. We assume to be interested to the decay mechanisms of the time correlation function of a given dynamical variable and to be able to identify a set of other dynamical variables, independent one from the other but all strongly coupled to the reference dynamical variable. We introduce an extension of the formalism discussed in Sec. **3.1** by generalizing it to a multi-variable case (Schepper *et al.* 1988; Hansen and McDonald 1990).

Let $\mathbf{A}$ be a set of independent variables, $\mathbf{A} = \{A_1, A_2, \ldots, A_n\}$. The n×n matrix of correlation functions $\mathbf{F} \doteq [F_{ij}] = \langle A_j(t)A_i^* \rangle$ and the equation ruling its time evolution can be derived by the same passages leading to Eq. (16) (Balucani and Zoppi 1995),

$$\dot{\mathbf{F}}(t) - i\mathbf{\Omega} \cdot \mathbf{F}(t) + \int_0^t \mathbf{M}(t - t') \cdot \mathbf{F}(t')dt' = 0 \tag{24}$$

Note that now $\Omega_{ij} = \langle A_i \dot{A}_j^* \rangle \langle A_i A_j^* \rangle^{-1}$ is different from zero and cannot be neglected. By Laplace-transforming Eq. (24) we obtain

$$\tilde{\mathbf{F}}(z) = \left[z\mathbf{I} - i\mathbf{\Omega} + \tilde{\mathbf{M}}(z)\right]^{-1} \mathbf{F}(0). \tag{25}$$

The memory matrix describes the decay of the time correlation of the random force, which is in turn a vector orthogonal at any time to $\mathbf{A}$. If $\mathbf{A}$ is properly chosen such that it includes all

the slowly decaying variables coupled to the reference one, the Markovian approximation for the memory function can be used. The elements of $\mathbf{M}$ becomes, under this approximation, instantaneously time-decay functions and, in the Laplace space, constant functions of z. The hydrodynamic matrix $\mathbf{T}(Q)$ is defined as

$$\mathbf{T}(Q) \doteq -i\mathbf{\Omega}(Q) + \tilde{\mathbf{M}}(Q, z = 0), \tag{26}$$

where the memory function matrix has been represented by its value at zero time times an instantaneously decaying function of time. The Markovian approximation states that

$$\tilde{\mathbf{F}}(Q, z) = [z\mathbf{I} + \mathbf{T}(Q)]^{-1} \mathbf{F}(Q, 0) = \mathscr{T}^{-1}\mathbf{F}(Q, 0) \tag{27}$$

A generalization of the concept of dispersion introduced in Sec. **2** is possible in terms of the poles of the inverse of $\mathscr{T}$. The equation $\mathrm{Det}\mathscr{T} = 0$, corresponds to the eigenvalue equation for $\mathbf{T}$ in the variable $\zeta = -z$. The Q-dependent imaginary parts of its m$<$n non-real eigenvalues correspond to m dispersion relations $\omega^{(k)}(Q)$, $k = 1, \ldots, $ m. In general, including also the purely relaxing modes, *i.e.*, purely real eigenvalues, we can speak of n generalized collective modes (Bryk and Mryglod 2000). The problem of solving Eq. (27), *i.e.*, to assign an explicit z dependence to the elements of $\tilde{\mathbf{F}}(Q, z)$ in Markovian approximation, is trivial. Let z_α be the eigenvalues of $\mathbf{T}$, and $X_{i\alpha}$ be the matrix whose i-th column represent the α-th eigenvector of $\mathbf{T}$,

$$\sum_j^n T_{ij}(Q)X_{j\alpha} = z_\alpha(Q)X_{i\alpha}. \tag{28}$$

The matrix $\mathbf{X}$ is the change of basis matrix from $\mathbf{A}$ to the diagonal basis for $\mathbf{T}$. Let $\tilde{\mathbf{F}}'(z)$ and $\mathbf{F}'$ be the matrices representing $\tilde{\mathbf{F}}(z)$ and $\mathbf{F}$ in the new coordinates, while $\mathbf{T}'$ is the diagonal matrix with elements $\delta_{ij}z_j(Q)$. In the new representation Eq. (27) has a straightforward solution,

$$\tilde{F}'_{ij}(Q, z) = \frac{F'_{ij}}{z + z_i(Q)} \tag{29}$$

Since $\tilde{\mathbf{F}}(Q, z) = \mathbf{X}\tilde{\mathbf{F}}'\mathbf{X}^{-1}$ we find

$$
\begin{aligned}
\tilde{F}_{ij}(Q, z) &= \sum_{\alpha k} X_{i\alpha}\tilde{F}'_{\alpha k}\left[X^{-1}\right]_{kj} = \sum_{\alpha k} X_{i\alpha}\frac{\sum_{lm}[X^{-1}]_{\alpha l}F_{lm}X_{mk}}{z + z_\alpha}\left[X^{-1}\right]_{kj} \\
&= \sum_\alpha \frac{G_{ij}^\alpha(Q)}{z + z_\alpha(Q)},
\end{aligned}
\tag{30}
$$

where they have defined the weight coefficients describing the relevant contributions from each mode $z_\alpha(Q)$ (Bryk and Mryglod 2000), *i.e*,

$$G_{ij}^\alpha(Q) = \sum_{l=1}^n X_{i\alpha}\left[X^{-1}\right]_{\alpha l}F_{lj} \tag{31}$$

In the time representation the Markovian expression for the correlation matrix is a sum, with the weights $\mathbf{G}^\alpha$, of n exponential terms, each one associated with the α-th collective mode $z_\alpha(Q)$, *i.e*,

$$F_{ij}(Q,t) = \sum_{\alpha=1}^{n} G_{ij}^\alpha(Q)e^{-z_\alpha(Q)t} \tag{32}$$

The expression of the hydrodynamic matrix in its Markovian approximation can be derived by fixing $F_{ij}(Q,t=0) = \langle A_i A_j^* \rangle$ and $\tilde{F}_{ij}(Q,z=0) = \int_0^\infty F_{ij}(Q,t)dt$. From Eq. (27) with z=0 it is obtained

$$\mathbf{T}(Q) = \mathbf{F}(Q,t=0) \cdot \left[\tilde{\mathbf{F}}(Q,z=0) \right]^{-1}. \tag{33}$$

We turn to the problem of deriving the hydrodynamic correlation functions in Markovian approximation. A reasonable choice for $\mathbf{A}$ would be the set of conserved densities $\mathbf{A} = \{\rho, J, e\}$, *i.e.*, number density, longitudinal current and energy. An equivalent but more convenient choice to easy calculations is to define a local temperature as a linear combination of energy and density: $(Q,t) = e(Q,t) - \frac{\langle \rho e^* \rangle}{\langle \rho \rho^* \rangle} \rho(Q,t)$. The expression for the zero-time correlation function can be easily obtained by considering that $J_{\mathbf{q}}^l$ is orthogonal both to $\rho_{\mathbf{q}}$ and $e_{\mathbf{q}}$ because of its different simmetry under time reversal, while $\rho_{\mathbf{q}}$ and $h_{\mathbf{q}}$ are orthogonal by construction,

$$\mathbf{F}(Q,t=0) = \begin{pmatrix} \langle \rho \rho^* \rangle & 0 & 0 \\ 0 & \langle JJ^* \rangle & 0 \\ 0 & 0 & \langle hh^* \rangle \end{pmatrix} \tag{34}$$

Given the selected set of dynamical variables the elements of the matrix $\tilde{\mathbf{F}}(Q,z=0)$ can be obtained by exploiting, where possible, the continuity equations. Taking into account density and longitudinal current, for instance, it is found

$$\begin{aligned} \tilde{F}_{\rho J}(Q,0) &= \int_0^\infty dt \left\langle \rho J^{l*}(t) \right\rangle = -\frac{i}{Q} \int_0^\infty dt \left\langle \rho \dot{\rho}(t) \right\rangle \\ &= -\frac{i}{Q} \left\langle \rho(0) \left[\rho^*(\infty) - \rho^*(0) \right] \right\rangle = \frac{i}{Q} \left\langle \rho \rho^* \right\rangle. \end{aligned} \tag{35}$$

We furthermore define the following quantities with the dimensions of a time,

$$\tau_{ij}(Q) = \frac{1}{F_{ij}(Q,0)} \int_0^\infty F_{ij}(Q,t)dt \tag{36}$$

The matrix $\tilde{\mathbf{F}}(Q,z=0)$ takes finally the expression

$$\tilde{\mathbf{F}}(Q,0) = \begin{pmatrix} \tau_{\rho\rho} \langle \rho \rho^* \rangle & \frac{i}{Q} \langle \rho \rho^* \rangle & (\tau_{\rho e} - \tau_{\rho\rho}) \langle \rho e^* \rangle \\ \frac{i}{Q} \langle \rho \rho^* \rangle & 0 & 0 \\ (\tau_{\rho e} - \tau_{\rho\rho}) \langle \rho e^* \rangle & 0 & \tau_{hh} \langle hh^* \rangle \end{pmatrix} \tag{37}$$

The hydrodynamic matrix is then easily obtained from Eq. (33). We note that $\langle JJ^* \rangle Q^2 / \langle \rho\rho^* \rangle$ $= K_B T Q^2 / m S(Q)$. In the hydrodynamic limit $K_B T / m S(Q \to 0) = c_T^2$ is the isothermal sound speed, thus

$$\frac{\langle JJ^* \rangle}{\langle \rho\rho^* \rangle} \xrightarrow{Q \to 0} \gamma^{-1} c_S^2. \tag{38}$$

The following expression for the hydrodynamic matrix is thus retrieved

$$\mathbf{T}(Q) = \begin{pmatrix} 0 & -iQ & 0 \\ -iQ\gamma^{-1}c_S^2 & \gamma^{-1}c_S^2 Q^2 \left[\tau_{\rho\rho} - \frac{(\tau_{\rho e} - \tau_{\rho\rho})^2}{\tau_{hh}} \cdot \frac{\langle \rho h^* \rangle^2}{\langle \rho\rho^* \rangle \langle hh^* \rangle} \right] & iQ\gamma^{-1}c_S^2 \frac{(\tau_{\rho e} - \tau_{\rho\rho})}{\tau_{hh}} \frac{\langle \rho e^* \rangle}{\langle hh^* \rangle} \\ 0 & iQ\frac{(\tau_{\rho e} - \tau_{\rho\rho})}{\tau_{hh}} \frac{\langle \rho e^* \rangle}{\langle \rho\rho^* \rangle} & \frac{1}{\tau_{hh}} \end{pmatrix} \tag{39}$$

We give in the following the expression of the second order memory function corresponding to a Markovian first order memory matrix, *i.e*, that function of Q and t that, if inserted in Eq. (20) yields the correct expression for the intermediate scattering function as computed in the GCM framework when the hydrodynamic matrix Eq. (39) is used,

$$M_{\mathbf{m}}^{(2)}(Q,t) = 2\omega_0^2 \left(\tau_{\rho\rho} - \frac{(\tau_{\rho e} - \tau_{\rho\rho})^2}{\tau_{hh}} \cdot \frac{\langle \rho e^* \rangle^2}{\langle \rho\rho^* \rangle \langle hh^* \rangle} \right) \delta(t) +$$
$$\omega_0^2 \frac{(\tau_{\rho e} - \tau_{\rho\rho})^2}{\tau_{hh}} \cdot \frac{\langle \rho e^* \rangle^2}{\langle \rho\rho^* \rangle \langle hh^* \rangle} \cdot \left(\frac{e^{-t/\tau_{hh}}}{\tau_{hh}} \right) \tag{40}$$

The expression above of the second order memory function is isomorphic to the hydrodynamic form with respectively an instantaneous and an exponential decaying contribution. It should be compared with Eq. (23) in order to establish a correspondence between the coefficients entering the two expressions of the second order memory function. A direct comparison shows that

$$\tau_{hh} = \langle hh^* \rangle^{-1} \int_0^\infty \langle h(t)h^* \rangle \, dt = \frac{1}{\gamma D_T Q^2}$$

$$\tau_{\rho\rho} = \langle \rho\rho^* \rangle^{-1} \int_0^\infty \langle \rho(t)\rho^* \rangle \, dt = \frac{\gamma\nu}{c_S^2} + \frac{(\gamma-1)}{\gamma} \frac{1}{D_T Q^2} \tag{41}$$

$$[\langle \rho\rho^* \rangle \langle hh^* \rangle]^{-1/2} |\int_0^\infty \langle \rho(t)h^* \rangle \, dt| = \frac{(\gamma-1)^{1/2}}{\gamma} \frac{1}{D_T Q^2}$$

The second of Eqs. (44) can be derived by noting that

$$\int_0^\infty \frac{F(Q,t)}{S(Q)} dt = \frac{\tilde{F}(Q,0)}{S(Q)} \tag{42}$$

Again, starting from the hydrodynamic matrix Eq. (6) via the solution Eq. (8) for $\langle h(Q,z)h(Q)^* \rangle / \langle h(Q)h^*(Q) \rangle$ we are able to derive the first of Eqs. 41.

The fact that we able to derive the correct hydrodynamic behaviour of the density autocorrelation function in Markovian approximation means that the first order memory matrix, written for the set **A**, has exactly the Markovian form of an instantaneously decaying function of time in the long wavelength limit. Such a property stems from our choice of three *quasi-conserved* variables, *i.e*, variables becoming constant functions of time in the $Q \to 0$ limit. The continuity equation for $A_i \in \mathbf{A}$ indeed reads

$$\dot{A}_i(Q,t) = i\mathbf{Q} \cdot \mathbf{J}_i(Q,t). \tag{43}$$

A_i approaches thus the limit of a slowly decaying function of time in the limit $Q \to 0$, while the elements $M_{ij}(Q,t)$ of the memory matrix, which can be eventually considered as time correlation functions, keep the decaying properties of correlations of non-conserved variables and their rate of change is much greater than the one of A_i. The Markovian description for M_{ij} thus becomes exact when $Q \to 0$.

Similar results than Eqs. (41) can be obtained by using the analytical hydrodynamic asymptotes of the time correlation functions of the conserved dynamical variables and exploiting Eq. (36) . We note that in the present treatment of hydrodynamics an approximate solution of the roots of the dispersion equation is used leading to correlation functions where terms of the order $\frac{aQ}{c_s}$, being a a generic transport coefficient, are neglected (Mountain and Deutch 1969; Cohen *et al.* 1971). These terms give rise to non-Lorentzian contributions to the Rayleigh-Brillouin spectra. By taking into account also those terms the times τ_{hh} and $\tau_{\rho\rho}$, directly calculated from the hydrodynamic correlation functions, are

$$\tau_{hh} = \langle hh^* \rangle^{-1} \int_0^\infty \langle h(t)h^* \rangle \, dt = \frac{1}{\gamma D_T Q^2} + \frac{\gamma-1}{\gamma} \frac{2\Gamma - D_T(\gamma+1)}{c_s^2 + \Gamma^2 Q^2}$$

$$\tau_{\rho\rho} = \langle \rho\rho^* \rangle^{-1} \int_0^\infty \langle \rho(t)\rho^* \rangle \, dt = \frac{\gamma-1}{\gamma D_T Q^2} + \frac{1}{\gamma} \frac{4\Gamma - \nu}{c_s^2 + \Gamma^2 Q^2} \tag{44}$$

Going beyond the hydrodynamics, the analytical expression for the first correction to the hydrodynamic linear dispersion law can be obtained within the five-variable thermo-viscoelastic model of GCM approach (Bryk *et al.* 2010), and results in

$$\omega_s(Q) = c_s Q + \beta Q^3 + ..., \tag{45}$$

which gives evidence of the first correction proportional to Q^3 with analytical expression for coefficient β (Bryk *et al.* 2010), responsible for positive sound dispersion (Bryk *et al.* 2017)

4. Sound speed

In the previous section it has been derived the hydrodynamic expression of the intermediate scattering function within the scheme of three equivalent frameworks, Eq. (9), which yields, according to Eq. (11), an expression for the dynamic structure factor $S(Q,\omega)$. In the following we will introduce and compare three different "definitions" of the generalized velocity of sound and discuss the implications of the three different definitions on the analysis of hydrodynamic and generalized hydrodynamic sound dispersion.

The dynamic structure factor can be expressed as a function of the poles of the intermediate scattering function (Boon and Yip 1991). Such poles can be derived by solving the equation $\text{Det}\mathscr{T} = 0$, being $\mathscr{T}$ the hydrodynamic matrix (6), *i.e.*:

$$
\begin{aligned}
\mathrm{Det}\,\mathscr{T} \quad &= z^3 + Az^2 + Cz + D = 0 \\
A \quad &= \gamma D_\mathrm{T} Q^2 + \nu Q^2 \\
C \quad &= \gamma D_\mathrm{T} \nu Q^4 + c_\mathrm{S}^2 Q^2 \\
D \quad &= D_\mathrm{T} c_\mathrm{S}^2 Q^4
\end{aligned}
\tag{46}
$$

We already looked the poles in the limit $Q \to 0$, now we turn to the general case, so that we have to solve Eq. (46). We define the quantities

$$
\begin{aligned}
\psi \quad &= \frac{2}{27}A^3 - \frac{AC}{3} + D \\
\varphi \quad &= C - \frac{A^2}{3}
\end{aligned}
$$

and the discriminant

$$
\begin{aligned}
\Delta = \left(\frac{\psi}{2}\right)^2 + \left(\frac{\varphi}{3}\right)^3 &= -\frac{1}{180}\left[\gamma D_\mathrm{T}\nu(\nu - \gamma D_\mathrm{T})\right]^2 Q^{12} + \\
\frac{2}{108}D_\mathrm{T}c_\mathrm{S}^2\left[3\left(\nu^3 + (\gamma D_\mathrm{T})^3\right) - (\nu + \gamma D_\mathrm{T})^3\right] Q^{10} &+ \left(\frac{D_\mathrm{T}c_\mathrm{S}^2}{2}\right)^2 Q^8
\end{aligned}
\tag{47}
$$

For small values of Q the discriminant $\Delta = \left(\frac{D_\mathrm{T}c_\mathrm{S}^2}{2}\right)^2 Q^8 + O\left(Q^{10}\right)$ is positive, which implies that Eq. (46) admits one real, z_0, and two complex conjugate roots, $z_\pm = z_\mathrm{S} \pm i\omega_\mathrm{S}$, where

$$
\begin{aligned}
z_0 \quad &= \left(-\frac{\varphi}{3}\right)^{\frac{1}{2}}\left[(\cosh\theta + \sinh\theta)^{\frac{1}{3}} + (\cosh\theta - \sinh\theta)^{\frac{1}{3}}\right] - \frac{A}{3} \\
Re(z_\pm) \quad &= \left(\frac{\varphi}{6}\right)^{\frac{1}{2}}\left[(\cosh\theta + \sinh\theta)^{\frac{1}{3}} + (\cosh\theta - \sinh\theta)^{\frac{1}{3}}\right] \\
\pm Im(z_\pm) \quad &= \left(-\frac{\varphi}{4}\right)^{\frac{1}{2}}\left[(\cosh\theta + \sinh\theta)^{\frac{1}{3}} - (\cosh\theta - \sinh\theta)^{\frac{1}{3}}\right] \\
\theta \quad &= \frac{1}{2}\ln\frac{\psi + 2\sqrt{\Delta}}{\psi - 2\sqrt{\Delta}}
\end{aligned}
\tag{48}
$$

$S(Q,\omega)$ can now be written in terms of real, frequency independent, amplitudes A_h, A_s and b_s,

$$
\frac{S(Q,\omega)}{S(Q)} = \frac{1}{\pi}\left[A_\mathrm{h}\frac{z_\mathrm{h}}{\omega^2 + z_\mathrm{h}^2} + A_\mathrm{s}\frac{z_\mathrm{S} + b_\mathrm{S}(\omega + \omega_\mathrm{S})}{(\omega + \omega_\mathrm{S})^2 + z_\mathrm{S}^2} + A_\mathrm{s}\frac{z_\mathrm{S} - b_\mathrm{S}(\omega - \omega_\mathrm{S})}{(\omega - \omega_\mathrm{S})^2 + z_\mathrm{S}^2}\right],
\tag{49}
$$

where $z_\mathrm{h} = -z_0$, $z_\mathrm{S} = -Re z_+$ and $\omega_\mathrm{S} = |Im z_+|$. A first definition of generalized sound speed arises quite naturally from Eq. (49), *i.e*, $\Omega_{(A)} = \omega_\mathrm{S}$, and consequently $c_{(A)} = \frac{\omega_\mathrm{S}}{Q}$. The other two definitions, used in the literature, identify the frequencies of the inelastic excitations with the maxima of inelastic features of $S(Q,\omega)$ (Belyayev *et al.* 1989; Witte *et al.* 2017;

Harbour *et al.* 2018), $\Omega_{(B)}$, or the maxima of the current function $J(Q,\omega)$ (Scopigno *et al.* 2000a; Cunsolo *et al.* 2001; Scopigno *et al.* 2005; Bolmatov *et al.* 2015; Bryk *et al.* 2017; Kryuchkov *et al.* 2019), called $\Omega_{(C)}$. In the following we will analyze the behaviour of these three quantities in the hydrodynamic case. We will first calculate $\Omega_{(A)}$, $\Omega_{(B)}$ and $\Omega_{(C)}$ in the simple case $\gamma = 1$. Subsequently we will remove this approximation, and finally we will treat the case of non hydrodynamic limit in a specific example.

4.1. The special case $\gamma = 1$. In the case $\gamma = 1$ the coefficients of Eq. (9) become

$$
\begin{aligned}
A &= D_{\mathrm{T}}Q^2 + \nu Q^2 \\
B &= D_{\mathrm{T}}\nu Q^4 \\
C &= D_{\mathrm{T}}\nu Q^4 + c_{\mathrm{S}}^2 Q^2 \\
D &= D_{\mathrm{T}}c_{\mathrm{S}}^2 Q^4.
\end{aligned}
\tag{50}
$$

The expression of $\tilde{F}(Q,z)$ simplifies to

$$
\frac{\tilde{F}(Q,z)}{S(Q)} = \frac{z + \nu Q^2}{z^2 + \nu Q^2 z + c_{\mathrm{S}}^2 Q^2}.
\tag{51}
$$

Simple, exact expressions, follow for the poles of $\tilde{F}(Q,z)$,

$$
Rez_+ = -\frac{\nu Q^2}{2}
$$

$$
Imz_+ = \sqrt{c_{\mathrm{S}}^2 Q^2 - \left(\frac{\nu Q^2}{2}\right)^2}
\tag{52}
$$

We notice that Eq. (51) corresponds to reducing the hydrodynamic second order memory function to the simple form $M^{(2)}(Q,t) = 2\nu Q^2 \delta(t)$, yielding for the dynamic structure factor the expression

$$
\frac{S(Q,\omega)}{S(Q)} = \frac{1}{\pi} \frac{2\Gamma\omega_0^2}{\left(\omega^2 - \omega_0^2\right)^2 + 4\omega^2\Gamma^2}
\tag{53}
$$

where $\omega_0 = c_{\mathrm{S}}Q$ is the second frequency moment, *i.e*, the longitudinal current maximum because for a the Damped Harmonic Oscillator function, Eq. (53), the two quantities coincide, and $\Gamma = \frac{\nu Q^2}{2}$. This expression corresponds to Eq. (49) with $A_{\mathrm{h}} = 0$, $A_{\mathrm{S}} = 1/2$ and $b_{\mathrm{S}} = z_{\mathrm{S}}/\omega_{\mathrm{S}}$, *i.e*,

$$
\begin{aligned}
\frac{S(Q,\omega)}{S(Q)} &= \frac{1}{\pi}\left[\frac{1}{2}\frac{z_{\mathrm{S}} + b_{\mathrm{S}}(\omega + \omega_{\mathrm{S}})}{(\omega + \omega_{\mathrm{S}})^2 + z_{\mathrm{S}}^2} + \frac{1}{2}\frac{z_{\mathrm{S}} - b_{\mathrm{S}}(\omega - \omega_{\mathrm{S}})}{(\omega - \omega_{\mathrm{S}})^2 + z_{\mathrm{S}}^2}\right] \\
&= \frac{1}{\pi}\frac{2z_{\mathrm{s}}(\omega_{\mathrm{s}}^2 + z_{\mathrm{s}}^2)}{\left[\omega^2 - (\omega_{\mathrm{s}}^2 + z_{\mathrm{s}}^2)\right]^2 + 4z_{\mathrm{s}}^2\omega^2}
\end{aligned}
\tag{54}
$$

By comparing Eq. (53) and Eq. (54) we find $\Gamma = z_{\mathrm{s}} = -Rez_+$, $\omega_0^2 = \omega_{\mathrm{S}}^2 + z_{\mathrm{S}}^2$. The maxima of the dynamic structure factor and of the longitudinal current can be now easily found

basing on Eq. (54). In conclusion it is found,

$$\text{Poles of the hydrodynamic matrix} \quad \Omega_{(A)}(Q) = \sqrt{c_S^2 Q^2 - \left(\frac{vQ^2}{2}\right)^2}$$

$$\text{Dynamic structure factor maxima} \quad \Omega_{(B)}(Q) = \sqrt{c_S^2 Q^2 - \frac{(vQ^2)^2}{2}} \tag{55}$$

$$\text{Longitudinal current maxima} \quad \Omega_{(C)}(Q) = c_S Q$$

4.2. The general γ case. If $\gamma \neq 1$ it occurs a coupling between the thermal fluctuations and the density fluctuations. As a consequence, two distinct sound propagation regimes can be recognized: the low-Q adiabatic regime, characterizing the hydrodynamic behaviour, and the high-Q isothermal regime, occurring in a region of Q beyond the hydrodynamic limit. In particular, by defining the characteristic decay time of thermal diffusion as $\tau_{\text{th}} = \frac{1}{D_T Q^2}$, the adiabatic regime occurs when the decay time of thermal fluctuations is much slower than the time scale of the density fluctuations, *i.e*, in the limit $\omega \tau_{\text{th}} \gg 1$. In the case $\omega \tau_{\text{th}} \ll 1$, the characteristic time scale of the propagation of the density fluctuations is much slower than the decay time of thermal fluctuations, τ_{th}, so that local thermalization is allowed. In this limit we expect an isothermal regime to occur (Bencivenga *et al.* 2006; Bolmatov *et al.* 2015) We shall see that $\Omega_{(A)}$, $\Omega_{(B)}$ and $\Omega_{(C)}$ have the same simple expressions (55) in the adiabatic limit, while a simple generalization can be derived in the opposite limit of isothermal regime. For our purpose it is convenient to define a frequency-dependent parameter ε, which is much lower or much greater than 1 in the two limits of interest,

$$\varepsilon = \frac{D_T Q^2}{\omega}, \tag{56}$$

so that $\varepsilon \ll 1$ if $\omega \tau_{\text{th}} \gg 1$ and $\varepsilon \gg 1$ if $\omega \tau_{\text{th}} \ll 1$.

4.2.1. *Current maxima.* We remove the dependence from the thermal diffusion coefficient D_T in $J(Q, \omega)$ and replace it by ε. After some algebra one finds:

$$J(Q, \omega) = \frac{\omega (c_S Q)^2}{\gamma} \cdot \frac{\varepsilon^2 (\gamma^2 \omega v) + \varepsilon c_S^2 (\gamma - 1) + \omega v}{\varepsilon^2 \hat{F}(Q, \omega) + \varepsilon \hat{G}(Q, \omega) + \hat{H}(Q, \omega)}, \tag{57}$$

$$\frac{dJ(Q, \omega)}{d\omega} = \frac{2(c_S Q)^2}{\gamma} \cdot \frac{\varepsilon^4 \hat{A}(Q, \omega) + \varepsilon^3 \hat{B}(Q, \omega) + \varepsilon^2 \hat{C}(Q, \omega) + \varepsilon \hat{D}(Q, \omega) + \hat{E}(Q, \omega)}{\left[\varepsilon^2 \hat{F}(Q, \omega) + \varepsilon \hat{G}(Q, \omega) + \hat{H}(Q, \omega)\right]^2}, \tag{58}$$

where

$$
\begin{aligned}
\hat{A}(Q,\omega) &= \gamma^2 \omega v \left[(c_S Q)^4 - \gamma^2 \omega^4 \right] \\
\hat{B}(Q,\omega) &= \left[(\omega^2 \gamma)^2 - (c_S Q)^2 \right] (1 - \gamma) c_S^2 \\
\hat{C}(Q,\omega) &= 2 \left[\gamma \omega^2 (c_S Q)^2 (\gamma - 1) + ((c_S Q)^4 - \gamma^2 \omega^4) \right] \omega v \\
\hat{D}(Q,\omega) &= \left[2(\omega c_S^2 Q)^2 + (\omega v c_S Q^2)^2 - 2(\omega^2 c_S)^2 \right] (\gamma - 1) \\
\hat{E}(Q,\omega) &= \omega v \left[(c_S Q)^4 - \omega^4 \right] \\
\hat{F}(Q,\omega) &= (\gamma \omega^2 - (c_S Q)^2)^2 + (\omega v \gamma Q^2)^2 \\
\hat{G}(Q,\omega) &= 2\omega c_S^2 v Q^4 (\gamma - 1) \\
\hat{H}(Q,\omega) &= (\omega^2 - (c_S Q)^2)^2 + (\omega v Q^2)^2.
\end{aligned}
\tag{59}
$$

In the limit of diverging $\omega \tau_{\mathrm{th}}$ (adiabatic regime), ε becomes infinitesimal and

$$
\lim_{\varepsilon \to 0} \frac{dJ(Q,\omega)}{d\omega} = \frac{2(c_S Q)^2}{\gamma} \cdot \frac{\hat{E}}{\hat{H}^2} = \frac{2(c_S Q)^2}{\gamma} \cdot \frac{\omega v \left[(c_S Q)^4 - \omega^4 \right]}{\left[(\omega^2 - (c_S Q)^2)^2 + (\omega v Q^2)^2 \right]^2}.
\tag{60}
$$

In this limit the equation $\frac{dJ}{d\omega} = 0$ has one solution at $\omega = 0$ representing a minimum of the current, being $\frac{d^2 J(Q,\omega)}{d\omega^2}|_0 = 2\frac{(c_S Q)^2}{\gamma (v Q^2)^2} > 0$, and two degenerate solutions at $\omega = \pm c_S Q$ representing two maxima, being $\frac{d^2 J(Q,\omega)}{d\omega^2}|_{c_S Q} = -8\frac{(c_S Q)^2}{\gamma (v Q^2)^4} < 0$. On the other hand in an isothermal regime, when $\omega \tau_{\mathrm{th}} \to 0$, ε diverges and

$$
\lim_{\varepsilon \to \infty} \frac{dJ(Q,\omega)}{d\omega} = \frac{2(c_S Q)^2}{\gamma} \cdot \frac{\hat{A}}{\hat{F}^2} = 2(c_S Q)^2 \cdot \frac{\gamma \omega v \left[(c_S Q)^4 - \gamma^2 \omega^4 \right]}{\left[(\gamma \omega^2 - (c_S Q)^2)^2 + (\omega v \gamma Q^2)^2 \right]^2}.
\tag{61}
$$

In this limit the equation $\frac{dJ}{d\omega} = 0$ has one solution at $\omega = 0$ representing a minimum, and two solutions at $\omega = \pm c_T Q = \pm \frac{c_S}{\sqrt{\gamma}} Q$ representing maxima. We can easily recognize that the dispersion is always linear for each finite value of ε. In this case, indeed, each term in the numerator of (58) becomes zero or proportional to $\omega \left[(c_S Q)^4 - \omega^4 \right]$, in particular

$$
\begin{aligned}
\hat{A} &= \tfrac{1}{2}\hat{C} = \hat{E} = \omega v[(c_S Q)^4 - \omega^4] \\
\hat{B} &= \hat{D} = 0 \\
\hat{F} &= \hat{H} = [\omega^2 - (c_S Q)^2]^2 + (\omega v Q^2)^2 \\
\hat{G} &= 0,
\end{aligned}
\tag{62}
$$

and $\frac{dJ}{d\omega}$ does no longer depend on ε. This was somehow expected, since Eq. (9) can be decomposed according to Eq. (51), so that any dependence from D_T disappears.

4.2.2. *Dynamic structure factor maxima.* The function $S(Q,\omega)$ can be expressed as

$$
\frac{S(Q,\omega)}{S(Q)} = \frac{c_S^2 Q^4}{\gamma \omega} \cdot \frac{\varepsilon^2 (\gamma^2 \omega v) + \varepsilon c_S^2 (\gamma - 1) + \omega v}{\varepsilon^2 \hat{F}(Q,\omega) + \varepsilon \hat{G}(Q,\omega) + \hat{H}(Q,\omega)}
\tag{63}
$$

$$\frac{dS(Q,\omega)}{d\omega} = \frac{2c_S^2 Q^4}{\gamma\omega^2} \cdot \frac{\varepsilon^4 \hat{A}(Q,\omega) + \varepsilon^3 \hat{B}(Q,\omega) + \varepsilon^2 \hat{C}(Q,\omega) + \varepsilon \hat{D}(Q,\omega) + \hat{E}(Q,\omega)}{\left[\varepsilon^2 \hat{F}(Q,\omega) + \varepsilon \hat{G}(Q,\omega) + \hat{H}(Q,\omega)\right]^2}; \quad (64)$$

$$
\begin{aligned}
\hat{A}(Q,\omega) &= \gamma^3 \omega^3 \nu \left[2(c_S Q)^2 - \gamma \nu^2 Q^4 - 2\gamma\omega^2\right] \\
\hat{B}(Q,\omega) &= \gamma(\gamma-1)\omega^2 \left[-3\gamma(c_S Q)^2(\nu Q)^2 - 2\gamma\omega^2 c_S^2 + 2c_S^4 Q^2\right] \\
\hat{C}(Q,\omega) &= \omega\nu \left[2\gamma^2\omega^2 \left[2(c_S Q)^2 - 2\omega^2 - (\nu Q^2)^2\right] - (\gamma-1)(3\gamma-1)(c_S Q)^4\right] \\
\hat{D}(Q,\omega) &= \left[2(\omega c_S \nu Q^2)^2 + 3c_S^2\omega^4 + (c_S^2 Q)^2((c_S Q)^2 - 4\omega^2)\right](1-\gamma) \\
\hat{E}(Q,\omega) &= \omega^3\nu \left[2(c_S Q)^2 - 2\omega^2 - (\nu Q^2)^2\right] \\
\hat{F}(Q,\omega) &= (\gamma\omega^2 - (c_S Q)^2)^2 + (\omega\nu\gamma Q^2)^2 \\
\hat{G}(Q,\omega) &= 2\omega c_S^2 \nu Q^4 (\gamma-1) \\
\hat{H}(Q,\omega) &= (\omega^2 - (c_S Q)^2)^2 + (\omega\nu Q^2)^2
\end{aligned}
\quad (65)
$$

In the adiabatic region, when $\omega\tau_{th} \to \infty$ and $\varepsilon \to 0$:

$$\lim_{\varepsilon \to 0} \frac{dS(Q,\omega)}{d\omega} = \frac{2c_S^2 Q^4}{\gamma} \cdot \frac{\omega\nu \left[-2\omega^2 + 2(c_S Q)^2 - \nu^2 Q^4\right]}{[(\omega^2 - (c_S Q)^2)^2 + (\omega\nu Q^2)^2]^2}. \quad (66)$$

The dynamic structure factor maxima are at $\omega = \pm\sqrt{(c_S Q)^2 - \frac{(\nu Q^2)^2}{2}}$. In the isothermal regime, when $\omega\tau_{th} \to 0$ and $\varepsilon \to \infty$:

$$\lim_{\varepsilon \to \infty} \frac{dS(Q,\omega)}{d\omega} = 2c_S^2 Q^4 \gamma^2 \cdot \frac{\omega\nu \left[-2\gamma\omega^2 + 2(c_S Q)^2 - \gamma\nu^2 Q^4\right]}{[(\gamma\omega^2 - (c_S Q)^2)^2 + (\gamma\omega\nu Q^2)^2]^2}. \quad (67)$$

The dynamic structure factor maxima are at $\omega = \pm\sqrt{(c_T Q)^2 - \frac{(\nu Q^2)^2}{2}}$.

4.2.3. *Poles.* We define the complex quantity

$$\varepsilon = \frac{D_T Q^2}{z}. \quad (68)$$

The adiabatic and isothermal limits are now obtained respectively when $|\varepsilon| \to 0$ and $|\varepsilon| \to \infty$. The equation $\mathrm{Det}\,\mathcal{T} = 0$ becomes

$$
\begin{aligned}
&z^3 + Az^2 + Cz + D = 0 \\
&A = \gamma\varepsilon z + \nu Q^2 \\
&C = \gamma\varepsilon z\nu Q^2 + c_S^2 Q^2 \\
&D = z\varepsilon c_S^2 Q^2
\end{aligned}
\quad (69)
$$

In the adiabatic limit $|\varepsilon| \to 0$, Eq. (69) becomes, neglecting terms $O(|\varepsilon|)$:

$$z\left(z^2 + \nu Q^2 z + c_S^2 Q^2\right) = 0, \quad (70)$$

thus $z_\pm = -\frac{vQ^2}{2} \pm i\sqrt{c_S^2 Q^2 - \left(\frac{vQ^2}{2}\right)^2}$. In the isothermal limit $|\varepsilon| \to \infty$, Eq. (69) becomes, retaining only terms $O(|\varepsilon|)$:

$$z\varepsilon \left(\gamma z^2 + \gamma v Q^2 z + c_S^2 Q^2 \right) = 0 \tag{71}$$

and now $z_\pm = -\frac{vQ^2}{2} \pm i\sqrt{c_T^2 Q^2 - \left(\frac{vQ^2}{2}\right)^2}$.

4.2.4. *Comparison between different definitions of hydrodynamic sound speed.* Summarizing, the dispersion relations derived in the case $\gamma \neq 1$ in the two limiting situations of adiabatic and isothermal regime are

$$
\begin{array}{lll}
\varepsilon \to 0 & & \omega\tau_{\mathrm{th}} \to \infty \\[2ex]
\textit{Poles of the hydrodynamic matrix} & \Omega_{(A)}^S(Q) = \sqrt{c_S^2 Q^2 - \left(\frac{vQ^2}{2}\right)^2} \\[3ex]
\textit{Dynamic structure factor maxima} & \Omega_{(B)}^S(Q) = \sqrt{c_S^2 Q^2 - \frac{(vQ^2)^2}{2}} \\[3ex]
\textit{Longitudinal current maxima} & \Omega_{(C)}^S(Q) = c_S Q
\end{array} \tag{72}
$$

$$
\begin{array}{lll}
\varepsilon \to \infty & & \omega\tau_{\mathrm{th}} \to 0 \\[2ex]
\textit{Poles of the hydrodynamic matrix} & \Omega_{(A)}^T(Q) = \sqrt{c_T^2 Q^2 - \left(\frac{vQ^2}{2}\right)^2} \\[3ex]
\textit{Dynamic structure factor maxima} & \Omega_{(B)}^T(Q) = \sqrt{c_T^2 Q^2 - \frac{(vQ^2)^2}{2}} \\[3ex]
\textit{Longitudinal current maxima} & \Omega_{(C)}^T(Q) = c_T Q
\end{array} \tag{73}
$$

Note that $\Omega_{(C)}(Q) > \Omega_{(A)}(Q) > \Omega_{(B)}(Q)$. At the first order in Q the three definitions of adiabatic dispersion reduce to the same linear one, $\Omega(Q) = c_S Q + O(Q^2)$, and this is what is usually presented as hydrodynamic dispersion, derived both from the poles of $\mathscr{T}$ or from the maxima of the Brillouin doublet at $O(Q^2)$. For intermediate Q values (around $Q \approx \frac{c_S}{D_T}$) a transition between the limiting behaviours takes place. The general case $\gamma \neq 1$ can be view as an extension of the special case $\gamma = 1$, accounting also for the adiabatic to isothermal transition. It has to be noted, however, that the previous treatment holds in the hydrodynamic limit, while for all nonmetallic fluids, due to the low thermal diffusivity, this transition occurs at Q values well outside the long wavelength limit in a strictly non-hydrodynamic region.

4.3. The case $\gamma = 1$ with non-Markovian $M^{(2)}(Q,t)$. We will derive the expressions for the different definitions of the velocity of sound at finite values of Q and ω. In the generalized hydrodynamics frame a model for describing density fluctuations in a simple liquid at finite values of Q and ω stems from the modification of the simple viscoelastic ansatz, by allowing a more sophisticated decay of the longitudinal part of $M^{(2)}(Q,t)$. For instance, the following two exponential-decay ansatz for the longitudinal second order memory function proved to be a convenient model for describing experimental IXS spectra of liquid metals (Scopigno *et al.* 2000b,c, 2002; Scopigno *et al.* 2005):

$$
\begin{aligned}
M_L(Q,t) &= \Delta_L^2(Q)\left[(1-\alpha(Q))e^{-t/\tau_\mu(Q)} + \alpha(Q)e^{-t/\tau_\alpha(Q)}\right] \\
&= \Delta_\mu^2(Q)e^{-t/\tau_\mu} + \Delta_\alpha^2(Q)e^{-t/\tau_\alpha}
\end{aligned}
\tag{74}
$$

where the time $\tau_\alpha(Q)$ is larger than $\tau_\mu(Q)$ and the dimensionless quantity $\alpha(Q)$ measures the relative weight of slow and fast decay channels. Moreover, we require the total amplitude of the longitudinal memory function to be related to the longitudinal viscosity, *i.e*,

$$
\nu Q^2 = \Delta_L^2(Q)\left[(1-\alpha(Q))\tau_\mu + \alpha(Q)\tau_\alpha\right].
\tag{75}
$$

In order to simplify the task, we assume $\gamma = 1$, thus neglecting the thermal part of $M^{(2)}(Q,t)$. We furthermore restrict the treatment to the case $\omega\tau_\mu \ll 1$ so that

$$
M^{(2)}(Q,t) = 2\Delta_\mu^2(Q)\tau_\mu\delta(t) + \Delta_\alpha^2(Q)e^{-t/\tau_\alpha}.
\tag{76}
$$

Such a model is indeed well suited for treating the spectra of glass forming materials in the Brillouin Light Scattering window where the condition $\omega\tau_\mu \ll 1$ holds. The analytical form of Eq. (76) is exactly the same of Eq. (23). The calculation of the inelastic frequency in the hydrodynamic case with $\gamma \neq 1$ thus provides a solution also in this case, once the parameters are properly redefined. We thus find:

$\omega\tau_\alpha \to \infty$

Poles of the hydrodynamic matrix $\Omega_{(A)}^S(Q) = \sqrt{c_T^2 Q^2 - \left[\frac{1}{2}\Delta_\mu^2(Q)\tau_\mu(Q)\right]^2}$

Dynamic structure factor maxima $\Omega_{(B)}^S(Q) = \sqrt{c_T^2 Q^2 - \frac{1}{2}\left[\Delta_\mu^2(Q)\tau_\mu(Q)\right]^2}$

Longitudinal current maxima $\Omega_{(C)}^S(Q) = c_T Q$

$\omega\tau_\alpha \to 0$

Poles of the hydrodynamic matrix $\Omega_{(A)}^T(Q) = \sqrt{c_T^2 Q^2 + \Delta_\alpha^2(Q) - \left[\frac{1}{2}\Delta_\mu^2(Q)\tau_\mu(Q)\right]^2}$

Dynamic structure factor maxima $\Omega_{(B)}^T(Q) = \sqrt{c_T^2 Q^2 + \Delta_\alpha^2(Q) - \frac{1}{2}\left[\Delta_\mu^2(Q)\tau_\mu(Q)\right]^2}$

Longitudinal current maxima $\Omega_{(C)}^T(Q) = \sqrt{c_T^2 Q^2 + \Delta_\alpha^2(Q)}$

$$\tag{77}$$

Being related to the structural relaxation process (*i.e*, the usual diffusion process of the atoms in a liquid) the time $\tau_\alpha(Q)$ shows a roughly constant Q-trend and it is generally of

the order of ps, as for instance in the case of liquid metals under criticality. This means that the condition $\omega \tau_\alpha >> 1$ holds in the hydrodynamic limit, *i.e*, for $Q << (\tau_\alpha c_T)^{-1} \doteq Q_1$, in which case we recover no effects on the usual hydrodynamic sound speed as defined from $\Omega_{(A)}, \Omega_{(B)}, \Omega_{(C)}$ arising from the α relaxation (Balucani *et al.* 1993; Ruocco and Sette 2001; Bolmatov *et al.* 2015; Cunsolo 2015). A contribution to $\Omega_{(A)}$ and $\Omega_{(B)}$ is instead due, in the hydrodynamic limit, to the μ, fast, relaxation process. This is a reminiscence of what was found to hold in the long wavelength limit with the viscosity term entering Eqs. (55), (72) and (73).

If the approximation $\gamma = 1$ is removed, effects related to thermal relaxation enters into play. Since the timescales involved in thermal and structural processes always are several orders of magnitudes apart, Eqs. (77) are modified by the presence of a further relaxation process well separated from the α-process, causing the transition from c_S to c_T, at Q values around $Q_0 \sim \frac{c_S}{D_T} << Q_1$. In the case of simple liquid metals, e.g., $Q_0 \sim 0.1\ nm^{-1}$ and $Q_1 \sim 1\ nm^{-1}$.

5. Conclusions

We derived the hydrodynamic intermediate scattering function from the linearized Navier-Stokes equations, by which it is possible to account for the decay of density fluctuations in the limit of small exchanged momentum and small energy exchange. The features of a Raileigh-Brillouin spectrum can be derived. Nevertheless, this result is no longer valid for higher Q and ω values, as is the case in typical IXS or INS experiments, and an extension is necessary. We introduced two more, somehow complementary techniques for computing time correlation functions, based on Mori's generalized Langevin equation framework, *i.e*, the memory function approach and the Generalized Collective Modes approach. Both the techniques have been applied to the relevant hydrodynamic variables in order to compute hydrodynamic correlation functions. It was furthermore demonstrated that the two approaches are equivalent in the hydrodynamic limit where the hydrodynamics results are retrieved. In particular, the second order memory function approach reduces to simple hydrodynamics when the second order memory function takes the form of two distinct decaying contributions, an exponential one related to thermal diffusion processes, and an instantaneous one, related to microscopic structural relaxation characterized by timescales much shorter than the times probed in the hydrodynamic region. The Generalized Collective Modes approach reduces to simple hydrodynamics if the set of hydrodynamic quasi-conserved variables $\mathbf{A} = \left\{ \rho, J^l, e \right\}$ of density, longitudinal current and energy, is chosen. These results are relevant when the two approaches are used in order to set up an extension of hydrodynamics to higher values of Q and ω because any method setting this objective shall retrieve the correct hydrodynamics results in the hydrodynamic limit.

Three different expressions of sound of speed are usually found in literature, respectively related to the characteristic frequencies of inelastic excitations defined through the poles of the intermediate scattering function, $\Omega_{(A)}$, maxima of the dynamic structure factor, $\Omega_{(B)}$, or maxima of the current, $\Omega_{(C)}$. For all these definitions we obtained the related expressions as a function of the characteristic quantities characterizing the dynamic structure factor related to density fluctuations both within and outside the hydrodynamic region. A comparison of the three different expressions is also provided. Since the speed of sound shall be sensitive

to those relaxation processes which take place on time scale shorter than the charcteristic period of the acoustic excitations its dispersion can be used to pinpoint the crossover between different regimes where different decay channels are activated. The special cases of transition from adiabatic to isothermal regimes as well as the viscoelastic transition related to the structural relaxation are here treated explicitly, but similar stages can be developed for any relaxation process coupled to density fluctuations. Special care thus should be paid when dispersions obtained by different experimental studies, in particular in different wavevectors region, are compared because the same definition of speed of sound should be used. Furthermore, the more convenient definition in order to emphasize the phenomenon to be analyzed can be chosen. In a generalized hydrodynamic context the dispersion defined $\Omega_{(A)}$ splits into many branches, each of which associated to some *kinetic mode*, with the exception of the lower three branches approaching the hydrodynamic dispersion behaviour for $Q \to 0$. This choice can be thus the more suitable when one aim to detect the presence of non-hydrodynamic propagating modes. The dispersion obtained through $\Omega_{(B)}$ as well as through $\Omega_{(C)}$ simply deviates from its hydrodynamic Q dependence, as soon as the region of small Q is left. From the experimental point of view the insight one can gain about microscopic dynamics of a liquid (*i.e*, the dynamic structure factor), cannot usually account for the different contributions of each generalized mode. $\Omega_{(B)}$ and $\Omega_{(C)}$ can in principle always be derived from experimental inelastic scattering spectra. A convenient definition of the generalized velocity seems to be the one related to the current maxima, for at least two reasons of practical interest. First, in this case any deviation from hydrodynamic dispersion is more easily identified because it will be a deviation from linearity. Secondly, any elastic feature is absent in the current spectrum, so that two symmetric inelastic maxima are always well defined up to values of Q even near the main peak position of the static structure factor.

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