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Collective acoustic modes in liquids: A comparison between the generalized-hydrodynamics and memory-function approaches

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The most familiar approaches used to describe the dynamical structure factor from adiabatic density fluctuations in liquids are based on generalized hydrodynamics and on the memory function, respectively. We show that, contrary to the common belief, the two approaches are not fully equivalent. In particular, models based on the memory function of a normalized damped oscillator fail in reproducing the correct experimental spectral profiles of systems close to the relaxation process. The discrepancy is due to misleading interpretation of the theoretical memory-function expressions, producing an unavoidable mixing of spectral contribution at different wave vectors when the theory is forced beyond its limits of validity.

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I. INTRODUCTION

Brillouin spectroscopy represents a powerful tool for the investigation of the collective dynamics in fluids. Rigorously speaking, the term "Brillouin spectroscopy" refers to a light-scattering experiment. This implies that the system is investigated at very long wavelengths and over distances larger than the intermolecular distance. As a consequence, it can be described as a continuous and homogeneous fluid. The traditional theoretical description of the scattering phenomena, for a simple liquid, was obtained within the framework of the hydrodynamic approximation [1–3]. However, the model can be easily generalized to account for the occurrence of relaxation processes [1–4], i.e., when one of the transport coefficients becomes frequency dependent. This requires that the real transport coefficient involved in the linearized hydrodynamic expression is translated into a complex functional form. The real part is a dissipative coefficient which is the usual transport coefficient at zero frequency, while the imaginary part reflects the nondissipative response of the fluid. The frequency dependence of the generalized transport coefficient produces two distinct regimes; at high frequency the system behaves like an elastic medium while at low frequency it appears as a purely dissipative fluid. The transition between the different regimes occurs at a characteristic frequency, whose reverse marks the relaxation time of the generalized transport coefficient. The immediate consequence of introducing a generalized transport coefficient is that the velocity of propagation of the density fluctuations will assume a complex functional form too. As a result, a relaxing system will exhibit a dispersion of the sound velocity.

During the last three decades, the power of the Brillouin technique improved due to the remarkable development of the inelastic neutron and x-ray scattering at the large-scale facilities. The new techniques allowed investigators to extend by orders of magnitude the ranges of energy and momentum exchanged between the probe and the sample, including situations well outside the limits of the traditional hydrodynamic approximation. Together with the experimental techniques, computer simulation also advanced, becoming an essential tool thanks to the continuous increase of available computing power. The huge amount of collected data triggered theoretical interest for the description and interpretation of the experimental spectral profiles. An approach alternative to the generalized-hydrodynamic model is the standard Mori-Zwanzig memory-function approximation of the microscopic time evolution of dynamical variables [4–9]. Within this framework, the dynamical structure factor is derived by the corresponding expression for the complex susceptibility. It was originally proposed as a way to get access to information about any relaxation process taking place in a system by the full spectrum analysis of a single Brillouin spectrum, recorded over a wide frequency region. In addition, this approach can provide a correct k dependence of relevant dynamical parameters and seems to represent a unique way to handle the data obtained from molecular dynamics simulations or from neutron and x-ray experiments.

Both experimental and computer simulation techniques furnish the same quantity, i.e., the dynamical structure factor $S(k,\omega)$, which is the frequency spectrum of the autocorrelation function of the density fluctuations at a given value of the exchanged wave vector. In analyzing the experimental or calculated spectra, a fitting procedure is adopted with the theoretical expression for $S(k,\omega)$, where ω is the variable while k plays the role of a parameter that must be fixed at the corresponding experimental value. Only density fluctuations at a wave vector $\boldsymbol{k}$ matching the selection rule $\boldsymbol{k} = \boldsymbol{k}_1 - \boldsymbol{k}_0$ ($\boldsymbol{k}_1$ and $\boldsymbol{k}_0$ being the wave vectors of the scattered photons and of the probe, respectively) contribute to the experimental spectrum.

To be consistent, both approaches must produce the same result within the limit of validity of the hydrodynamic approximation. In effect, it can be demonstrated that both the linearized hydrodynamic and the generalized-hydrodynamic expressions are retrieved from the adoption of suitable expressions for the memory functions [10].

The aim of this article is to compare the outcomes from the two approaches, under the assumption of the same memory function. Obviously, the comparison will be made only within the limit of validity of the hydrodynamic approximation. Without loss of generality, in comparing the two formalisms

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we will assume a single relaxation process of the bulk viscosity. Any extension to more complicated and realistic situations is straightforward.

We will show that, contrary to the common belief, the theoretical description that can be obtained by the complex susceptibility, after the selection of the appropriate model of the memory function, is not able to reproduce the full spectrum of density fluctuations occurring in the system and that its adoption should be limited to the description of the Brillouin doublet only.

In particular, any attempt for extracting information about the thermal relaxation by fitting a single experimental spectrum with equations obtained within the above framework is wrong or misleading.

This should be taken as a general result which also remains valid outside the hydrodynamic limits.

II. THEORY AND MODELS

A. The linearized hydrodynamic model

Following the formalism of Ref. [1], the linearized hydrodynamic expression for the dynamical structure factor at given wave vector k_s is given by

$$\begin{aligned} I(k_s,\omega) = \frac{S(k_s,\omega)}{S(k_s)} &= \frac{\gamma-1}{\gamma}\frac{2\chi k_s^2}{\omega^2+\left(\chi k_s^2\right)^2} \\ &+ \frac{1}{\gamma}\left[\frac{\Gamma k_s^2}{(\omega+ck_s)^2+\left(\Gamma k_s^2\right)}+\frac{\Gamma k_s^2}{(\omega-ck_s)^2+\left(\Gamma k_s^2\right)}\right] \\ &+ \frac{k_s}{c\gamma}[\Gamma+(\gamma-1)\chi]\cdot\left[\frac{\omega+ck_s}{(\omega+ck_s)^2+\left(\Gamma k_s^2\right)}\right. \\ &\left. - \frac{\omega-ck_s}{(\omega-ck_s)^2+\left(\Gamma k_s^2\right)}\right]. \end{aligned} \tag{1}$$

Equation (1) describes a spectral profile consisting of three components. The central (Rayleigh) peak arises from fluctuations at constant pressure and corresponds to the thermal diffusivity mode (γ is the ratio of the constant volume and constant pressure-specific heats; χ is the thermal diffusivity). The two Lorentzian lines, symmetrically shifted at $\pm ck_s$, are the result of fluctuations at constant entropy and correspond to the longitudinal acoustic modes. These modes propagate with the adiabatic sound velocity c with a lifetime Γ^{-1}, where $\Gamma = 1/2[\upsilon_l + (\gamma–1)\chi]$ (υ_l = kinematic longitudinal viscosity). The remaining two asymmetric terms are needed to satisfy the first moment sum rule $\int_{-\infty}^{+\infty}\omega I(\omega,k_s)d\omega = 0$, which is the necessary condition for having a converging second moment of the spectral distribution. Although these terms are often disregarded because their contribution is considered negligible, they become relevant to produce the correct spectral shape at high frequency shifts.

B. The generalized-hydrodynamic model

The generalized-hydrodynamic expression for the dynamical structure factor at given wave vector k_s is obtained after introduction of the concept of relaxation process into the linearized hydrodynamic equations. Following the formalism of Ref. [1], it can be written as

$$\begin{aligned} I(k_s,\omega) = \frac{S(k_s,\omega)}{S(k_s)} &= \left(1-\frac{1}{\gamma}\right)\frac{2\chi k_s^2}{\omega^2+\left(\chi k_s^2\right)^2} + R_C\frac{2\frac{c_{s,0}^2}{c_s^2\tau}}{\omega^2+\left(\frac{c_{s,0}^2}{c_s^2\tau}\right)^2} + R_B\left[\frac{\Gamma_s k_s^2}{(\omega+c_sk_s)^2+\left(\Gamma_s k_s^2\right)^2}+\frac{\Gamma_s k_s^2}{(\omega-c_sk_s)^2+\left(\Gamma_s k_s^2\right)^2}\right] \\ &+ \frac{k_s}{c_s}\left[\left(1-\frac{1}{\gamma}\right)\chi + R_C\frac{c_{s,0}^2}{c_s^2k_s^2\tau}+R_B\Gamma_s\right]\left[\frac{\omega+c_sk_s}{(\omega+c_sk_s)^2+\left(\Gamma_s k_s^2\right)^2}-\frac{\omega-c_sk_s}{(\omega-c_sk_s)^2+\left(\Gamma_s k_s^2\right)^2}\right], \end{aligned} \tag{2}$$

where $c_{s,0}$ is the low frequency (relaxed) speed of sound, $c_s = \omega_s/k_s$ is the speed of sound at the frequency $\omega_s/2\pi$ and τ is the relaxation time. The quantity $\Gamma_s k_s^2$ is the half width at half maximum of the experimental Brillouin line which contains both nonrelaxing, Γ, and relaxing contributions and can be written as

$$\Gamma_s = \Gamma + \frac{1}{2}\chi\left(1-\frac{c_{s,0}^2}{c_{s,\infty}^2}\right) + \frac{1}{2}\left(1+\gamma\chi k_s^2\tau\right)\frac{c_{s,\infty}^2-c_{s,0}^2}{1+(\omega_s\tau)^2}\tau, \tag{3}$$

where $c_{s,\infty}$ is the high frequency (unrelaxed) value of the sound velocity. The value of ω_s in Eq. (2) is immediately obtained as [1]

$$\begin{aligned} \omega_s = c_sk_s = c_{s,0}k_s\sqrt{S+\sqrt{S^2+\frac{1}{(c_{s,0}k_s\tau)^2}}}; \\ S = \frac{1}{2}\left[\frac{c_{s,\infty}^2}{c_{s,0}^2}-\frac{1}{(c_{s,0}k_s\tau)^2}\right]. \end{aligned} \tag{4}$$

The generalization of hydrodynamic equations leads to a light-scattering spectrum Eq. (2) consisting of four components. The origin of the Rayleigh line and the symmetric Brillouin peaks is the same as in the above described linearized model. The additional nonshifted component (Mountain mode), whose linewidth is of the order of τ^{-1}, arises from the thermal relaxation. In Eq. (2), the quantities R_c and R_B are the amplitudes of the unshifted contribution arising from the relaxation [4] and of the Brillouin lines, respectively (see Ref. [1] for suitable expressions for these quantities).

C. The damped harmonic oscillator model

The first suggestions for alternative formulations [4,5] were mainly regarding Brillouin scattering in nonrelaxing fluids. They followed from the fact that in a Brillouin scattering experiment the thermal diffusion contribution is usually much narrower than the instrumental resolution. On this basis, any contribution from thermal diffusion to the acoustic damping can be disregarded and the equation of motion for the density fluctuations, at a given wave vector, is written as

$$\ddot{\rho}_{k_s} + \left(\frac{\eta_l}{\rho}k_s^2\right)\dot{\rho}_{k_s} + \left(\frac{M}{\rho}k_s^2\right)\rho_{k_s} = 0, \tag{5}$$

where M is the compressibility modulus related to the velocity of propagation, c_0, of the undamped density fluctuation through the relations $c_0 = \sqrt{M/\rho}$ and $\omega_0 = c_0 k_s$. In Eq. (5), the quantity $\eta_l = \upsilon_l/\rho$ is the longitudinal viscosity. Defining $\Gamma = (1/2)\upsilon_l$, Eq. (5) can be rewritten as

$$\ddot{\rho}_{k_s} + 2\Gamma k_s^2 \dot{\rho}_{k_s} + \omega_0^2 \rho_{k_s} = 0. \tag{6}$$

The fluctuation dissipation theorem allows us to obtaining the corresponding spectral distribution, $I(k_s,\omega)$, from the complex susceptibility, $X(k_s,\omega)$, leading to [3]

$$\begin{aligned} I(k_s,\omega) &= \frac{1}{\pi}\frac{\langle\omega_{k_s}^2\rangle}{\omega}\mathrm{ImX}(k_s,\omega) \\ &= \frac{1}{\pi}\langle\omega_{k_s}^2\rangle \frac{2\Gamma k_s^2}{\left(\omega^2-\omega_0^2\right)^2 + \left(2\omega\Gamma k_s^2\right)^2}, \end{aligned} \tag{7}$$

where the quantity $\langle\omega_{k_s}^2\rangle$ denotes the second frequency moment of the distribution $I(k_s,\omega)$, the nth moment being defined as

$$\langle\omega_k^n\rangle = \int_{-\infty}^{+\infty} d\omega\, \omega^n I(k,\omega). \tag{8}$$

In the absence of any relaxation ($c_s = c_{s,0} = c_{s,\infty}$) Eq. (2) reduces to the linearized hydrodynamic expression Eq. (1) and it collapses over Eq. (7), when the central diffusive mode is disregarded. In fact, if we introduce the quantity ω_s given by $\omega_s^2 = \omega_0^2 - (\Gamma k_s^2)^2$, assuming the condition $(\Gamma k_s^2)^2 \ll (2\omega_s)^2$, Eq. (7) is reduced to

$$\begin{aligned} &I(k_s,\omega) \\ &= \frac{\langle\omega_{k_s}^2\rangle}{4\pi\omega_s^2}\left[\frac{\Gamma k_s^2 + (\omega+\omega_s)\frac{\Gamma k_s^2}{\omega_s}}{(\omega+\omega_s)^2 + \left(\Gamma k_s^2\right)^2} + \frac{\Gamma k_s^2 - (\omega-\omega_s)\frac{\Gamma k_s^2}{\omega_s}}{(\omega-\omega_s)^2 + \left(\Gamma k_s^2\right)^2}\right]. \end{aligned} \tag{9}$$

Equation (9) just produces two Brillouin lines symmetrically shifted to the frequencies $\pm\omega_s = \pm c_s \mathrm{k}_s$, while no unshifted contribution is generated. It is not surprising since Eq. (5) implies that the density is only a function of the time and does not depend on the temperature. As a consequence, the thermal expansion coefficient α is zero and Eq. (9) describes an isothermal spectrum or the spectrum of a system for which adiabatic, β_s, and isothermal, β_T, compressibilities coincide. As a result $\gamma = C_p/C_v = \beta_T/\beta_s = 1$.

D. The generalized damped harmonic oscillator model (viscoelastic model)

Equation (9) can be easily modified taking into account a relaxation process. We will assume, as an example, a Debye relaxation of the bulk viscosity (under the condition $\gamma = 1$) and we will compare the indication of the modified Eq. (9) against that of Eq. (2). Under this condition, the damping coefficient Γ is translated into a generalized friction coefficient:

$$\begin{aligned} \Gamma(\omega) &= \mathrm{Re}[\Gamma(\omega)] + i\,\mathrm{Im}[\Gamma(\omega)] = \Gamma'(\omega) + i\Gamma''(\omega) \\ &= \Gamma + \frac{1}{2}\left(c_{s,\infty}^2 - c_{s,0}^2\right)\int_0^\infty e^{i\omega t} M_\Gamma(t)dt, \end{aligned} \tag{10}$$

where Γ is related to the nonrelaxing part of the kinematic viscosity [and corresponds to the quantity Γ in Eqs. (1), (2), and (8)] and $M_\Gamma(t) = \exp(-t/\tau)$ is the memory function for damping. Based on these assumptions, Eq. (10) becomes

$$\Gamma(\omega) = \Gamma + \frac{1}{2}\left(c_{s,\infty}^2 - c_{s,0}^2\right)\frac{\tau}{1 - i\omega\tau}, \tag{11}$$

whose real part is consistent with Eq. (3) (disregarding the thermal diffusion). It must be noticed that the function $\Gamma(\omega)$ is also a function of k through the sound velocity. In the following, the values of this function and of its real and imaginary parts calculated at the wave vector k_s will be indicated by the subscript s.

The substitution of Eq. (11) into Eq. (7) produces the required spectral density. Taking into account that, in the ω space, the memory function can be written as

$$\begin{aligned} M(k,\omega) &= \left(2\Gamma + \frac{c_{s,\infty}^2 - c_{s,0}^2}{1+\omega^2\tau^2}\tau\right)k^2 - i\frac{c_{s,\infty}^2 - c_{s,0}^2}{1+\omega^2\tau^2}\omega\tau^2 k^2 \\ &= M'(k,\omega) + iM''(k,\omega), \end{aligned} \tag{12}$$

we obtain

$$\begin{aligned} I(k_s,\omega) &= \frac{\langle\omega_0^2\rangle}{\pi}\frac{M'(k_s,\omega)}{\left[\omega^2 - \omega_0^2 + \omega M''(k_s,\omega)\right]^2 + [\omega M'(k_s,\omega)]^2} \\ &= \frac{\langle\omega_0^2\rangle}{\pi}\frac{2\Gamma_s'(\omega)k_s^2}{\left[\omega^2 - c_s^2(\omega)k_s^2 - \left(\Gamma_s k_s^2\right)^2\right]^2 + \left[2\omega\Gamma_s'(\omega)k_s^2\right]^2}, \end{aligned} \tag{13}$$

where we made use of the above relation between ω_0 and the frequency $\omega_s = \omega_{s,0}$ corresponding to the relaxed value of the sound velocity. In Eq. (13), the quantity $c_s(\omega)$ is given by

$$c_s(\omega) = \sqrt{c_{s,0}^2 + \frac{c_{s,\infty}^2 - c_{s,0}^2}{1+\omega^2\tau^2}\omega^2\tau^2} = \sqrt{c_{s,\infty}^2 - \frac{c_{s,\infty}^2 - c_{s,0}^2}{1+\omega^2\tau^2}}. \tag{14}$$

Equation (13) represents the widely adopted model for the fitting of experimental data obtained over very wide frequency ranges. Besides its above mentioned ability of reproducing the correct k dependence of the involved parameters, a further advantage comes for its apparent ability of reproducing, with a simple and compact notation, the whole spectral distribution including the central component, which relates with nonpropagating modes originated by the relaxation phenomenon occurring in the system.

III. DIFFERENCES BETWEEN THE DIFFERENT APPROACHES

A. The linearized hydrodynamic model and the damped oscillator model

It can be shown [10] that Eq. (2) can be derived from the memory function $M(k,t) = \upsilon_l k^2 \delta(t) + (\gamma - 1)\langle\omega_0^2\rangle \exp(-\chi k^2 t)$, where $\langle\omega_0^2\rangle = c_s^2 k^2/\gamma$ is the value of the second moment in the hydrodynamic regime (which means at low k values).

This occurrence is enough for asserting that, for a nonrelaxing system and under the condition $\gamma = 1$ within the hydrodynamic approximation, Eq. (1) is fully equivalent to Eq. (9).

B. The generalized-hydrodynamic model and the viscoelastic model

Equation (13) can be rearranged leading to expressions formally equivalent to Eq. (2) [10]. In the low or high frequency limits, Eq. (14) is reduced to one of the two frequency-independent values, $c_{s,0}$ or $c_{s,\infty}$. In these limits the hypersonic velocity does not exhibit dispersion and Eq. (13) is reduced to Eq. (7), which is equivalent to Eq. (1). However, when the explored frequency range includes a relaxation, Eq. (14) produces a distribution of sound velocities. Each component of this distribution corresponds to a density fluctuation at a different frequency and at a different wave vector. But actually only the waves propagating at the frequency $\omega_s = c_s \mathrm{k}_s$, corresponding to phonons matching the experimentally selected wave vector, bring contributions to Eq. (1) and to the experimental spectrum. Analogously, $\Gamma(\omega)$ is the generalized frequency-dependent damping function while the quantity $\Gamma_s k^2$ is the lifetime of the density fluctuation at the frequency $\omega_s(k)$. It now becomes clear that the whole distribution of sound velocities described by Eq. (14) contributes to Eq. (13). As a consequence, Eq. (13) does not describe a spectral profile at a fixed k value and hence does not correspond to any experimental situation. In order to match with the given definition of $I(k,\omega)$, the quantity k should play the role of a parameter. Unfortunately, the quantity $c_s(\omega)$ is implicitly dependent on k even when the value of this parameter is fixed at a given value in Eq. (13). As a consequence the left- and the right-hand sides of Eq. (13) become inconsistent with each other.

As a result, Eq. (13) is unable to describe the correct shape of the experimental Brillouin profile of a system close to the relaxation. In particular, $I(k_s,\omega)$ given by Eq. (13) is a broader spectral distribution than that described by Eq. (2), which is rigorously calculated at $k = k_s$ (defined by the experimental geometry).

We can make an attempt to reproduce the experimental $I(k_s,\omega)$, putting into Eq. (13) only the component of the distribution $c_s(\omega)$ which satisfies the relation $c_s = \omega_s/k_s$. From Eq. (14) we obtain

$$\omega_s = k_s \sqrt{c_{s,\infty}^2 - \frac{c_{s,\infty}^2 - c_{s,0}^2}{1 + \omega_s^2 \tau^2}}. \tag{15}$$

Equation (15) produces only two real solutions for ω_s:

$$\omega_s = \pm c_{s,0} k_s \sqrt{S + \sqrt{S^2 + \frac{1}{(c_{s,0} k_s \tau)^2}}}. \tag{16}$$

This is exactly the same result which was obtained within the generalized-hydrodynamic approach [1] [see Eq. (4)]. As a result, the function $\Gamma'(\omega)$ in Eq. (13) assumes the value

$$\Gamma'(\omega)_{k=k_s} = \Gamma_s = \Gamma + \frac{1}{2}\frac{c_{s,\infty}^2 - c_{s,0}^2}{1 + \omega_s^2 \tau^2}\tau. \tag{17}$$

Finally, Eq. (13) is reduced to

$$\begin{aligned} I(k_s,\omega) &= \frac{\langle\omega_0^2\rangle}{\pi} \frac{2\Gamma_s k_s^2}{\left[\omega^2 - \omega_s^2 - \left(\Gamma k_s^2\right)^2\right]^2 + \left(2\omega\Gamma_s k_s^2\right)^2} \\ &= \frac{\langle\omega_0^2\rangle}{\pi} \frac{2\Gamma_s k_s^2}{\left(\omega^2 - \omega_0^2\right)^2 + \left(2\omega\Gamma_s k_s^2\right)^2}, \end{aligned} \tag{18}$$

which is equivalent to Eq. (7), describing the spectrum of a damped harmonic oscillator without any contribution from the Mountain mode.

IV. COMPARISON AND DISCUSSION

In Fig. 1 we plot, as an example, the dynamical structure factors for a simulated system calculated in agreement with Eqs. (2) and (13), at three different temperatures.

The following assumptions have been made throughout the calculations: $\gamma = 1$, $\rho = 1000$ kg m^{-3}, $k = 2.221\times10^7$ m^{-1}, $\upsilon_l(T) = (8\times10^{-6} + 10^{-7}T)$ m^2 s^{-1}, $v_0(T) = (1400 + 0.5T)$ m s^{-1}, $v_\infty(T) = v_0(T) + 700$ m s^{-1}. A single Debye process has been assumed with an Arrhenius temperature dependence of the relaxation time, $\tau(T) = \tau_0\exp(-\Delta H/RT)$, where R is the gas constant, $\Delta H = -18\times10^3$ J mole^{-1} is the activation enthalpy and $\tau_0 = 10^{-13}$ s. The calculated dependence of the hypersonic velocity is presented in the inset of the same figure, together with its limit behaviors at low and high frequencies. The inflection point of the $c_s(T)$ curve clearly indicates the temperature at which the spectral density will be affected by

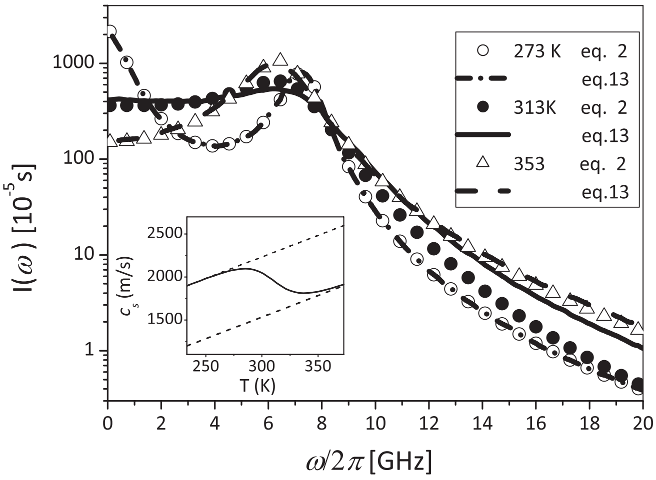

FIG. 1. Calculated spectrum for the simulated system with $\gamma = 1$ at three different temperatures (see text for details). Inset: calculated temperature dependence of the hypersonic velocity.

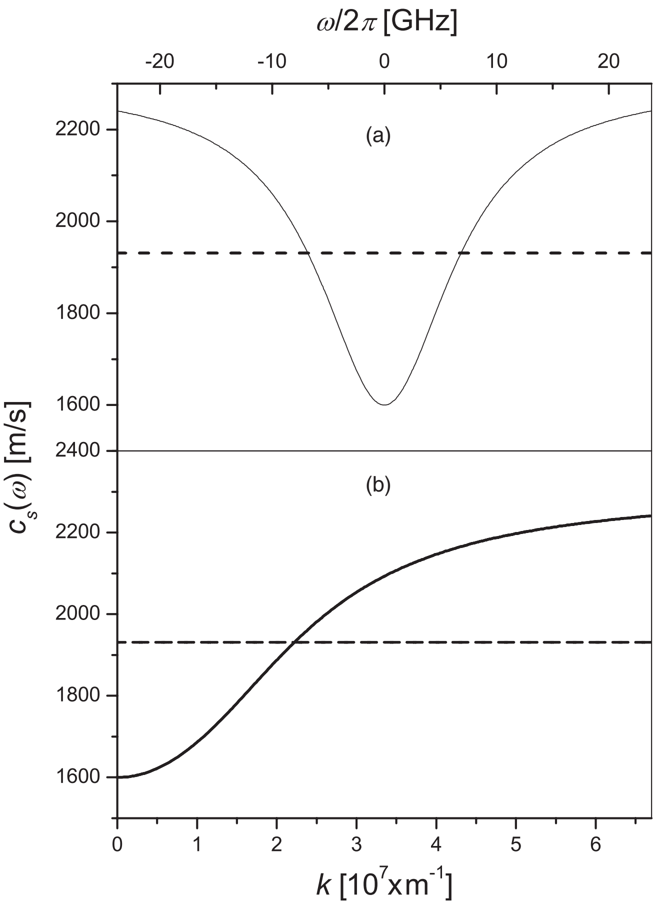

FIG. 2. (a) Frequency dependence of the function $c_s(\omega)$, calculated through Eq. (13) for $T = 313$ K under the assumption of a single Debye process (see text for further details). The dashed line represents the value of the sound velocity at the wave vector k_s, calculated through Eq. (14). (b) k dependence of $c_s(\omega)$. The dashed line represents the sound velocity at the wave vector k_s, calculated through Eq. (14).

the relaxation phenomenon. Figure 1 unambiguously shows how the predictions of the two approaches almost perfectly match at temperatures far enough from the relaxation. In contrast, at temperatures close to the relaxation, the spectral distribution given by Eq. (13) becomes definitely broader than that produced by Eq. (2).

In Fig. 2(a) we report the frequency dependence of the function $c_s(\omega)$, calculated through Eq. (14), at $T = 313$ K. The dashed line represents the value of the sound velocity at the wave vector k_s, calculated through Eq. (15) and relation $c_s = \omega_s/k_s$. In Fig. 2(b), we report the k dependence of the same quantity $c_s(\omega)$. The dashed line represents the sound velocity at the wave vector k_s, calculated through Eq. (15). The value of k_s corresponds to the point where the dashed line intercepts the $c_s(\omega)$ curve. The plot shows unambiguously that the function $c_s(\omega)$ in Eq. (13) is also a function of k, and clearly demonstrates that Eq. (13) cannot correspond to the spectral profile calculated at a fixed k value.

The above reported comparison between the hydrodynamics and the memory-function approaches refers to a system for which $C_p = C_v$.

However, Eq. (13) can be easily modified in order to include thermal diffusion. To obtain this result, the memory function should be rewritten as

$$M(k,t) = \upsilon_{l,0}k^2\delta(t) + \left(c_{s,\infty}^2 k^2 - \gamma\langle\omega_0^2\rangle\right)\exp\left(-\frac{t}{\tau}\right) + (\gamma-1)\langle\omega_0^2\rangle\exp(-\chi k^2 t), \tag{19}$$

which leads to the following expressions for the quantities $M'(k,\omega)$ and $M''(k,\omega)$:

$$\begin{aligned} M'(k,\omega) &= \left(2\Gamma + \frac{c_{s,\infty}^2 - c_{s,0}^2}{1+\omega^2\tau^2}\tau\right)k^2 + \frac{(\gamma-1)\langle\omega_0^2\rangle\chi k^2}{\omega^2+(\chi k^2)^2}, \\ M''(k,\omega) &= -\frac{c_{s,\infty}^2 - c_{s,0}^2}{1+\omega^2\tau^2}\omega\tau^2 k^2 - \frac{(\gamma-1)\langle\omega_0^2\rangle}{\omega^2+(\chi k^2)^2}\omega. \end{aligned} \tag{20}$$

In principle, Eq. (13) with Eq. (20) can be used to fit experimental data taking into account all the contributions to damping of the adiabatic density fluctuations. However, the arguments about its inability to reproduce the correct behavior close to a relaxation still remain valid.

In Fig. 3, we report the isotropic experimental [11,12] spectrum, I_{vv}, of a polyethylene glycol aqueous solution together with the fitting results with the convolution of Eqs. (2) and (13) with the instrumental resolution function. Both the fitting procedures involve the determination of the values of six independent parameters. In the case of Eq. (1) the parameters are γ, $\Gamma_1 = c_{s,0}{}^2 c_s{}^{-2}\tau^{-1}$, Γ_s, R_C, R_B, and ω_s. In adopting Eq. (13) the free parameters are γ, Γ, $\Delta = c_{s,\infty}{}^2 - c_{s,0}{}^2$, $\langle\omega_0^2\rangle$, ω_0, and τ. In both cases, the thermal diffusion contribution is considered within the instrumental resolution. It was shown [11,12] that the system exhibits a relaxation which, at temperature = 298 K indicated in Fig. 3, takes place on a time scale of 14ps. It is quite evident that, while Eq. (2) is able to reproduce the experimental spectrum, Eq. (13) fails in reproducing the correct decay at large ω values [11,12]. In addition, the estimated relaxation time value turns out to be 2.4 ps which is much lower than the result obtained by the analysis of a set of data over a wide temperature range [11,12].

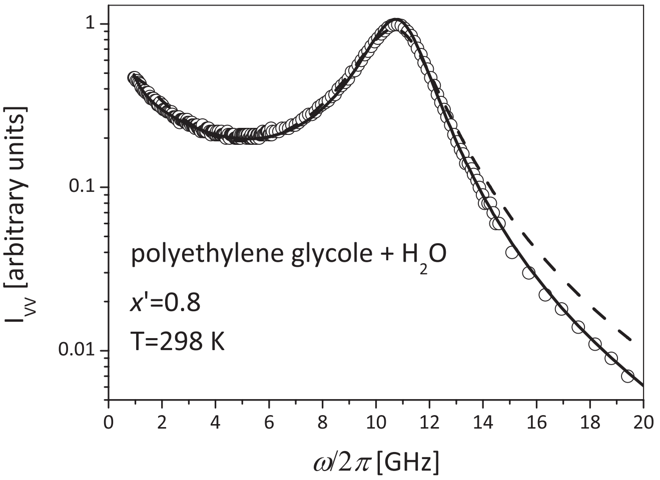

FIG. 3. Circles: Experimental Brillouin spectrum (molecular weight 400, monomer molar fraction $x' = 0.8$) at temperature $T = 298$ K (see Refs. [11] and [12] for details). Continuous line: Eq. (1). Dashed line: Eq. (12).

Finally, the descriptions of the dynamic structure factor related to adiabatic density fluctuations, as obtained from generalized hydrodynamics Eq. (2) and from generalized damped harmonic oscillator Eq. (13) are not equivalent. The generalized-hydrodynamic formalism correctly describes the experimental situation where only fluctuations preserving the exchanged wave-vector selection rule contribute to the spectrum. On the contrary, the expression given in Eq. (13) is not the correct $S(k_s,\omega)$ since it contains spectral components at $k\neq k_s$. However, these two approaches become indistinguishable when no relaxation process takes place or when the system is investigated at frequencies largely different from the relaxation frequency. The indications from models based on Eq. (13) become consistent with those from Eq. (2) only when the condition $k = k_s$ is preserved. In such a case, however, Eq. (13) assumes the same form of Eq. (7) which describes only the Brillouin doublet profile. Any fitting of the experimental spectrum with such model will require the addition of a further unshifted term. From a practical point of view, the experimental data are often fitted with Eq. (7) plus a Lorentzian centered at $\omega = 0$. Even if such a procedure can appear able to satisfactorily fit the experimental data, it has no advantage over Eq. (2). Furthermore, it introduces an unnecessary inconsistence since the theoretical spectral distribution obtained in such a way has an undefined first moment.

V. CONCLUDING REMARKS

We want to stress that the divergence between the different approaches is not related to the adoption of different models, i.e., different memory functions. The same memory functions have been used in both cases. The difference originates from the incorrect use of Eq. (13) when it is adopted to describe the full experimental spectral profile. In fact, the differences between the models disappear when the correct components are taken from Eq. (13). The price to pay is that we lose any description of the central unshifted contribution.

Contrary to the common belief, there is no way to extract information about any relaxation process by means of the full spectrum analysis of a single experimental structure factor at a fixed k_s value, irrespective of the assumptions taken in different models [5–8]. The values of $\omega_s(k_s)$ and $\Gamma_s(k_s)$ are the only information that can be obtained by such a procedure. The acquisition of data over a wide k range and the subsequent fitting with a suitable model of relaxation are mandatory for extracting nonmisleading information about any process taking place in the system.

We remark that we are not claiming that the memory-function approach is wrong. We are simply asserting that the approach is able to produce only the spectral contributions from density fluctuations at constant entropy. This limitation stems from Eq. (5), which describes density as a function of time only, disregarding any dependence on the temperature. The correct spectrum resulting from the memory-function approach is represented by Eq. (18). Any attempt for reproducing the full experimental spectral features by Eq. (13) is wrong and reflects a misleading interpretation of this equation.

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

[2] B. J. Berne and R. Pecora, *Dynamic Light Scattering* (J. Wiley & Sons, New York, 1976).

[3] U. Balucani and M. Zoppi, *Dynamics of the Liquid State* (Clarendon Press, Oxford, 1994).

[4] R. Mountain, J. Res. Natl. Bur. Stand. **70A**, 207 (1966).

[5] M. Fuchs, W. Götze, and A. Latz, Chem. Phys. **149**, 185 (1990).

[6] J. Börjesson, M. Elmorth, and L. M. Torrell, Chem. Phys. **149**, 209 (1990).

[7] N. J. Tao, G. Li, and H. Z. Cummins, Phys. Rev. B **45**, 686 (1992).

[8] G. Li, W. M. Du, J. Hernandez, and H. Z. Cummins, Phys. Rev. E **48**, 1192 (1993).

[9] G. Monaco, G. Ruocco, L. Comez, and D. Fioretto, J. Non-Cryst. Solids **235–237**, 208 (1998).

[10] U. Bafile, E. Guarini, and F. Barocchi, Phys. Rev. E **73**, 061203 (2006).

[11] M. Pochylski, F. Aliotta, R. C. Ponterio, F. Saija, and J. Gapiński, J. Phys. Chem. B **114**, 1614 (2010).

[12] M. Pochylski, F. Aliotta, Z. Błaszczak, and J. Gapiński, Macromol. Symp. **251**, 47 (2007).