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Collective acoustic modes as renormalized damped oscillators: Unified description of neutron and x-ray scattering data from classical fluids

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In the Q range where inelastic x-ray and neutron scattering are applied to the study of acoustic collective excitations in fluids, various models of the dynamic structure factor $S(Q,\omega)$ generalize in different ways the results obtained from linearized-hydrodynamics theory in the $Q\to 0$ limit. Here we show that the models most commonly fitted to experimental $S(Q,\omega)$ spectra can be given a unified formulation. In this way, direct comparisons among the results obtained by fitting different models become now possible to a much larger extent than ever. We also show that a consistent determination of the dispersion curve and of the propagation Q range of the excitations is possible, whichever model is used. We derive an exact formula which describes in all cases the dispersion curve and allows for the first quantitative understanding of its shape, by assigning specific and distinct roles to the various structural, thermal, and damping effects that determine the Q dependence of the mode frequencies. The emerging picture describes the acoustic modes as Q-dependent harmonic oscillators whose characteristic frequency is explicitly renormalized in an exact way by the relaxation processes, which also determine, through the widths of both the inelastic and the elastic lines, the whole shape of collective-excitation spectra.

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I. INTRODUCTION

Significant progress has been made in the last two decades in the field of the experimental investigation of the collective dynamics of fluids at the atomic scale. This advance is the consequence of an impressing improvement in the performances of the two techniques that are most relevant to the study of microscopic dynamics: first, neutron and, more recently, x-ray inelastic scattering. These spectroscopies have in this way firmly established themselves as complementary methods to the older light (i.e., Brillouin) scattering technique, extending by orders of magnitude the ranges of energy and momentum exchanged between the probe and the sample. In parallel with the experimental advances, computer simulation techniques have also been developed to become a major tool for dynamics investigations thanks to the increase of available computing power.

This situation, by stimulating the production of a large amount of accurate data on a wide variety of fluids, has also revived the interest in the theoretical methods for the description and interpretation of experimental results. Most of the theoretical tools had already been developed since the 1960s, or earlier. However, the need for methods to extract reliable and significant information from new experimental data sets has become a common concern to experimentalists and computer simulators, besides remaining of course a specific subject of study for theoreticians. For those who have had data to analyze, this problem has taken the form of being able to understand fit models [1–4]. The analysis of experimental results is, in fact, typically performed by fitting to the spectral data a model function that is believed to incorporate the relevant features of the dynamics under study. Truly theoretical approaches to the calculation of spectra exist, among which one can mention the extension of kinetic theories to dense fluids and the mode-coupling theory [1,2]. In this respect, the use of fit models could rather be considered a phenomenological approach. Undoubtedly, however, the comparison of experimental results to theoretical calculations is not the favored option in the great majority of published works.

It is quite a remarkable and fortunate case that, in the field we are interested in here, both all experimental techniques and computer simulations produce results for exactly the same physical quantity, which also is of central importance in the theory. This quantity is the dynamic structure factor $S(Q,\omega)$, i.e., the frequency spectrum of the autocorrelation function of density fluctuations with wave vector $\mathbf{Q}$, where $Q=|\mathbf{Q}|$. The discussion of model representations of $S(Q,\omega)$ has, therefore, assumed great relevance, including the comparison of the performance of different models in various situations, the assignment of physical meaning to the parameters that characterize the models, and their generalization and extension to more detailed, or more powerful, expressions.

In most cases, data are taken directly in, or reduced through a preliminary analysis to, the form of constant-Q frequency spectra, and model fitting is carried out separately at each investigated Q value. By collecting the values found at the various Q's, one obtains an experimental Q dependence for each fit parameter, which is the basis for further developments and speculations, or for comparisons with other works or other systems. The goodness of the fit, assessed too as a function of Q with standard means such as the χ^2 evaluation, can then be taken as an evidence supporting, for example, the superiority of a model, or revealing the onset of a different dynamical process.

A few models of $S(Q,\omega)$ [2] are of common use for such a kind of analysis on a large variety of fluids, in the Q-range

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characteristic of neutron and x-ray inelastic scattering investigations (broadly speaking, between 0.1 and 20 nm^{-1}, to be compared with the value $Q \simeq 0.01\ \mathrm{nm}^{-1}$, typical of Brillouin light scattering). Essentially, they are based either on the generalization of the known behavior of fluid systems in the linearized-hydrodynamics regime, or on expressions derived within the memory function approach to the microscopic dynamics. A generalization of the Rayleigh-Brillouin triplet was used, for example, for the analysis of liquid and gaseous Ar [5] and N_2 [6], liquid Ne [7], CD_4 [8], Li [9], and Al_2O_3 [10], and the He-Ne gas mixture [11]. The so-called damped harmonic oscillator model, enriched with an additional spectral term centered at $\omega=0$, most usually in the Lorentzian form, was fitted to data on liquid metals as Ga [12], K [13], Hg [14], Ni [15], on liquid alloys Li_4Pb [16] and K-Cs [17], on liquid para-hydrogen and deuterium [18], water [19], NH_3 [20], glycerol [21], on molten NaCl [22], on the metal solution Li-$(ND_3)_4$ [23] and on Hg vapor [24]. Other models, belonging to a family generally named after the theory of viscoelasticity and formulated in various versions, were fitted to spectra of gaseous He [25], liquid and gaseous Ne [26], the molecular liquids H_2 and D_2 [27], CCl_4 [28], SO_2 [29], water [30], HF [31], the liquid metals Rb [32], Cs [33], Li [34], Na [35], K [36], Al [37], and Ga [38], and the liquid alloy Rb-Sb [39]. Also, in some cases different models were used with the same data to describe different Q ranges, such as for compressed gaseous and liquid Ne [40] and He [41], and liquid Rb [42], Si [43], and methanol [44]. An extended review of results for liquid metals was recently published [45]. The above list includes neutron or x-ray investigations only, with no claim of completeness.

Given the effort made in this field, and the favorable condition of having all data presented in the form of $S(Q,\omega)$ spectra at constant Q, it is regretful that the task of comparing data analyzed by means of different models is usually difficult, simply because the formulation of these models and their parametrization are not reduced to a common scheme.

A typical example of this undesirable variety is provided by the different methods with which the so-called dispersion curve, i.e., the way the frequency of the excitations depends on Q, is extracted from experimental data. This ambiguity derives from the lack of a generally accepted criterion to obtain this quantity, which in turn reflects a lack of agreement on its definition, or at least on an operative definition.

This paper aims at establishing a common, more general basis on which all the frequently used models can be set, by reformulating them in a unified way. As one of the consequences, we will show that, whichever fit model is employed, the excitation frequency can be consistently defined and directly obtained from the fit, thus enabling a much easier and direct comparison among data analyzed by means of different models. Also, a deeper understanding of the properties of the dispersion curve will be shown to be possible if the fit models are expressed in the way proposed here. We stress, however, that it is not the purpose of this paper to go into the discussion of which model is more appropriate in one or another situation.

In this work we will refer to the data to which models are fitted as "experimental" data, including in this denomination the output of molecular-dynamics simulations. As said before, "data" generally means $S(Q,\omega)$ spectra as functions of ω at a given Q. However, equivalent information is stored in the corresponding time correlation functions $F(Q,t)$. We will show that, if formulated in the way presented here, all fit models can be immediately converted for application to the time domain.

Measurements on real systems reflect their fundamental quantum nature in at least one respect, namely the detailed-balance effect, that characterizes the spectra with an asymmetric intensity distribution. However, all models considered here are based on theories developed for "classical" fluids, leading to spectra which are even functions of ω. It is then common practice to symmetrize, by means of appropriate (though in principle never exact) prescriptions [46], the experimental spectra before the fit session. Alternatively, the original, symmetric, fit model is modified, usually with an ω-dependent multiplicative factor, to produce the required asymmetry. In this work we will assume that the data to be analyzed have been either converted to, or produced in, the form of symmetric spectra. Accordingly, we will denote by $S(Q,\omega)$ and $F(Q,t)$ the symmetric frequency spectra and time correlations, respectively, of a classical fluid.

Also, we will not be concerned in this paper with the effects of the finite resolution power of the instrumental apparatus or of the simulation algorithm. Usually, the spectral broadening induced by resolution effects is applied to the model within the fit procedure. In this way, the best agreement between the original model and the data is assessed taking into account the resolution effect, while the extracted information, in terms of fitted parameters, can be considered as being resolution free.

A few figures will illustrate some of the relevant points discussed in this paper by using as an example the results of a recent [8] molecular-dynamics simulation of the center-of-mass dynamics of liquid deuterated methane (CD_4) at a thermodynamic state close to the triple point. The paper is structured in the following way. We briefly recall in Sec. II a few fundamental results of the theory of microscopic dynamics in the framework of the memory function approach. These basic formulas will be used in Sec. III for the analysis of the Rayleigh-Brillouin triplet and in Sec. IV for the discussion of various fit models. In Sec. V we address the problem of the determination of the frequency and propagation Q range of the excitations. Section VI reports on a general formula which describes exactly the dispersion curve as obtained from the various fit models. Section VII contains a comparison of the results obtained by analyzing the mentioned simulation data set [8] with two models. The conclusions form the content of Sec. VIII. Two Appendixes, A and B, contain results whose derivation would not properly fit in the text.

II. GENERAL FORMULAS IN THE MEMORY FUNCTION FRAMEWORK

A unified description of the various models applied to the interpretation of spectra of the density autocorrelation function in a classical fluid can be obtained in the framework of the memory function approach. Here we will only report a few basic formulas that are relevant for our purposes, referring the reader to Refs. [1,2] for a general introduction and details of the memory function theory.

We are interested in the time autocorrelation of the Fourier components, with wave vector $\mathbf{Q}$, of the microscopic density, that is, the so-called intermediate scattering function

$$F(Q,t) = \frac{1}{N}\sum_{\alpha,\beta=1}^{N} \langle e^{-i\mathbf{Q}\cdot\mathbf{R}_\alpha(0)} e^{i\mathbf{Q}\cdot\mathbf{R}_\beta(t)}\rangle$$

of a fluid composed of N identical particles located at positions $\mathbf{R}_\alpha(t)$. Here and in the following we exploit the macroscopically isotropic behavior of a fluid by dropping the dependence of $F(Q,t)$ on the direction of $\mathbf{Q}$.

A fundamental result of the theory we are referring to is that the time evolution of $F(Q,t)$ is described with the help of a memory function $M(Q,t)$, leading to the integro-differential equation

$$\ddot{F}(Q,t) + \int_0^t dt' M(Q,t-t')\dot{F}(Q,t') + \langle\omega_Q^2\rangle F(Q,t) = 0, \tag{1}$$

where the dots denote time derivatives. More precisely, $M(Q,t)$ is the second-order memory function in a hierarchy of equations describing the time dependence of the density autocorrelation. Equation (1) is derived [2,45] by using an equation for $\dot{F}(Q,t)$ in terms of a first-order memory function $M^{(1)}(Q,t)$, namely,

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

together with an equation for the time evolution of $M^{(1)}(Q,t)$ itself in terms of $M(Q,t)$,

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

We also introduce the frequency spectrum of $F(Q,t)$, i.e., the dynamic structure factor

$$S(Q,\omega) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} dt\, e^{-i\omega t}F(Q,t), \tag{3}$$

with the static structure factor

$$S(Q) = \int_{-\infty}^{+\infty} d\omega\, S(Q,\omega) = F(Q,0), \tag{4}$$

and use in the following the symbol $I(Q,\omega)$ to denote the normalized dynamic structure factor $S(Q,\omega)/S(Q)$. Its kth frequency moment (kth moment, for short) is written as

$$\langle\omega_Q^k\rangle = \int_{-\infty}^{+\infty} d\omega\, \omega^k I(Q,\omega). \tag{5}$$

The second moment appearing in (1) has, in classical systems, the value [1]

$$\langle\omega_Q^2\rangle = \frac{k_B T Q^2}{m S(Q)}, \tag{6}$$

where k_B is the Boltzmann constant, T is the temperature and m is the mass of the particles. We immediately recall that, at low Q, $\langle\omega_Q^2\rangle$ tends to the Q^2-dependent quantity $\langle\omega_0^2\rangle$ obtained by replacing $S(Q)$ with its limit value $S(0)=nk_BT\chi_s\gamma_0$, where n is the number density, χ_s is the adiabatic compressibility, and γ_0 is the ratio of the constant pressure (c_p) to the constant-volume (c_v) specific heat, so that $\langle\omega_0^2\rangle$ can be related to the adiabatic sound velocity $c_s = 1/\sqrt{nm\chi_s}$ by the simple formula

$$\langle\omega_0^2\rangle = \frac{c_s^2 Q^2}{\gamma_0}. \tag{7}$$

We also define the symbol $\omega_L^2(Q)$ through the relationship [2,45]

$$\langle\omega_Q^4\rangle = \omega_L^2(Q)\langle\omega_Q^2\rangle, \tag{8}$$

with the low-Q behavior $\omega_L^2(Q) \simeq c_L^2 Q^2$, where $c_L = c_\infty(0)$ is the $Q=0$ value of the infinite-frequency sound velocity [1].

Since the developments that lead to (1) are carried out within the general framework of a classical theory, with $F(Q,t)$ having the property of being real and even in time, the theory intrinsically assigns to $F(Q,t)$ the fundamental property $\dot{F}(Q,0)=0$, as it is immediately seen from (2). This implies the existence of a finite second moment. In fact, being $\dot{F}(Q,t)$ an odd function of t, for $t=0$ it either has a zero value or is not defined. However, if $\dot{F}(Q,0)=0$ then surely $\ddot{F}(Q,0)$ also exists and is finite. Then, the well-known relation between the zero-time properties of $F(Q,t)$ and the moments of $I(Q,\omega)$,

$$\left[\frac{d^k}{dt^k}\left(\frac{F(Q,t)}{F(Q,0)}\right)\right]_{t=0} = i^k\langle\omega_Q^k\rangle, \tag{9}$$

is applicable with $k=2$, yielding $\ddot{F}(Q,0)/F(Q,0) = -\langle\omega_Q^2\rangle$, as is also shown by (1). It must be noted that, in general, the theory expressed by (1) does not ensure the applicability of (9) for any $k>2$. In particular, for the models considered here, all derived from (1) with specific choices of $M(Q,t)$, it will be seen that (9) ceases to be applicable, because the left-hand side is not defined, for $k=3$ (see Secs. III, IV A, and IV B) or $k=5$ (see Secs. IV C and IV D), and that the fourth or sixth moment diverge, respectively.

Equation (1) is solved via Laplace transformation with initial conditions given by (4) and by $\dot{F}(Q,0)=0$, yielding

$$\frac{\widetilde{F}(Q,z)}{S(Q)} = \left(z + \frac{\langle\omega_Q^2\rangle}{z+\widetilde{M}(Q,z)}\right)^{-1}, \tag{10}$$

where $\widetilde{F}(Q,z)$ and $\widetilde{M}(Q,z)$ are the Laplace transforms of $F(Q,t)$ and $M(Q,t)$. The dynamic structure factor is then obtained from [2]

$$\frac{S(Q,\omega)}{S(Q)} = \frac{1}{\pi}\,\mathrm{Re}\,\frac{\tilde{F}(Q,i\omega)}{S(Q)}. \tag{11}$$

In the framework of the memory function theory, attempts at grasping the main features of the microscopic dynamics of fluids are made by exploiting the known properties of the memory function [essentially its $t=0$ value, given by $M(Q,0)=\omega_L^2(Q)-\langle\omega_Q^2\rangle$ [2]] and by modeling, through reasonable guesses, the unknown time dependence of $M(Q,t)$. All the models we will be concerned with here express $M(Q,t)$ as a sum of terms with two basic types of time dependence: either a δ-function, which amounts to assuming no memory effects at all, or an exponential decay. We remark that the use of a δ-function in $M(Q,t)$ actually violates the just given prescription for $M(Q,0)$. The models where this is done (see Secs. III, IV A, and IV B) are to be understood as limit cases, where a $\delta(t)$-term is introduced to express the fact that the decay of the memory function (or at least of a part of it) becomes extremely fast compared to the slower and slower decay of $F(Q,t)$ when approaching the hydrodynamic limit. The memory function formalism, however, permits to treat these cases as well, reproducing the theoretical results of hydrodynamics that were historically derived by different routes. In any case, models of $M(Q,t)$ containing a $\delta(t)$-term give rise to spectra that do not possess a finite fourth moment.

Reminding that the Laplace transforms of $\delta(t)$ and of $\exp(-at)$ are $1/2$ and $1/(z+a)$, respectively, we note that, with these kinds of terms, simple algebraic steps can always put Eq. (10) in the form

$$\frac{\tilde{F}(Q,z)}{S(Q)} = \frac{V(z)}{W(z)}, \tag{12}$$

where V and W are polynomials in the variable z (with real, Q-dependent coefficients). The degree of W, denoted by p, is the number of exponential terms in $M(Q,t)$ plus two, and the degree of V is $p-1$. Moreover, the second-highest-degree terms in the two polynomials necessarily have the same coefficient, a fact that can be shown to be related to the condition of finiteness of the second moment. For example, a memory function

$$M(Q,t) = 2k_1(Q)\,\delta(t) + k_2(Q)\exp[-a(Q)t] \tag{13}$$

produces

$$\frac{\tilde{F}(Q,z)}{S(Q)} = \frac{z^2 + f_1(Q)z + f_2(Q)}{z^3 + g_1(Q)z^2 + g_2(Q)z + g_3(Q)} \tag{14}$$

with $f_1(Q)=g_1(Q)=k_1(Q)+a(Q)$, $f_2(Q)=k_1(Q)a(Q)+k_2(Q)$, $g_2(Q)=f_2(Q)+\langle\omega_Q^2\rangle$, and $g_3(Q)=a(Q)\langle\omega_Q^2\rangle$.

An explicit expression of the dynamic structure factor can then be obtained in more ways. One can set $z=i\omega$ in (10) and use (11) to get

$$I(Q,\omega) = \frac{1}{\pi}\frac{\langle\omega_Q^2\rangle M'(Q,\omega)}{[\omega^2 - \langle\omega_Q^2\rangle + \omega M''(Q,\omega)]^2 + [\omega M'(Q,\omega)]^2}, \tag{15}$$

where $\tilde{M}(Q,i\omega)=M'(Q,\omega)+iM''(Q,\omega)$. In particular, one has $M'(Q,\omega)=k_1$ and $M''(Q,\omega)=0$ for $M(Q,t)=2k_1\delta(t)$, and $M'(Q,\omega)=k_2 a/(\omega^2+a^2)$ and $M''(Q,\omega)=-\omega k_2/(\omega^2+a^2)$ for $M(Q,t)=k_2\exp(-at)$. Formula (15) is quite general and written in a very compact form. It tends, however, to hide some important properties of the specific memory-function model, that are better appreciated when $I(Q,\omega)$ is expressed in other equivalent forms.

Another expression for $I(Q,\omega)$ is found if one applies (11) with $\tilde{F}(Q,z)/S(Q)$ in the polynomial-ratio form (12). It is easily seen that $I(Q,\omega)$ too is obtained as a ratio of polynomials in the variable ω^2, where the highest-degree term in the denominator is of order ω^{2p}, and the highest-degree term in the numerator is, at most, of order ω^{2p-4}. Thus, $I(Q,\omega)$ appears immediately to have the required properties of being an even function of ω and of going to zero, for $\omega\to\pm\infty$, at least as fast as ω^{-4}.

A third, useful, way of writing the dynamic structure factor is obtained as follows. Starting again from (12), let $z_j(Q)$ be the p complex solutions of the equation

$$W(z) = 0. \tag{16}$$

Since the solutions of (16) are, in general, all distinct, one can find p complex coefficients $I_j(Q)$ such that

$$\frac{\tilde{F}(Q,z)}{S(Q)} = \sum_{j=1}^{p}\frac{I_j(Q)}{z - z_j(Q)}, \tag{17}$$

from which, using again (11), one finds

$$I(Q,\omega) = \frac{1}{\pi}\sum_{j=1}^{p}\frac{-\mathrm{Re}\,I_j\,\mathrm{Re}\,z_j + \mathrm{Im}\,I_j(\omega - \mathrm{Im}\,z_j)}{(\mathrm{Re}\,z_j)^2 + (\omega - \mathrm{Im}\,z_j)^2}. \tag{18}$$

Here and throughout this paper the Q dependence of z_j and I_j is omitted for simplicity. This last form of $I(Q,\omega)$ will be used repeatedly in the following.

The intermediate scattering function is, from (17),

$$\frac{F(Q,t)}{F(Q,0)} = \sum_{j=1}^{p} I_j\exp(z_j|t|), \tag{19}$$

which for $t=0$ gives the normalization

$$\sum_{j=1}^{p} I_j = 1. \tag{20}$$

The first time derivative of (19) is $\dot{F}(Q,t)/F(Q,0)$ $=\Sigma_{j=1}^{p}I_j(\pm z_j)\exp(z_j|t|)$, where the sign is in accord with the sign of t. Thus, the condition for the existence of a finite second moment of $I(Q,\omega)$ translates into

$$\sum_{j=1}^{p} I_j z_j = 0. \tag{21}$$

Further differentiation yields $\ddot{F}(Q,t)/F(Q,0) = \Sigma_{j=1}^{p} I_j z_j^2 \exp(z_j|t|)$, and from (9)

$$\langle \omega_Q^2 \rangle = -\sum_{j=1}^{p} I_j z_j^2. \tag{22}$$

If the third time derivative of $F(Q,t)/F(Q,0)$ is also zero at $t=0$, i.e., if $\Sigma_{j=1}^{p} I_j z_j^3 = 0$, a finite fourth moment is ensured and given by

$$\langle \omega_Q^4 \rangle = \sum_{j=1}^{p} I_j z_j^4. \tag{23}$$

This happens when the memory function has the correct starting value $M(Q,0)=\omega_L^2(Q)-\langle \omega_Q^2 \rangle$.

We end this section by noting that Eq. (19) implies that the real roots and the real part of the complex roots must be negative for the physical constraint that $F(Q,t)$ must decay to zero at large t. Also, from (12) and (17) it can be shown that [47]

$$I_j = \lim_{z \to z_j} \sum_{k=1}^{p} \frac{I_k}{z - z_k}(z - z_j) = \frac{V(z_j)}{\prod\limits_{k \neq j}^{p} (z_j - z_k)}. \tag{24}$$

For all the models of $I(Q,\omega)$ considered here, it will be shown that a value $Q_{\max}$ exists such that, for $0 < Q < Q_{\max}$, Eq. (16) has two complex conjugated solutions, which will be denoted throughout the paper as

$$z_A = z' + iz'', \quad z_B = z' - iz'', \tag{25}$$

where without loss of generality we can take $z'' > 0$. The other roots, if existing, are real, and will be referred to by means of subscripts C, D, … . Equation (24) shows that I_A and I_B are complex conjugated too

$$I_A = I' + iI'', \quad I_B = I' - iI'', \tag{26}$$

while if z_j is real, so is I_j. Finally, one easily realizes that the conjugated pair $z' \pm iz''$ contributes to (19) with a term that can be written as

$$2I' \exp(z'|t|) \frac{\cos(z''|t| - \varphi)}{\cos \varphi} \tag{27}$$

with $\tan \varphi = -I''/I'$. Thus, we will be dealing with an $F(Q,t)/F(Q,0)$ which is the sum of $p-2$ exponentially decaying terms plus one exponentially damped phase-shifted oscillation. The most frequently used expressions for $I(Q,\omega)$, considered in the following, are obtained from memory functions with $p=2$, 3, 4, or 5.

III. THE RAYLEIGH-BRILLOUIN TRIPLET

Before reviewing the various models adopted for the interpretation of $I(Q,\omega)$ data in classical fluids, it is convenient to begin with a detailed discussion of the Rayleigh-Brillouin (RB) triplet expression of $I(Q,\omega)$, since this is known to be an exact theoretical expression, although only valid asymptotically in the limit case $Q \to 0$. In fact, it is obtained from the linearized-hydrodynamics theory of a fluid continuum, which not only predicts the general form of $I(Q,\omega)$ but also establishes the explicit low-Q-dependence of the parameters in terms of products of Q^2 times an appropriate quantity related to well-defined thermophysical properties of the system. In practice, in the whole Q range that is typical of light scattering studies, the RB triplet is a working theory that accounts extremely well for the observed dynamics of dense fluids, so that it has actually been used to carry out spectroscopic measurements of various thermophysical quantities in a large number of substances.

The hydrodynamic theory [1,47,48] that leads to the expression of the RB spectrum is not formulated in terms of a memory function. Here, however, we highlight the underlying similarity among the various models of $I(Q,\omega)$ by recalling the derivation of the RB line shape from an appropriate expression for $M(Q,t)$. This has exactly the form (13),

$$M(Q,t) = 2\nu Q^2 \delta(t) + (\gamma_0 - 1)\langle \omega_0^2 \rangle \exp(-\gamma_0 D_T Q^2 t), \tag{28}$$

where $\nu = [(4/3)\eta_s + \eta_b]/mn$ is the kinematic longitudinal viscosity, defined through the shear (η_s) and bulk (η_b) viscosities, and $D_T = \lambda / nc_p$ is the thermal diffusivity with λ the thermal conductivity. Inserting the Laplace transform of (28) into (10) gives

$$\frac{\tilde{F}(Q,z)}{S(Q)} = \left(z + \frac{\langle \omega_0^2 \rangle}{z + \nu Q^2 + \dfrac{(\gamma_0 - 1)\langle \omega_0^2 \rangle}{z + \gamma_0 D_T Q^2}} \right)^{-1}, \tag{29}$$

or, equivalently, expression (14) with the coefficients

$$f_1(Q) = g_1(Q) = (\gamma_0 D_T + \nu) Q^2, \tag{30a}$$

$$f_2(Q) = (1 - 1/\gamma_0) c_s^2 Q^2 + \gamma_0 D_T \nu Q^4, \tag{30b}$$

$$g_2(Q) = c_s^2 Q^2 + \gamma_0 D_T \nu Q^4, \tag{30c}$$

$$g_3(Q) = D_T c_s^2 Q^4. \tag{30d}$$

Following the procedure outlined in Sec. II, we consider the cubic equation (16) obtained by setting, for each Q, the denominator of (14) equal to zero:

$$z^3 + g_1(Q) z^2 + g_2(Q) z + g_3(Q) = 0. \tag{31}$$

We demonstrate in Appendix A the existence of one real and two complex conjugated roots of (31) for a certain range $0 < Q < Q_{\max}$. Being the three roots necessarily distinct, it is possible to write (14) in the form (17) with $j=A,B,C$,

$$\frac{\widetilde{F}(Q,z)}{S(Q)} = \frac{I_A}{z-z_A} + \frac{I_B}{z-z_B} + \frac{I_C}{z-z_C}, \tag{32}$$

where, as shown in Sec. II, z_C denotes the real root and I_C is real. The solutions of (31) obey the well-known Viète relations

$$z_A + z_B + z_C = 2z' + z_C = -g_1(Q), \tag{33a}$$

$$z_A z_B + (z_A + z_B) z_C = z'^2 + z''^2 + 2z' z_C = g_2(Q), \tag{33b}$$

$$z_A z_B z_C = (z'^2 + z''^2) z_C = -g_3(Q). \tag{33c}$$

The conditions of normalization (20) and of existence of a finite second moment (21) give

$$2I' + I_C = 1, \tag{34a}$$

$$2I' z' - 2I'' z'' + I_C z_C = 0. \tag{34b}$$

For later use we define the quantity $b = -I''/I'$, which from (34) is found to be $b = -[I_C z_C/(1-I_C) + z']/z''$. Moreover, from (24), (30d), and (33c), one obtains

$$I_C = \frac{z'^2 + z''^2}{(z_C - z')^2 + z''^2}\left(1 + \frac{z_C}{\gamma_0 D_T Q^2}\right). \tag{35}$$

Thus, once the roots z_j are found, expression (32) is fully determined. Finally, making use of (22), (34), (30d), and (33c), one finds that $-\Sigma I_j z_j^2$ gives the second moment value (7), while the condition of existence of a finite fourth moment is not satisfied, since $\Sigma I_j z_j^3 = \nu Q^2 \langle \omega_0^2 \rangle$ which is a nonzero quantity.

By taking the real part of (32) with $z = i\omega$, introducing the positive quantities

$$z_h = -z_C, \quad z_s = -z', \quad \omega_s = z'', \tag{36}$$

and defining

$$I_h = I_C, \quad I_s = I', \quad b_s = b, \tag{37}$$

the usual formula for the RB triplet [1–3,47]

$$I(Q,\omega) = \frac{1}{\pi}\left(I_h \frac{z_h}{\omega^2 + z_h^2} + I_s \frac{z_s + b_s(\omega + \omega_s)}{(\omega + \omega_s)^2 + z_s^2} + I_s \frac{z_s - b_s(\omega - \omega_s)}{(\omega - \omega_s)^2 + z_s^2} \right) \tag{38}$$

is obtained. Subscripts h and s remind the identification of the central (Rayleigh) Lorentzian line with a *heat* mode, and of the side (Brillouin) peaks with *sound* modes, following the notation of Ref. [5]. In (38) ω_s is the frequency shift of the inelastic lines, z_h and z_s have the usual meaning of half-width at half-maximum of the central and shifted Lorentzian lines, respectively, I_h and I_s are the corresponding amplitudes, given by (35) and (34a) as

$$I_h = \frac{z_s^2 + \omega_s^2}{(z_h - z_s)^2 + \omega_s^2}\left(1 - \frac{z_h}{\gamma_0 D_T Q^2}\right), \tag{39}$$

$$I_s = \frac{1 - I_h}{2}, \tag{40}$$

while

$$b_s = \frac{1}{\omega_s}\left(\frac{I_h}{1 - I_h} z_h + z_s\right) \tag{41}$$

is an "asymmetry parameter" which distorts the pure Lorentzian shape of the Brillouin lines and has the right expression to ensure a convergent second moment of $I(Q,\omega)$. The corresponding intermediate scattering function is, in agreement with (19) and (27),

$$\frac{F(Q,t)}{F(Q,0)} = I_h e^{-z_h|t|} + 2I_s e^{-z_s|t|} \frac{\cos(\omega_s|t| - \varphi)}{\cos\varphi} \tag{42}$$

with the phase shift φ given by $\tan\varphi = b_s$.

The values of z_h, z_s, ω_s, I_h, I_s, and b_s for an arbitrary Q value (provided that $Q < Q_{\max}$) can only be obtained from the solution of (31) and use of (36) and (37). However, the asymptotic $Q \to 0$ behaviors have explicit expressions (see Appendix A),

$$z_h = D_T Q^2 - (\gamma_0 - 1)(\nu - D_T)\frac{D_T^2 Q^4}{c_s^2} + O(Q^6), \tag{43}$$

$$z_s = \frac{[(\gamma_0 - 1)D_T + \nu]Q^2}{2} + \frac{(\gamma_0 - 1)(\nu - D_T)D_T^2 Q^4}{2c_s^2} + O(Q^6), \tag{44}$$

$$\omega_s = c_s Q - [(\gamma_0 - 1)(\gamma_0 + 3)D_T^2 - 2(\gamma_0 - 1)D_T \nu + \nu^2]\frac{Q^3}{8c_s} + O(Q^5), \tag{45}$$

and, using (39)–(41), $I_h = (1 - 1/\gamma_0) + O(Q^2)$, $I_s = 1/(2\gamma_0) + O(Q^2)$, and $b_s = [3(\gamma_0 - 1)D_T + \nu]Q/(2c_s) + O(Q^3)$.

IV. MODELS FOR THE DYNAMIC STRUCTURE FACTOR

A. The generalized hydrodynamic model

Based on the fact that the RB triplet is the exact behavior predicted by the linearized-hydrodynamics theory in the $Q \to 0$ limit, it is a straightforward generalization to take it as a possible model of $I(Q,\omega)$ also for situations where its application with exact hydrodynamic coefficients cannot account properly for the spectral shape. The RB triplet so becomes a fit function which we will refer to as the "generalized hydrodynamic model" [49]. The memory function is still written in the form (28),

$$M(Q,t) = 2B(Q)\delta(t) + (\gamma(Q) - 1)\langle \omega_Q^2 \rangle \exp[-\Gamma_T(Q)t], \tag{46}$$

but the four parameters become unknown functions of Q to be determined, which at small Q can be represented by series expansions with dominant, lowest-order, terms fixed by the exact RB theory. Thus, for $Q \to 0$ we have $\gamma(Q) \sim \gamma_0$,

$B(Q) \sim \nu Q^2$, $\Gamma_T(Q) \sim \gamma_0 D_T Q^2$, and $\langle \omega_Q^2 \rangle \sim \langle \omega_0^2 \rangle$. Equation (14) is still valid, with coefficients given now by the generalization of (30),

$$f_1(Q) = g_1(Q) = B(Q) + \Gamma_T(Q), \tag{47a}$$

$$f_2(Q) = B(Q)\Gamma_T(Q) + (\gamma(Q) - 1)\langle \omega_Q^2 \rangle, \tag{47b}$$

$$g_2(Q) = B(Q)\Gamma_T(Q) + \gamma(Q)\langle \omega_Q^2 \rangle, \tag{47c}$$

$$g_3(Q) = \Gamma_T(Q)\langle \omega_Q^2 \rangle. \tag{47d}$$

The spectrum $I(Q,\omega)$ is still given by (38), where, however, the Q dependence of the quantities z_h, z_s, ω_s, I_h, I_s, and b_s will be, in general, different from that of linearized hydrodynamics. Expression (42) for the intermediate scattering function remains also valid. The mathematical structure underlying (29) and (38) is preserved and ensures the persisting validity of the result (33), (40), and (41), with (39) rewritten as

$$I_h = \frac{z_s^2 + \omega_s^2}{(z_h - z_s)^2 + \omega_s^2}\left(1 - \frac{z_h}{\Gamma_T(Q)}\right). \tag{48}$$

It is then clear that, in order to fit (38) to experimental data at a given Q value, one needs to let four parameters free: the frequency ω_s, the line widths z_h and z_s, and one amplitude parameter, say I_h, accounting for the actually observed distribution of intensity among the three lines of the spectrum. (In addition, an overall normalization constant should also be fitted if the spectral data are not normalized or normalizable.) From the fitted parameters, it is easy to derive the original parameters of (46): once $\Gamma_T(Q)$ is found from (48), and rewriting (33) in terms of z_h, z_s, ω_s, one obtains $B(Q)$ and $\langle \omega_Q^2 \rangle$ from (47a) and (47d), and finally, (47c) can be inverted to yield $\gamma(Q)$. The results are

$$\Gamma_T(Q) = z_h\left(1 - I_h\frac{(z_h - z_s)^2 + \omega_s^2}{z_s^2 + \omega_s^2}\right)^{-1}, \tag{49a}$$

$$B(Q) = z_h + 2z_s - \Gamma_T(Q), \tag{49b}$$

$$\langle \omega_Q^2 \rangle = \frac{z_h(z_s^2 + \omega_s^2)}{\Gamma_T(Q)}, \tag{49c}$$

$$\gamma(Q) = \frac{2z_h z_s + z_s^2 + \omega_s^2 - B(Q)\Gamma_T(Q)}{\langle \omega_Q^2 \rangle}. \tag{49d}$$

B. The damped harmonic oscillator model

In the context of the collective dynamics of liquids, the damped harmonic oscillator (DHO) model can be viewed as a simplified version of the hydrodynamic theory, corresponding to the special case of an RB triplet with $\gamma_0 = 1$. If the other parameters are given the same Q dependence as in (28), the resulting spectrum is therefore only suitable for describing the very-low-Q dynamics of a system with $\gamma_0 = 1$, a rather special case indeed. The DHO model is, as a fact, typically used, at larger Q values, as a fit function with Q-dependent free parameters. However, its properties can be more easily understood if one first assumes for the memory function the explicit Q dependence of (28), obtaining simply $M(Q,t) = 2\nu Q^2 \delta(t)$. The presence of the δ-function qualifies the DHO as another model for which no even moment of $I(Q,\omega)$ of higher-than-second order is finite. Equation (10) becomes $\widetilde{F}(Q,z)/S(Q) = [z + \langle \omega_0^2 \rangle/(z + \nu Q^2)]^{-1}$, and (12) is obtained as

$$\frac{\widetilde{F}(Q,z)}{S(Q)} = \frac{z + f_1(Q)}{z^2 + g_1(Q)z + g_2(Q)}, \tag{50}$$

with the coefficients $f_1(Q) = g_1(Q) = \nu Q^2$ and $g_2(Q) = c_s^2 Q^2$. Note that now, because $\gamma_0 = 1$, $\langle \omega_0^2 \rangle = c_s^2 Q^2$, and the adiabatic sound speed coincides here with the isothermal one. The second-degree polynomial in the denominator of (50) has, in the range $0 < Q < Q_{\max} = 2c_s/\nu$, two complex conjugated roots written as in (25) with

$$z' = -\frac{\nu Q^2}{2}, \tag{51a}$$

$$z'' = c_s Q\sqrt{1 - \left(\frac{\nu Q^2/2}{c_s Q}\right)^2}. \tag{51b}$$

Thus, thanks to its simplicity, the DHO model with fixed Q dependence of the parameters has explicit expressions for the roots z_j. It must be noted that, with $\gamma_0 = 1$, all higher-order terms in (44) can be shown to vanish leaving (51a), while (45) reduces exactly to the series expansion of the square root of (51b).

Expression (50) can be written as $\widetilde{F}(Q,z)/S(Q) = I_A/(z - z_A) + I_B/(z - z_B)$ with I_A and I_B defined as in (26), $I_A + I_B = 1$ (or $I' = 1/2$), and $b = -I''/I' = -z'/z''$. The spectrum $I(Q,\omega)$, using again the identifications (36) and (37) for z_s, ω_s, and b_s, is

$$I(Q,\omega) = \frac{1}{\pi}\left(\frac{1}{2}\frac{z_s + b_s(\omega + \omega_s)}{(\omega + \omega_s)^2 + z_s^2} + \frac{1}{2}\frac{z_s - b_s(\omega - \omega_s)}{(\omega - \omega_s)^2 + z_s^2}\right), \tag{52}$$

as it was recognized in Ref. [50]. This shows that the DHO line shape is a doublet of inelastic lines having the same formal expression as in the RB triplet (38). We will come back to this point later in this section. Here we remind that the form (52) should not induce one to expect an always evident two-peak spectrum, since, with increasing Q, the amount of overlap of the two lines increases until they merge into a single central line. The intermediate scattering function is simply

$$\frac{F(Q,t)}{F(Q,0)} = e^{-z_s|t|}\frac{\cos(\omega_s|t| - \varphi)}{\cos\varphi} \tag{53}$$

with $\tan\varphi = b_s = z_s/\omega_s$.

The DHO model is customarily written not as in (52) but in the form (15),

$$I(Q,\omega)=\frac{1}{\pi}\frac{2\Gamma\Omega^2}{(\omega^2-\Omega^2)^2+4\Gamma^2\omega^2}, \tag{54}$$

where Ω^2 is an usual substitute for $\langle\omega_0^2\rangle$. The parameters in (52) and (54) are related by

$$\Gamma=\frac{\nu Q^2}{2}=z_s, \tag{55}$$

$$\Omega^2=\omega_s^2+z_s^2. \tag{56}$$

As already noticed, the DHO line shape has only found practical application, in the form (54), as a fit model corresponding to the memory function $M(Q,t)=4\Gamma(Q)\delta(t)$, by letting Γ and Ω be free Q-dependent parameters (with Ω^2 now standing, in general, for $\langle\omega_Q^2\rangle$). However, the lack of a central peak makes it too rough a model in most cases. Thus, it is usual practice to let the DHO doublet play the role of describing the inelastic peaks due to the viscous relaxation, and to supplement the model with an extra central line, most often of Lorentzian shape. The result is nothing else than recovering the generalized hydrodynamic model of Sec. IV A, except for the introduction of an unnecessary inconsistency. Indeed, the addition of a Lorentzian line to a spectrum having a finite second moment unavoidably makes the latter diverge to infinity. The asymmetry parameter b_s in (52) has, in fact, the correct value for the situation where no central line is present, a value that cannot be maintained when a Lorentzian line is added to $I(Q,\omega)$. In other words, the fit model obtained by such a modification of the pure DHO spectrum has inelastic peaks with a wrong asymmetry. Despite the formal identity of (52) with the inelastic part of the generalized hydrodynamic model, in order to recover the latter by modifying the DHO expression, one should add to this not only the missing central Lorentzian line, but also another symmetric term, centered at $\omega=0$, that restores the correct large-ω behavior. It is, in fact, easy to rewrite (38) as

$$I(Q,\omega)=\frac{1}{\pi}\frac{I_h z_h}{\omega^2+z_h^2}+\frac{2I_s}{\pi}\frac{2\Gamma\Omega^2}{(\omega^2-\Omega^2)^2+4\Gamma^2\omega^2}+\frac{I_h z_h}{\pi}\frac{\Omega^2-\omega^2}{(\omega^2-\Omega^2)^2+4\Gamma^2\omega^2},$$

with Γ and Ω given by (55) and (56). The second term is a DHO spectrum (normalized to $1-I_h$), while the last term does not contribute to the zeroth moment.

C. The viscoelastic model

The so-called viscoelastic model is a widely used representation of the dynamics of collective modes. The physical reasons behind the introduction of this model are clearly exposed in Ref. [2] and will not be recalled here. We only mention one distinctive property of the model, that marks its difference from those of Secs. IV A and IV B, namely the fact that the memory function now has the correct, finite, zero-time value $M(Q,0)=\omega_L^2(Q)-\langle\omega_Q^2\rangle$, which implies the existence of a finite fourth moment of $I(Q,\omega)$. This result is simply the consequence of having removed the δ-function term from (46), by replacing it with an exponentially decaying term, so that

$$M(Q,t)=\Delta_L^2(Q)\exp[-t/\tau(Q)]+[\gamma(Q)-1]\langle\omega_Q^2\rangle\times\exp[-\Gamma_T(Q)t], \tag{57}$$

where we have set $\Delta_L^2(Q)=\omega_L^2(Q)-\gamma(Q)\langle\omega_Q^2\rangle$ following the notation of Ref. [34]. The term "viscoelastic" was originally attributed to a simpler model where $\gamma(Q)=1$ in the above formula, so that $M(Q,t)$ is made of only the first exponential term [51]. We will not consider this model here, reserving the name "viscoelastic" to the more general case of (57). In (57) $\tau(Q)$ denotes the new time constant, $\omega_L^2(Q)$ is defined as in (8), and all other symbols retain the same meaning as in (46). All the parameters entering (57) are to be fitted to the data, and are unknown functions of Q except for the $Q\to 0$ behavior, which, as for the generalized hydrodynamic model, is known to be $\gamma(Q)\sim\gamma_0$, $\Gamma_T(Q)\sim\gamma_0 D_T Q^2$, and $\langle\omega_Q^2\rangle\sim\langle\omega_0^2\rangle$, and moreover, $\omega_L^2(Q)\sim c_L^2 Q^2$.

As for the low-Q behavior of $\tau(Q)$, an important feature of the viscoelastic model is that $1/\tau(Q)$ does not vanish for $Q\to 0$ [2], but tends to a limit value $1/\tau_0$. Inserting the Laplace transform of (57) into (10) gives

$$\frac{\tilde{F}(Q,z)}{S(Q)}=\left(z+\frac{\langle\omega_Q^2\rangle}{z+\dfrac{\Delta_L^2(Q)}{z+1/\tau(Q)}+\dfrac{[\gamma(Q)-1]\langle\omega_Q^2\rangle}{z+\Gamma_T(Q)}}\right)^{-1}. \tag{58}$$

Then, for the viscoelastic model to go over onto the RB triplet predicted by theory for $Q\to 0$, the term $\Delta_L^2(Q)/[z+1/\tau(Q)]$ in (58) should behave as the corresponding term of (29), namely as νQ^2. Since $\Delta_L^2(Q)$ goes to zero as Q^2, this condition implies a nonzero limit for $1/\tau(Q)$, so that, being the spectrum confined to lower frequencies the lower is Q, when the condition $\omega\tau\ll 1$ is fulfilled $1/\tau(Q)$ dominates over z and the denominator tends to a constant. This argument fixes the value of τ_0 through the relationship $1/\tau_0=(c_L^2-c_s^2)/\nu$ [2].

The viscoelastic expression of $I(Q,\omega)$ is usually written in the form (15) with

$$M'(Q,\omega)=\frac{\Delta_L^2(Q)\dfrac{1}{\tau(Q)}}{\omega^2+\left(\dfrac{1}{\tau(Q)}\right)^2}+\frac{[\gamma(Q)-1]\langle\omega_Q^2\rangle\Gamma_T(Q)}{\omega^2+\Gamma_T^2(Q)}, \tag{59a}$$

$$M''(Q,\omega)=-\omega\frac{\Delta_L^2(Q)}{\omega^2+\left(\dfrac{1}{\tau(Q)}\right)^2}-\omega\frac{[\gamma(Q)-1]\langle\omega_Q^2\rangle}{\omega^2+\Gamma_T^2(Q)}. \tag{59b}$$

Here, proceeding as in Sec. IV A, we write

$$\frac{\widetilde{F}(Q,z)}{S(Q)}=\frac{z^3+f_1(Q)z^2+f_2(Q)z+f_3(Q)}{z^4+g_1(Q)z^3+g_2(Q)z^2+g_3(Q)z+g_4(Q)}\tag{60}$$

with

$$f_1(Q)=g_1(Q)=\frac{1}{\tau(Q)}+\Gamma_T(Q),\tag{61a}$$

$$f_2(Q)=\frac{\Gamma_T(Q)}{\tau(Q)}+\omega_L^2(Q)-\langle\omega_Q^2\rangle,\tag{61b}$$

$$f_3(Q)=\Delta_L^2(Q)\Gamma_T(Q)+\frac{[\gamma(Q)-1]\langle\omega_Q^2\rangle}{\tau(Q)},\tag{61c}$$

$$g_2(Q)=\frac{\Gamma_T(Q)}{\tau(Q)}+\omega_L^2(Q),\tag{61d}$$

$$g_3(Q)=\Delta_L^2(Q)\Gamma_T(Q)+\langle\omega_Q^2\rangle\left(\Gamma_T(Q)+\frac{\gamma(Q)}{\tau(Q)}\right),\tag{61e}$$

$$g_4(Q)=\frac{\langle\omega_Q^2\rangle\Gamma_T(Q)}{\tau(Q)},\tag{61f}$$

and we set to zero the denominator of (60) to get the quartic equation (16),

$$z^4+g_1(Q)z^3+g_2(Q)z^2+g_3(Q)z+g_4(Q)=0.\tag{62}$$

We show in Appendix B that, for $0<Q<Q_{\max}$, two of the four solutions of (62) are real and different (z_C,z_D) and the other two are complex conjugated, so that all four roots are distinct. Then one can write

$$\frac{\widetilde{F}(Q,z)}{S(Q)}=\frac{I_A}{z-z_A}+\frac{I_B}{z-z_B}+\frac{I_C}{z-z_C}+\frac{I_D}{z-z_D},\tag{63}$$

with real I_C and I_D, and I_A and I_B given by (25). Equations (20) and (21) give

$$2I'+I_C+I_D=1,\tag{64a}$$

$$2I'z'-2I''z''+I_Cz_C+I_Dz_D=0.\tag{64b}$$

Using again (36) and (37) and introducing the two new symbols $z_2=-z_D$ and $I_2=I_D$, (64) gives

$$b_s=\frac{1}{\omega_s}\left(\frac{I_hz_h+I_2z_2}{1-I_h-I_2}+z_s\right).\tag{65}$$

It can also be shown that

$$I_h=\frac{z_s^2+\omega_s^2}{(z_h-z_s)^2+\omega_s^2}\left(\frac{z_2}{z_2-z_h}\right)\left(1-\frac{z_h(2z_s+z_2)}{\Gamma_T(Q)/\tau(Q)}\right),\tag{66}$$

$$I_2=\frac{z_s^2+\omega_s^2}{(z_2-z_s)^2+\omega_s^2}\left(\frac{z_h}{z_h-z_2}\right)\left(1-\frac{z_2(2z_s+z_h)}{\Gamma_T(Q)/\tau(Q)}\right),\tag{67}$$

so that, by solving, for example, (66) for $\Gamma_T(Q)/\tau(Q)$ and substituting into (67), and using (64) and (65), I_2, I_s, and b_s can all be expressed in terms of I_h. The Viète formulas for Eq. (62) are

$$2z_s+z_h+z_2=g_1(Q),\tag{68a}$$

$$z_s^2+\omega_s^2+2z_s(z_h+z_2)+z_hz_2=g_2(Q),\tag{68b}$$

$$(z_s^2+\omega_s^2)(z_h+z_2)+2z_sz_hz_2=g_3(Q),\tag{68c}$$

$$(z_s^2+\omega_s^2)z_hz_2=g_4(Q).\tag{68d}$$

By using (65), (66), (68d), and (61f), it can be shown that $-\Sigma I_jz_j^2$ coincides with $\langle\omega_Q^2\rangle$, as dictated by (22), and that $\Sigma I_jz_j^3=0$, ensuring a finite fourth moment whose value, using (8), turns out to be the expected (23).

The whole development expressed by formulas (60)–(68) follows closely the analogous treatment of Sec. IV A. It is then clear that, by pursuing it one step further, (63) can be translated, by means of (11), into an expression for $I(Q,\omega)$ alternative to the usual one and similar to (38),

$$I(Q,\omega)=\frac{1}{\pi}\left(I_h\frac{z_h}{\omega^2+z_h^2}+I_2\frac{z_2}{\omega^2+z_2^2}+I_s\frac{z_s+b_s(\omega+\omega_s)}{(\omega+\omega_s)^2+z_s^2}+I_s\frac{z_s-b_s(\omega-\omega_s)}{(\omega-\omega_s)^2+z_s^2}\right).\tag{69}$$

The spectrum (69) has thus a four-line structure, which, compared to (38), has one more central Lorentzian. Appendix B shows that for $Q\to 0$ the widths z_h and z_s behave as the corresponding quantities of the generalized hydrodynamic model, while z_2 does not vanish as Q^2 but tends to $1/\tau_0$. The asymmetry parameter b_s has, as for the other models, the right value to ensure finiteness of the second moment. I_h, I_s, and b_s also behave for $Q\to 0$ as in the hydrodynamic model. The presence of the second central line ensures a finite fourth moment, and it is therefore not surprising that, in the $Q\to 0$ limit, I_2 goes to zero as Q^4 in order to recover expression (38), as also shown in Appendix B. The intermediate scattering function is immediately written as

$$\frac{F(Q,t)}{F(Q,0)}=I_he^{-z_h|t|}+I_2e^{-z_2|t|}+2I_se^{-z_s|t|}\frac{\cos(\omega_s|t|-\varphi)}{\cos\varphi},\tag{70}$$

where, as usual, $\tan\varphi=b_s$ with b_s given by (65).

When the viscoelastic model is applied in the form given by (15) and (59), the five quantities appearing in (57) are used as fit parameters. We observe that, alternatively and in full analogy with what is done in Sec. IV A, one can use (69) as a fit function, for each given Q value, with free parameters z_h, z_2, z_s, ω_s, and I_h. In terms of these, the original parameters of the memory function can be derived as follows. The product $P=\Gamma_T(Q)[1/\tau(Q)]$ is taken from (66), while the sum $S=\Gamma_T(Q)+1/\tau(Q)$ is obtained by equating (61a) and (68a). Then $\Gamma_T(Q)$ and $1/\tau(Q)$ are immediately calculated as the solutions of $x^2-Sx+P=0$. From (61f), one has $\langle\omega_Q^2\rangle=g_4(Q)\tau(Q)/\Gamma_T(Q)$, with $g_4(Q)$ given by (68d), while, analogously, $\omega_L^2(Q)$ can be taken, for example, from (61d) using (68b). Finally, $\gamma(Q)$ is obtained through (61e) and (68c). The results are

$$\frac{\Gamma_T(Q)}{\tau(Q)} = z_h(2z_s + z_2)\left[1 - I_h \frac{(z_h - z_s)^2 + \omega_s^2}{z_s^2 + \omega_s^2}\left(\frac{z_2 - z_h}{z_2}\right)\right]^{-1}, \tag{71a}$$

$$\Gamma_T(Q) + \frac{1}{\tau(Q)} = z_h + z_2 + 2z_s, \tag{71b}$$

$$\omega_L^2(Q) = z_h z_2 + 2z_s(z_h + z_2) + z_s^2 + \omega_s^2 - \frac{\Gamma_T(Q)}{\tau(Q)}, \tag{71c}$$

$$\langle \omega_Q^2 \rangle = \frac{z_h z_2 (z_s^2 + \omega_s^2)}{\Gamma_T(Q)/\tau(Q)}, \tag{71d}$$

$$\gamma(Q) = \frac{1}{\Gamma_T(Q) - \dfrac{1}{\tau(Q)}}\left(\Gamma_T(Q) - \frac{1}{\langle \omega_Q^2 \rangle}[2z_h z_2 z_s + (z_h + z_2) \times (z_s^2 + \omega_s^2) - \omega_L^2(Q)\Gamma_T(Q)]\right). \tag{71e}$$

The formulation (69) of the viscoelastic model as a four-line fit function was not reported before. Nonetheless, a nearly identical expression for $I(Q,\omega)$ had been derived earlier in a different context. The linearized-hydrodynamics theory that leads to the RB triplet was indeed modified by Mountain [52] to account for the thermal relaxation that arises in molecular fluids because of the coupling between translational and intramolecular degrees of freedom. A theoretical expression for $I(Q,\omega)$, to be used in the typical Q range of Brillouin light scattering, was thus obtained. Similarly to the case of the RB triplet, this expression was not derived in the framework of the memory function theory, but it can be shown to correspond to the assumption that

$$M(Q,t) = 2\nu_1 Q^2 \delta(t) + \frac{\nu_2 Q^2}{\tau_0}\exp(-t/\tau_0) + (\gamma_0 - 1)\langle \omega_0^2 \rangle \times \exp(-\gamma_0 D_T Q^2 t). \tag{72}$$

The theory determines the parameters as explicit functions of Q as in (28), from which (72) differs for the fact that the viscosity contribution is split in two terms. The first, where ν_1 plays the same role as ν in (28), contributes to $\widetilde{M}(Q,z)$ with a z-independent term, while the second accounts for a frequency-dependent viscosity, with $1/\tau_0=(c_L^2-c_s^2)/\nu_2$ [47,52]. If one takes in (72) $\nu_1=0$ and identifies ν_2 with the total viscosity, one obtains immediately the $Q\to 0$ behavior of (57). Apart from the presence in (72) of the $\delta(t)$-term, which, as usual, produces an infinite fourth moment, the mathematical structure of $I(Q,\omega)$ is the same as in the viscoelastic model. In particular, it was shown that, under the approximation $D_T Q^2 \tau_0 \ll 1$ [52], the spectrum is made of two central Lorentzian lines, corresponding to nonpropagating modes, and two shifted Brillouin lines, also represented by undistorted Lorentzians. However, the expression of $I(Q,\omega)$ can be derived exactly, recovering the correct asymmetric shape of the inelastic peaks and obtaining a result formally identical to (69). The low-Q behavior is given by $z_h=D_T Q^2+O(Q^4)$, $z_2=1/\tau_0-\nu_2 Q^2+O(Q^4)$, and $z_s=[(\gamma_0-1)D_T+(\nu_1+\nu_2)]Q^2/2+O(Q^4)$ for the line widths, $\omega_s=c_s Q+O(Q^3)$ for the Brillouin frequency, and $I_h=(1-1/\gamma_0)+O(Q^2)$, $I_2=\nu_2 Q^2\langle\omega_0^2\rangle\tau_0^3+O(Q^6)$, $I_s=1/(2\gamma_0)+O(Q^2)$, and $b_s=[3(\gamma_0-1)D_T+(\nu_1+\nu_2)]Q/(2c_s)+O(Q^3)$ for the amplitude parameters. The second central Lorentzian behaves thus, for $Q\to 0$, as in the viscoelastic fit model, with an amplitude vanishing as Q^4 and a width tending to $1/\tau_0$. The $I(Q,\omega)$ expression of the Mountain theory has not been used as a fit model, with freely Q-dependent parameters, in Q ranges outside the Brillouin light scattering regime.

D. The "two-time" viscoelastic model

The viscoelastic model has also found application as a fit function for $I(Q,\omega)$ in an extended version allowing for the presence of one more relaxation mechanism on a time scale quite different from that given by $\tau(Q)$ in (57). From physical intuition it is expected [2,45] that such an additional relaxation should play a significant role in the low-Q regime. The memory function for this model, named here the "two-time" viscoelastic model, reads [2]

$$M(Q,t) = \Delta_L^2(Q)\left[[1-\alpha(Q)]\exp\left(-\frac{t}{\tau_1(Q)}\right) + \alpha(Q) \times \exp\left(-\frac{t}{\tau_2(Q)}\right)\right] + [\gamma(Q)-1]\langle\omega_Q^2\rangle\exp[-\Gamma_T(Q)t],$$

where $\tau_1(Q)$ is the relaxation time already introduced in (57), $\tau_2(Q)$ is a second, larger, time constant, and $\alpha(Q)$ is a weight factor determining the relative strength of the two relaxation processes, with $0\leqslant\alpha(Q)\leqslant 1$. All other symbols are the same as in (57). This model will not be discussed in detail in this work. We only recall that Eq. (16) is now of fifth degree, and that by the method applied in Appendix B one finds for $0<Q<Q_{\max}$ the usual pair of complex conjugated solutions z_A and z_B plus three real solutions z_C, z_D, and z_E, giving rise to a spectrum composed of five lines. The argument that in Sec. IV C led to the result that, for $Q\to 0$, $1/\tau(Q)$ has the nonzero limit $1/\tau_0$ can be repeated here to show that both $1/\tau_1(Q)$ and $1/\tau_2(Q)$ must tend to nonzero limits $1/\tau_{10}$ and $1/\tau_{20}$, which, however, cannot be uniquely determined. One finds, in fact [45], $1/t_0=(c_L^2-c_s^2)/\nu$ where $1/t_0=(1-\alpha_0)/\tau_{10}+\alpha_0/\tau_{20}$ and α_0 is the $Q\to 0$ limit of $\alpha(Q)$.

The lowest-order terms in the power expansions of the parameters of the model for $I(Q,\omega)$, with the usual symbols, are obtained as $z_h\sim D_T Q^2$, $z_2\sim 1/\tau_{10}$, and $z_3=-z_E\sim 1/\tau_{20}$ for the widths of the central lines, while the Brillouin frequency behaves as $\omega_s\sim c_s Q$. For the width of the inelastic lines one finds $z_s\sim[(\gamma_0-1)D_T+K\nu]Q^2/2$, where $K=1+\alpha_0(1-\alpha_0)(\tau_{20}-\tau_{10})^2/\tau_{10}\tau_{20}$. Note that $K>1$ always, unless $\alpha_0=0$ or 1, or $\tau_{10}=\tau_{20}$. The amplitudes are, to lowest order, $I_h\sim(1-1/\gamma_0)$, $I_2\sim\nu Q^2\langle\omega_0^2\rangle(1-\alpha_0)\tau_{10}^4/t_0$, and $I_3=I_E\sim\nu Q^2\langle\omega_0^2\rangle\alpha_0\tau_{20}^4/t_0$, and

TABLE I. Number of spectral lines for $0<Q<Q_{\max}$ in the various expressions for $I(Q,\omega)$ considered in the paper. p is the degree of Eq. (16) and the total number of lines, $p-2$ is the number of Lorentzian lines in the central peak.

Model	p	$\langle\omega_Q^4\rangle$	No of central lines	Section
RB triplet (from theory)	3	∞	1	III
Mountain theory	4	∞	2	IV C
Generalized hydrodynamic	3	∞	1	IV A
DHO	2	∞	0	IV B
Simplified viscoelastic	3	Finite	1	IV C
Viscoelastic	4	Finite	2	IV C
“Two-time” viscoelastic	5	Finite	3	IV D

also $I_s \sim 1/(2\gamma_0)$ with $b_s \sim [3(\gamma_0-1)D_T+K\nu]Q/(2c_s)$. Thus, in the asymptotic $Q\rightarrow 0$ regime, this model does not tend to the behavior of the RB triplet or of the generalized hydrodynamic model, unless it reduces, with $K=1$, to the viscoelastic model with one relaxation time described in Sec. IV C.

E. Summary of the properties of the various fit models

By writing in the form (17) the various models reviewed in this section, one sees that in all cases two complex roots of Eq. (16) correspond to a pair of inelastic lines. The number of elastic Lorentzian lines that build up the central peak of the spectrum is equal to the number $p-2$ of exponential terms present in the assumed form of $M(Q,t)$. We remark that the presence of a $\delta(t)$-term in the memory function has no relation with the number of modes, but only with the absence or existence of a finite fourth moment. The situation is summarized in Table I, where for completeness we also include the exact theoretical results expressed by the RB triplet and the Mountain theory [47,52], and the simplified viscoelastic fit model mentioned at the beginning of Sec. IV C [formula (57) with $\gamma(Q)=1$].

V. ENERGY AND DAMPING OF THE ACOUSTIC EXCITATIONS

The question of how to determine in an unambiguous way the frequencies of the acoustic modes as a function of Q, i.e., the so-called “dispersion curve,” though obviously a fundamental one, is not settled yet. Indeed, different authors assign the role of representing the excitation frequency to different fit parameters or other quantities.

In the Q range where $I(Q,\omega)$ shows clear and well-separated peaks, as it happens in the light scattering case unless the fluid is a very dilute gas [53–55], the assignment of frequencies to such peaks is a rather trivial task, that can be carried out in different ways, even including visual inspection, all leading to virtually indistinguishable results. This observation may misleadingly suggest to apply the same criteria for the determination of the excitation frequencies in other dynamical situations at larger Q's. However, in the Q range typical of neutron or x-ray scattering, instead of a three-sharp-line spectrum, a less structured line shape is often observed, where the presence of the excitations is indicated by, at most, weak side shoulders. In these cases, different methods give rise, for the same data, to a variety of dispersion curves. As a consequence, the comparison of works performed by authors employing different criteria has been in many cases rendered very hard, if not impossible at all.

In addition to the problem of determining the mode frequencies, an analogous confusion exists on how to evaluate the Q range where collective excitations have a propagating nature, ranging from the rather naive point of view that modes only propagate when they give rise to evident inelastic spectral features to the distinction between underdamped and overdamped excitations based on various, sometimes qualitative, criteria. Here too, use of a common language would facilitate comparisons between works on different (classes of) systems and help to gain an overall view of the microscopic dynamics of fluids.

We will here consider in more detail the two problems mentioned above, starting from the determination of the mode frequencies. We first recall that, as shown by (45), the $Q\rightarrow 0$ limit behavior of the dispersion curve has the linear form c_sQ [47]. However, at $Q>0$, the hydrodynamic theory introduces, through the prescripted Q dependence of the parameters entering (28), a deviation from linearity, as shown by the presence of the viscosities and thermal diffusion in the next-order term of (45). Moreover, it is clear that a linear dependence on Q cannot be exact at any $Q>0$, since this would require zero curvature of the dispersion curve in a Q-range of nonzero extent, and therefore a discontinuity in its second derivative at some Q if the dispersion curve has somewhere to deviate, as it is experimentally observed, from a trivial straight line. In other words, the correct low-Q behavior of the dispersion curve must include higher-order terms in addition to c_sQ.

At the onset of nonhydrodynamic behavior, the memory function (28) ceases to provide a valid description and needs to be amended through either a different, unknown, Q dependence of the parameters (the generalized hydrodynamic model) or, also, by a different time behavior (the viscoelastic model). Nevertheless, it is to be expected that the dispersion relation should analogously maintain a close link to the damping parameters, while ensuring a smooth transition into the asymptotic linear form c_sQ with decreasing Q.

Some confusion on the issue under discussion comes from a misleading use of the DHO fit model, where $\sqrt{\langle\omega_Q^2\rangle}=\Omega(Q)=\omega_m(Q)$ exactly. Here $\omega_m(Q)$ is the position of the maximum in the longitudinal-current autocorrelation spectrum, which is proportional to $\omega^2I(Q,\omega)$. Since the multiplication by ω^2 is an effective way of obliterating the central line of the spectrum to enhance its inelastic part, $\omega_m(Q)$ is a traditionally employed criterion for assigning the excitation frequencies. The above equation has then induced the use of two other quantities, namely the fit parameter $\Omega(Q)$ and $\sqrt{\gamma(Q)\langle\omega_Q^2\rangle}$, as estimators of the mode frequencies in the general case. The latter includes $\sqrt{\gamma(Q)}$ to correct for the fact that, being in general $\gamma_0\neq 1$, $\sqrt{\langle\omega_Q^2\rangle}$ has the wrong lowest-order $Q \to 0$ behavior $\sqrt{\langle \omega_Q^2 \rangle} \sim \sqrt{\langle \omega_0^2 \rangle} = c_s Q / \sqrt{\gamma_0}$ instead of the correct $c_s Q$.

However, in the special case of the low-Q DHO model, where $\gamma_0 = 1$ and the parameters are not fitted but have an explicit and fixed Q dependence, the above-mentioned quantities correspond to the same, exactly linear, function of Q, $\Omega(Q) = \sqrt{\langle \omega_0^2 \rangle} = c_s Q$, which is to be excluded as shown before. On the contrary, it was recalled in Sec. IV B that the correct hydrodynamic result for a system with $\gamma_0 = 1$ is given by the nonlinear law [see (56)]

$$\omega_s = \sqrt{\Omega^2 - \Gamma^2} \tag{73}$$

with $\Gamma = \nu Q^2 / 2$. Moreover, when $\sqrt{\langle \omega_Q^2 \rangle}$ needs to be replaced by $\sqrt{\gamma(Q) \langle \omega_Q^2 \rangle}$ because of the presence of a central peak, one should immediately realize that the DHO model is being abandoned, and the equalities $\omega_m(Q) = \Omega(Q) = \sqrt{\langle \omega_Q^2 \rangle}$ lose validity. Thus, even if $\omega_m(Q)$ were considered a correct estimator of the mode frequency, the use of $\Omega(Q)$ or $\sqrt{\gamma(Q) \langle \omega_Q^2 \rangle}$ would not be justified for any realistic fit model including a central line to account for a γ_0 value different from unity. There are, however, more reasons to consider $\omega_m(Q)$ and $\sqrt{\gamma(Q) \langle \omega_Q^2 \rangle}$ as improper determinations of the excitation frequency.

As for the position $\omega_m(Q)$ of the maximum of the longitudinal current autocorrelation spectrum, there is no theoretical justification to take it as the correct measure of the excitation energy. Moreover, this procedure may suffer from a problem of a different kind, reflecting the weakness of a method that attempts to determine a frequency position through the analysis of the spectral intensity. The problem is that the multiplication of $I(Q,\omega)$ by ω^2 always creates a maximum at nonzero frequency even when a central line is the only contribution to $I(Q,\omega)$, if the second moment has to be finite. When a true inelastic feature is present, it may or may not give rise to a maximum of $\omega^2 I(Q,\omega)$ depending on its strength: indeed, if it is weak enough, it may only produce a slight modification of the spectral shape on one side of the always present maximum. This phenomenon was, for example, recognized to lead to a wrong dispersion curve for the so-called slow sound in a simulated gaseous He-Ne mixture [56].

Concerning the use of $\sqrt{\gamma(Q) \langle \omega_Q^2 \rangle}$ as a measure of the mode frequency, we note that the resulting dispersion curve, apart from the trivial explicit Q^2 factor in (6) and the weak Q dependence of $\gamma(Q)$, would be mostly determined by the variation with Q of the static structure factor and completely independent of fundamental quantities, like D_T, ν, and τ_0, that account for the damping. Thus, the Q dependence of the excitation energy would essentially reduce to a disguised static property. Structural effects are indeed important, since the so-called de Gennes narrowing, occurring just because of the maximum of $S(Q)$, is the main cause of the downward bending of $\sqrt{\gamma(Q) \langle \omega_Q^2 \rangle}$. Nevertheless, we believe that the dispersion curve is a truly dynamical feature of a fluid, of which the damping mechanisms are essential ingredients, and that the way they affect the propagation of collective modes is at the core of the problem under study. One effect of the damping is, in particular, the slowing down of the oscillatory behavior of $F(Q,t)$, which can in no way be attributed to structural reasons only. We will return to this important point in the next section.

It should also be noted that, if the frequency of the excitations were defined through either $\sqrt{\gamma(Q) \langle \omega_Q^2 \rangle}$ or $\omega_m(Q)$, one would need another criterion to decide up to which Q value such a frequency represents a real collective mode. In fact, such quantities are defined and positive at any Q, thus also in the high-Q regime where only the single-particle part of $S(Q,\omega)$ survives and collective excitations no longer appear in a dynamical behavior approaching that of a free gas.

A generally valid criterion for the determination of the excitation frequencies is the one that relies on the existence of complex poles of $\tilde{F}(Q,z)$. As long as a pair of complex conjugated roots exists, the imaginary part ω_s is the frequency parameter that appears directly in the time evolution of the correlation of interest, that is $F(Q,t)$, as in (42), (53), and (70). Rigorously speaking, a characteristic frequency ω^* is well defined only when a time correlation consists of a purely harmonic oscillation, the corresponding spectrum being of the form $\delta(\omega - \omega^*)$. If the presence of damping makes the time dependence no longer periodic, giving rise to a line broadening, the concept of characteristic frequency can be, and usually is, maintained by operatively defining one parameter to effectively represent the position of such a spectral line. For an $F(Q,t)$ having the form of one oscillation modulated by a decaying amplitude, it is just a natural choice to assume as such a parameter the frequency that defines the oscillating term.

This approach is further clarified if the dynamics of a mechanical oscillator is considered. The motion of a point mass connected to a spring working in the Hooke's law regime obeys, in the presence of friction, the equation

$$\ddot{x}(t) + 2\mu \dot{x}(t) + \Omega_0^2 x(t) = 0 \tag{74}$$

which is formally identical to (1) when the memory function reduces to a δ-function. (This justifies the name of the DHO model.) From elementary mechanics it is known that for $\mu < \Omega_0$ the solution of (74) with initial conditions $x(0) = 1$ and $\dot{x}(0) = 0$ is $x(t) = \exp(-\mu t)\cos(\omega t - \varphi)/\cos \varphi$ with $\tan \varphi = \mu / \omega$ and $\omega^2 = \Omega_0^2 - \mu^2$. ω is then the actual frequency, in the presence of damping, of the phase-shifted exponentially modulated oscillation, while Ω_0 represents the frequency of the "free," i.e., undamped, oscillator. In the DHO fit model, then, $\Omega(Q)$ or $\sqrt{\langle \omega_Q^2 \rangle}$ play the role of the "undamped" frequency Ω_0, while ω_s corresponds to the true frequency ω.

The close analogy with the damped harmonic mechanical oscillator also clarifies the problem of the damping and propagation range of the acoustic excitations in a fluid. In the mechanical counterpart of the problem, it is customary to define the three situations corresponding to $\mu^2 - \Omega_0^2$ being negative, zero, or positive as the regimes of "underdamped," "critically damped," or "overdamped" oscillations, respectively. Thus, the criticality is defined as the transition from the existence to the absence of oscillatory solutions of (74), marked by the vanishing of $\omega^2 = \Omega_0^2 - \mu^2$. The application of

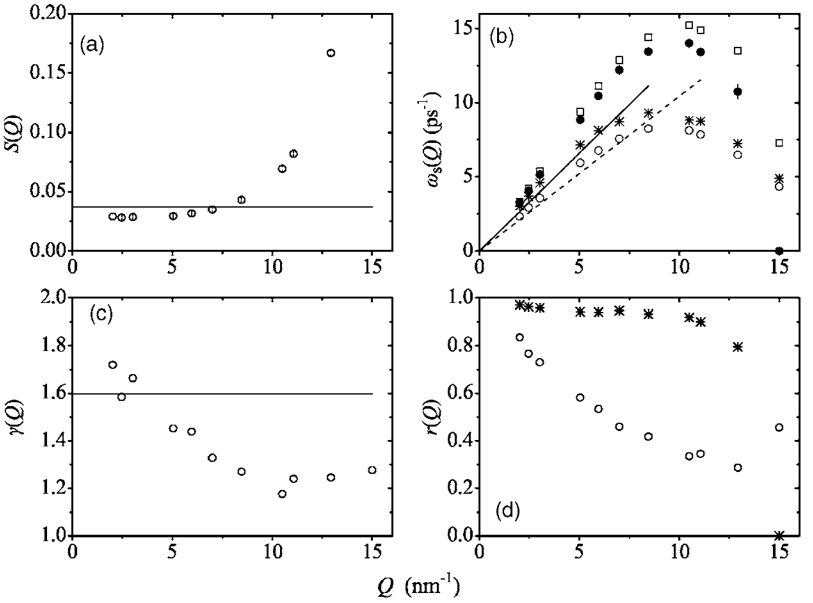

FIG. 1. Results of the viscoelastic analysis of liquid-CD$_4$ simulated spectra [8]. (a) Fitted $S(Q)$ (circles; error bars are smaller than the symbols); the line marks the value of $S(0)$. (b) Dispersion curve. Fitted ω_s (dots with error bars); the other symbols refer to quantities calculated from the fit parameters using (71) and (76)–(78): $\sqrt{\langle\omega_Q^2\rangle}$ (circles), $\sqrt{\gamma(Q)\langle\omega_Q^2\rangle}$ (stars), and $\Omega(Q)$ (squares). The straight lines are $\sqrt{\langle\omega_0^2\rangle}=c_sQ/\sqrt{\gamma_0}$ (dashed) and c_sQ (solid). (c) $\gamma(Q)$ (circles) derived from fit parameters using (71e); the line marks the value of γ_0. (d) $r(Q)$ (circles) and $\sqrt{1-z_s^2/\Omega^2(Q)}$ (stars), from (78).

this criterion to the DHO model of collective-mode dynamics is straightforward. In the more general cases represented by the hydrodynamic or the viscoelastic models, where more damping mechanisms are active, a similar criterion can be maintained by simply noting that if an acoustic excitation propagates, there must exist an oscillatory, though damped, behavior in $F(Q,t)$. In these cases formula (73) is no longer valid, and needs to be generalized as done in the next section.

It can thus be concluded that if the spectrum $I(Q,\omega)$ is described in terms of any one of the models considered in this paper, the parameters ω_s and z_s are the quantities to be taken for a correct evaluation of the frequency and width of the inelastic lines representing acoustic modes. This is the natural choice when fitting the generalized hydrodynamic model, but we have shown above that all used models can be written so as to display explicitly the presence of such parameters. Instead, in works where use was made of models not including ω_s and z_s in their usual fit parameter set, the excitation energy and damping were given values not theoretically well founded. Also, the propagation Q range can be consistently defined as that of existence of imaginary parts in the solutions of Eq. (16) [57].

VI. A FORMULA FOR THE DISPERSION CURVE

We show in this section that, if the parameters z_j are obtained from the fit, and the memory-function parameters are derived from them using, for example, (49) or (71), a detailed study of the dispersion curve $\omega_s(Q)$ can be performed, based on an exact formula.

In the dispersion relation (51b) of the DHO model, here rewritten for convenience in the form

$$\omega_s=\sqrt{\langle\omega_0^2\rangle}\sqrt{1-\frac{z_s^2}{\langle\omega_0^2\rangle}}, \qquad (75)$$

the downward curvature of $\omega_s(Q)$, expressed by the second square root, is only due to the increase with Q of the damping related to viscosities. In the more realistic case represented by the RB triplet, besides replacing $\sqrt{\langle\omega_0^2\rangle}$ with $\sqrt{\gamma_0\langle\omega_0^2\rangle}$, Eq. (75) must be modified in order to account for the presence of the damping due to thermal diffusion. From (7), (30d), (33c), and (36) one obtains

$$\omega_s=\sqrt{\frac{\langle\omega_0^2\rangle\gamma_0 D_T Q^2}{z_h}-z_s^2}.$$

Outside the hydrodynamic regime the RB triplet no longer provides an adequate description of the spectral shape, and (75) needs to be further modified. Using (49c) one finds for the generalized hydrodynamic model

$$\omega_s=\sqrt{\frac{\langle\omega_Q^2\rangle\Gamma_T(Q)}{z_h}-z_s^2}.$$

Analogously, for the viscoelastic model (71d) gives

$$\omega_s=\sqrt{\frac{\langle\omega_Q^2\rangle\Gamma_T(Q)}{z_h z_2\tau(Q)}-z_s^2}.$$

In the same way one obtains

$$\omega_s=\sqrt{\frac{\langle\omega_0^2\rangle\gamma_0 D_T Q^2}{z_h z_2\tau_0}-z_s^2}$$

for the Mountain theory of molecular fluids, and finally

$$\omega_s=\sqrt{\frac{\langle\omega_Q^2\rangle\Gamma_T(Q)}{z_h z_2 z_3\tau_1(Q)\tau_2(Q)}-z_s^2}$$

for the extended viscoelastic model of Sec. IV D. All these expressions can be rewritten in the general form

$$\omega_s = \sqrt{\Omega^2(Q)}\sqrt{1-\frac{z_s^2}{\Omega^2(Q)}}, \tag{76}$$

which, by comparison with (75), shows that, *in all cases*, the dispersion relation is that of a damped harmonic oscillator with a *renormalized* undamped-frequency parameter $\Omega(Q)$ defined by

$$\Omega^2(Q) = \frac{\gamma(Q)\langle\omega_Q^2\rangle}{r(Q)}, \tag{77}$$

where the renormalization function $r(Q)$ is given by

$$r(Q) = \begin{cases} 1, & \text{DHO model,} \\ \dfrac{z_h}{D_T Q^2}, & \text{RB triplet,} \\ \dfrac{z_h}{\left(\dfrac{\Gamma_T(Q)}{\gamma(Q)}\right)}, & \text{generalized hydrodynamic model,} \\ \dfrac{z_h}{D_T Q^2}\dfrac{z_2}{\left(\dfrac{1}{\tau_0}\right)}, & \text{Mountain theory,} \\ \dfrac{z_h}{\left(\dfrac{\Gamma_T(Q)}{\gamma(Q)}\right)}\dfrac{z_2}{\left(\dfrac{1}{\tau(Q)}\right)}, & \text{viscoelastic model,} \\ \dfrac{z_h}{\left(\dfrac{\Gamma_T(Q)}{\gamma(Q)}\right)}\dfrac{z_2}{\left(\dfrac{1}{\tau_1(Q)}\right)}\dfrac{z_3}{\left(\dfrac{1}{\tau_2(Q)}\right)}, & \text{“two-time” viscoelastic model.} \end{cases} \tag{78}$$

From the power expansions of the width(s) of the central line(s) in the various models [see, for example, (43) and (B2)], one sees that $r(Q)$ measures the variation, with increasing Q, of the damping associated to such lines with respect to the corresponding $Q\to 0$ limit values, with $r(0)=1$.

To our knowledge, formulas (76)–(78) were not reported before. Here we present some consequences of them. Before, however, we need to remark that these relationships express a mathematical property of the model fitted to the data, and that whether (76) represents a property of a real system or not, depends on the goodness of the fit.

The damping of the excitations is always described by z_s, which determines the exponential modulation of the oscillatory term in $F(Q,t)$. From (76) it is found that the existence of such oscillations is controlled by the ratio of z_s^2 to the quantity $\Omega^2(Q)$ that also incorporates the structural effects contained in $\langle\omega_Q^2\rangle$. However, a very rich dynamical behavior is included in the concise form of (76). For example, in the RB case (43) and (44) indicate that both z_s and $\Omega(Q)$ are determined by all the parameters entering the memory function (28), and the same can be shown to hold for all models of Sec. IV.

We are now in condition to understand quantitatively the dispersion curve of a realistic system, using (76)–(78) to display the various effects that contribute to define the shape of $\omega_s(Q)$. As an example, we summarize in Fig. 1 the results of the viscoelastic analysis, for which a good fit was obtained to the simulated $S(Q,\omega)$ of liquid methane [8], using the parameters appearing in (69) with the addition of $S(Q)$. We first note [Fig. 1(a)] that $S(Q)$ is nearly flat up to $Q\sim 6\ \text{nm}^{-1}$, but remains below $S(0)$ in the range $0<Q<7\ \text{nm}^{-1}$, where it has a minimum. This is a well-known property of dense classical liquids [58,59]. Thus, one can appreciate [Fig. 1(b)] the amount of purely structural effects by comparing $\sqrt{\langle\omega_Q^2\rangle}$ with $\sqrt{\langle\omega_0^2\rangle}$, the latter being simply the dashed straight line $c_sQ/\sqrt{\gamma_0}$. The initial decrease of $S(Q)$ produces an upward curvature of $\sqrt{\langle\omega_Q^2\rangle}$, which at higher Q displays, instead, the strong decrease corresponding to the de Gennes narrowing. The presence of $\gamma(Q)$ with $\gamma_0>1$ modifies $\sqrt{\langle\omega_Q^2\rangle}$ into $\sqrt{\gamma(Q)\langle\omega_Q^2\rangle}$, to be compared with its $Q\to 0$ linear behavior c_sQ (i.e., the solid straight line). Since $\gamma(Q)$ is a weakly decreasing function [Fig. 1(c)], the initial upward bending with respect to the low-Q straight line is reduced. However, this reduction is more than compensated by the further factor $\sqrt{1/r(Q)}$ entering the first square root of (76), with $r(Q)$ decreasing as shown in Fig. 1(d). Finally, the second square-root term in (76), also shown to decrease in Fig. 1(d), accounts for the abrupt fall down of the actual frequency ω_s at $Q>10\ \text{nm}^{-1}$, where the effect of the damping z_s is strongly enhanced by the decreasing of $\Omega(Q)$.

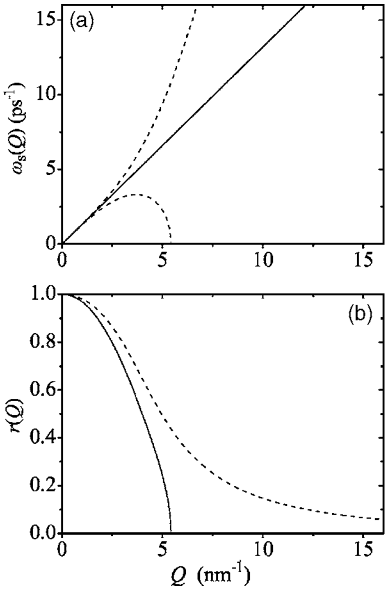

FIG. 2. Dispersion curve of the RB triplet calculated with the thermophysical coefficients of liquid CD$_4$ [8]. (a) $\sqrt{\gamma(Q)\langle\omega_Q^2\rangle} = \sqrt{\gamma_0\langle\omega_0^2\rangle} = c_s Q$ (solid line); $\Omega(Q)$ (upper dashed line); ω_s from solution of (31) (lower dashed line). (b) $r(Q)$ (dashed line) and $\sqrt{1-z_s^2/\Omega^2(Q)}$ (solid line).

A very important result of the above analysis is that the whole shape of the dispersion curve is due to the combination of structural, thermal, and damping effects, and that, by means of formulas (76)–(78), *each of these effects can be separately evaluated*. In particular, the initial upward bending of the dispersion curve, sometimes referred to as anomalous dispersion, is shown to be the effect of the initial decrease of both $S(Q)$ and $r(Q)$. This holds true for the model systems defined by the memory functions used in this paper, and for those real fluids whose $I(Q,\omega)$ is well represented by one of such models. We do not, however, exclude the existence of other possible causes of anomalous dispersion in real systems.

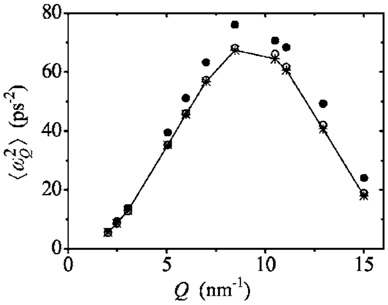

FIG. 3. Results of fitting the generalized hydrodynamic and viscoelastic models to the liquid-CD$_4$ simulated spectra [8]. $\langle\omega_Q^2\rangle$, calculated from fit parameters using (49) (dots) and (71) (circles), respectively. Theoretical values calculated from (6) are shown by stars (solid line as a guide for the eye).

Equations (76) also enables the use of the criterion described in Sec. V for the assessment of the Q range of propagation of the excitations. Being written in the form of the square-root relationship typical of a damped oscillator, the analogy can be pushed further to the statement that the existence of complex solutions to Eq. (16) is bound to the condition that the quantity under the second square-root symbol of (76) be positive.

If the same analysis is applied to the dispersion curve of the RB triplet, calculated for example with the thermophysical coefficients of liquid CD$_4$ [8], one sees (Fig. 2) that the upward bending of the curve is missing because (i) structural effects are absent, being in this model $\langle\omega_Q^2\rangle = \langle\omega_0^2\rangle$; (ii) thermal effects are also missing since $\gamma(Q) = \gamma_0$ is constant; (iii) the damping-variation effect expressed by $\sqrt{1/r(Q)}$ is compensated by the factor $\sqrt{1-z_s^2/\Omega^2(Q)}$ to the exact amount needed to make $\omega_s(Q)$ have a downward curvature everywhere with the correct initial straight-line behavior $c_s Q$. Although the RB triplet does not display the de Gennes narrowing, the quantity z_s^2 is increasing with Q so fast that the above square root determines a propagation range limited to a value of $Q_{\max}$ much smaller (by about a factor of 3) than

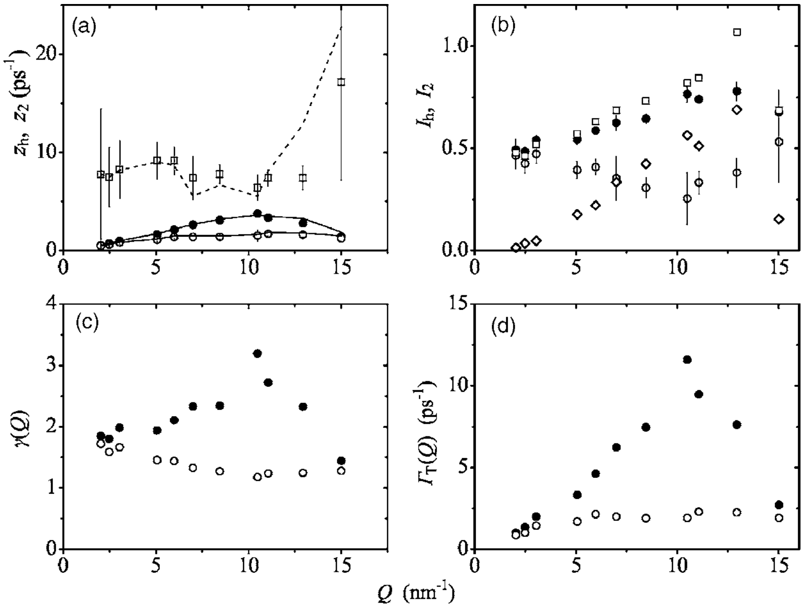

FIG. 4. Results of fitting the generalized hydrodynamic (dots) and viscoelastic (other symbols) models to the liquid-CD$_4$ simulated spectra [8]. Error bars are indicated for quantities obtained directly from the fit unless smaller than the symbol size. (a) Half-width at half-maximum of central Lorentzian lines: z_h and, for viscoelastic model, z_h (circles) and z_2 (squares). Lines show calculation of $\Gamma_T(Q)/\gamma(Q)$ [approximation (B2) to z_h, solid line] and of $1/\tau(Q) - \tau(Q)\Delta_L^2(Q)$ [approximation (B3) to z_2, dashed line]. (b) Amplitudes of central Lorentzian lines. I_h and, for viscoelastic model, I_h (circles), and calculated I_2 (diamonds) and I_h+I_2 (squares). (c) $\gamma(Q)$; (d) $\Gamma_T(Q)$.

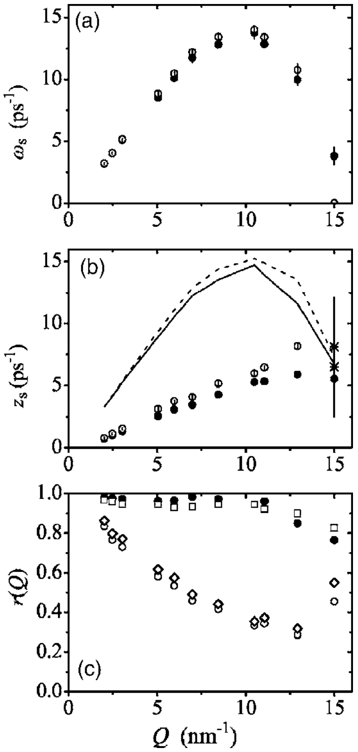

FIG. 5. Results of fitting the generalized hydrodynamic (dots) and viscoelastic (other symbols) models to the liquid-CD_4 simulated spectra [8]. Error bars are indicated for quantities obtained directly from the fit unless smaller than the symbol size. (a) Dispersion curve ω_s. (b) Half-width at half-maximum z_s of Brillouin lines. At $Q=15$ nm^{-1}, $-z_A$ and $-z_B$ (stars) replace the viscoelastic parameter z_s (circles). Lines show $\Omega(Q)$ (generalized hydrodynamic model, solid line; viscoelastic model, dashed line). (c) $r(Q)$. For viscoelastic model, the total (circles), and the two factors $z_h\gamma(Q)/\Gamma_T(Q)$ (squares) and $z_2\tau(Q)$ (diamonds) are separately shown.

what is actually observed in the simulations [8].

All the relationships obtained in this section can only be used if the parameters z_h, z_2, and z_s are available through the fitting, together with the derived memory-function parameters $\tau(Q)$, $\Gamma_T(Q)$, $\gamma(Q)$, and $\langle\omega_Q^2\rangle$. The possibility of carrying out a detailed study of the dispersion curve as done above is thus bound to the use of the viscoelastic fit model in the form (69).

VII. COMPARISON OF THE GENERALIZED HYDRODYNAMIC AND THE VISCOELASTIC MODELS IN A TEST CASE

We present in this section a detailed comparison between the results obtained by fitting both the generalized hydrodynamic and the viscoelastic model to the test $S(Q,\omega)$ data produced by the simulation of the CD_4 center-of-mass collective dynamics. The purpose of this section is not to discuss the microscopic dynamics in the specific case of liquid methane, but rather to show that writing the models in the common form (18) allows one to carry out comparisons much more easily and to draw more detailed conclusions.

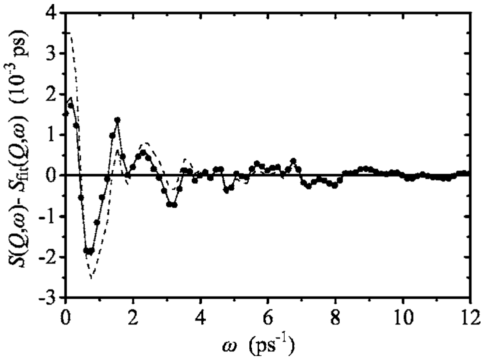

FIG. 6. Results of fitting the generalized hydrodynamic (dashed line) and viscoelastic (other symbols) models to the liquid-CD_4 simulated spectra [8]. Differences between the simulated and the fitted spectra at $Q=15$ nm^{-1} and $\omega\geqslant 0$. Viscoelastic fit with complex roots, dots; with all real roots, solid line. For comparison, the peak value is $S(Q,0)=95.8\times 10^{-3}$ ps.

The fitted $S(Q)$ already shown in Fig. 1(a) turned out to be the same for both models. The results for $\langle\omega_Q^2\rangle$ obtained from (22) [or using (49c) and (71d), respectively] are shown in Fig. 3, together with the exact value (6) calculated using the fitted $S(Q)$. One sees a small discrepancy between the two models starting at $Q\sim 5$ nm^{-1}, with the viscoelastic result in excellent agreement with the predicted value. This reveals a slight superiority of the viscoelastic model in the description of the simulated spectra, as it also is found by evaluating χ^2. From (38) and (69) it is clear that the main difference between the two models is the presence, in the second one, of an additional central Lorentzian contribution. It is therefore reasonable to attribute the reduced accuracy of the generalized hydrodynamic model to its inability to reproduce the central peak with one Lorentzian only. Indeed, the parameters z_h and z_2 in the viscoelastic model have quite different values [see Fig. 4(a)], and the parameter z_h in the generalized hydrodynamic model is therefore increased to compensate, in an effective way, the lack of an additional broader central line. This happens as soon as the amplitude I_2 becomes significant, i.e., for $Q\sim 5$ nm^{-1} [see Fig. 4(b)]. This interpretation is supported by the fact that the sum I_h+I_2 in the viscoelastic model follows very closely the behavior of I_h as fitted by the generalized hydrodynamic model. In this fit, the larger values of I_h reflect, in turn, into larger $\gamma(Q)$ and $\Gamma_T(Q)$, as shown in Figs. 4(c) and 4(d). In Fig. 4(a) we also show that z_h and z_2 are well approximated by the low-Q expressions (B2) and (B3).

Figure 5(a) displays the dispersion curve $\omega_s(Q)$. The two models give very similar results, with a slight discrepancy emerging again at $Q\sim 5$ nm^{-1}. The highest-Q point ($Q=15$ nm^{-1}) deserves here some more attention, since the viscoelastic fit produces a value $\omega_s=0$. This is not a spurious result due to the difficulty of fitting (69) when the Brillouin lines move towards the center of the spectrum because of the slowing down of the oscillation of $F(Q,t)$. We have verified that, if the viscoelastic model is fitted to the $Q=15$ nm^{-1} spectrum with the usual parametrization [see (15) and (59)] and the fitted memory-function parameters are inserted into (61), the quartic equation (62) does indeed have four real solutions. However, the two real roots z_A and z_B into which the complex ones have evolved turn out to be close to each other [and therefore with large uncertainties, see Fig. 5(b)], signaling that $Q_{\max}$ is just below the value of 15 nm^{-1}. This is consistent with the fact that, if the fit is performed forcing z_A and z_B to be complex conjugated, and therefore coincident when $\omega_s=0$, the fitted spectrum is practically indistinguishable from that obtained by using real z_A and z_B, as shown in Fig. 6.

Figure 5(b) shows the Brillouin linewidth z_s and the renormalized-DHO parameter $\Omega(Q)$. These quantities too begin to differ in the two fitted models around $Q=5$ nm^{-1}. At the highest Q, where the viscoelastic model requires to be fitted with four real roots, z_s is replaced by the parameters $-z_A$ and $-z_B$. At this Q value, all other fit parameters, and the memory function parameters derived from these ones, are not sensitive to the choice of fitting the viscoelastic model with either two complex roots or all real roots. We also note that with the generalized hydrodynamic model complex roots are found even at $Q=15$ nm^{-1}, with a fitted spectrum differing very little from the one obtained in the viscoelastic case (see Fig. 6). This means that the dynamical behavior at this value of Q is indeed very close to the transition to the zero-frequency situation, and the small difference in the representations of $I(Q,\omega)$ provided by the two models is sufficient to span the transition region. Clearly, more detailed and accurate data would be necessary to further elucidate this specific point.

Finally, Fig. 5(c) shows the function $r(Q)$. As already noted [see Fig. 4(a)], the factor $z_h\gamma(Q)/\Gamma_T(Q)$ in (78) is close to one for both models, but in the viscoelastic case the further factor $z_2\tau(Q)$ provides most of the damping variation effect. In the whole Q-range investigated here and with both models, $r(Q)$ is smaller than its initial value $r(0)=1$, a fact that, from (76) and (77), appears to favor the propagation of the excitations.

Thus, the results presented in this section show an overall slightly better performance of the viscoelastic model with respect to the generalized hydrodynamic one. This appears more evident in the parameters related to the central part of the spectrum, while rather small differences are found in the description of the inelastic lines. One can therefore conclude that, as far as this test case is concerned, the first exponential term in (57) provides, for $Q>5$ nm^{-1}, a more accurate modeling of $M(Q,t)$ than that obtained with the Markovian assumption of a $\delta(t)$ term as in (46). This important piece of information would be harder to recover by adopting the usual parametrization of the viscoelastic model and relying only, in comparing models, on the χ^2 evaluation.

VIII. CONCLUSIONS

We remind that the goal of this paper is not to discuss merits or drawbacks of the models here reviewed as far as the description of collective excitations is concerned, depending on the fluid, its thermodynamic state, and the studied Q range. We have tried, instead, to highlight the importance of a unified description that renders those models, and the results obtained by fitting them to experimental data, more easily comparable on a common basis. Moreover, we remind that the discussion presented here was restricted to the dynamical regime where the fluid does not necessarily behave as a hydrodynamic medium, but still shows the presence of propagating collective modes. In other words, we are concerned here with those situations where the concept of dispersion curve plays a significant role.

Given these premises, the conclusions of the present work are the following.

(a) The various models used so far in most, if not all, published works to describe and interpret spectral data on the dynamic structure factor of classical fluids are shown to be expressible in a unified formulation, which underlines the common features and highlights the differences among the models. This representation is based on the expression of the Laplace transform $\tilde{F}(Q,z)/S(Q)$ of the normalized intermediate scattering function in the form of a sum of as many terms of the type $I_j/(z-z_j)$ as are the poles of $\tilde{F}(Q,z)/S(Q)$. The properties of a specific model are then contained in the particular form of the second-order memory function $M(Q,t)$ that is taken to account for memory effects in the time evolution of $F(Q,t)$. Depending on the choice of $M(Q,t)$, one obtains ratios of polynomials with different degrees and coefficients. For all models considered here, in the Q range of propagation of the collective excitations, there are two terms of the type $I_j/(z-z_j)$ with pairs of complex conjugated roots z_j and amplitudes I_j. These terms contribute to the frequency spectrum $I(Q,\omega)$ with a pair of inelastic lines at positions $\pm\mathrm{Im}\, z_j$ which have a Lorentzian shape with half-width at half-maximum $-\mathrm{Re}\, z_j$, distorted by an asymmetric term dictated by the condition that the first time derivative of $F(Q,t)$ be zero at $t=0$. The other terms have real z_j and I_j and appear in the spectrum as symmetric Lorentzian lines centered at zero frequency. It is to be stressed, however, that the existence of two inelastic lines does not imply that such features are actually shaping the spectrum with a visible doublet.

(b) The generalized hydrodynamic model, being the extension to higher Q values of the Rayleigh-Brillouin triplet, is naturally and usually expressed in the form mentioned in (a). Other line shapes, however, and in particular the widely used viscoelastic model, are customarily referred to by means of formulas that have no apparent relation with a sum of lines. It is shown here that the viscoelastic model defines a four-line spectrum (again, irrespectively of whether a multiline structure is apparent or not), three of which correspond exactly, for $Q\to 0$, to the three lines of the generalized hydrodynamic model, with the addition of a second central line characterized by a width that does not go to zero in the $Q\to 0$ limit and an intensity which vanishes as Q^4. These properties of the viscoelastic model do not seem to have been recalled in the recent literature, though already suggested in the Mountain theory of Brillouin scattering from molecular fluids. In the extended version of the viscoelastic model with two relaxation times, one more central line is present, also with a nonvanishing width and a Q^4 dependent amplitude in the $Q\to 0$ limit, where, however, this model does not agree with the linearized-hydrodynamics theory unless it reduces to the simpler one-relaxation-time model.

(c) The use of the DHO fit model can only be justified in those cases where the specific-heat ratio γ_0 is unity. In all other cases, it needs, in fact, to be supplemented by the insertion of an extra central line, so that it works in practice as an effective version of the generalized hydrodynamic model flawed by the presence of an incorrect asymmetry parameter in the side lines.

(d) *The correct value of the acoustic excitation frequency is the imaginary part of the complex roots* z_j. This is the frequency with which the time correlation expressed by $F(Q,t)$ oscillates, modulated by an exponential decay, in the presence of the various damping processes that are active in the fluid at the specific Q-value under consideration.

(e) The other criteria for determining the excitation frequencies applied in many works on this subject are not justified theoretically, and have been shown to lead, in some cases, to an incorrect Q dependence in the asymptotic $Q \to 0$ regime. One of these estimators, namely the widely employed frequency position ω_m of the maximum of the longitudinal current autocorrelation spectrum, is, in addition, affected by another problem, arising from the interplay between spectral position and intensity, caused by the multiplication of $I(Q,\omega)$ by ω^2.

(f) As a consequence of (d) and (e), it is shown that, in order to determine the dispersion curve of the acoustic modes, the chosen fit model should be better set in the form $\widetilde{F}(Q,z)/S(Q)=\Sigma_j I_j/(z-z_j)$ with the poles z_j and one of the amplitudes I_j used as fit parameters, all other amplitudes being then univocally determined. We have shown that this is possible for all the models considered in this work, and, in general, in all the cases where $\widetilde{F}(Q,z)/S(Q)$ can be cast in the form of a ratio of polynomials in the variable z. This uniform way of analyzing data would provide a far easier comparison between different works than it has been the case so far. Moreover, we have shown that, if this parametrization is adopted, one can always derive the memory function parameters from the fitted quantities. For example, in the case of the viscoelastic model, we have given the formulas that give $\tau(Q)$, $\Gamma_T(Q)$, $\omega_L^2(Q)$, $\langle\omega_Q^2\rangle$, and $\gamma(Q)$ as functions of the four z_j's and one of the real amplitudes.

(g) If the models are parametrized as suggested in (f), the dispersion curve can be described by a formula, never reported before, that links the various parameters. This expression is very compact in form, but incorporates a wealth of dynamical features the combination of which determines the precise shape of the dispersion curve. The formula shows that the analogy with a mechanical damped oscillator, which amounts to a mathematical identity in the DHO case, can be extended to the other models, where more damping mechanisms are present, by a simple renormalization of the "free" oscillator frequency $\Omega(Q)$. As a consequence, the dispersion curve is seen to be the result of the interplay of (i) structural effects provided by the presence of $S(Q)$ in the second moment, (ii) thermal effects given by $\gamma(Q)$, (iii) the Q dependence of the width(s) of the central line(s), and (iv) the Q dependence of z_s. More important, the found formula allows for an explicit separation of each of these effects. Thus, provided that a given model is able to accurately reproduce the experimental spectra, i.e., if the quality of the fit is good, a full, quantitative, understanding of the dispersion curve of a fluid becomes possible.

(h) For the same reasons as given in (d), the correct measure of the damping of the acoustic modes is, to within the sign, the real part of the complex roots z_j, that is the inverse-time constant of the exponential decay that modulates the oscillatory part of $F(Q,t)$. The formula mentioned in (g) provides a unifying criterion for the definition of the transition from underdamped to overdamped, nonpropagating, excitations.

(i) The attachment of physical meaning to the fit parameters related to the width(s) of the central line(s) is a delicate issue, as far as their relations to the thermophysical properties of the fluid are concerned. A direct connection can be safely established only in the $Q \to 0$ limit. The Q-power expansion of any such fit parameter clearly displays in its higher-order terms the mixed presence of all thermal and transport-related quantities.

(j) A major result of this work is that the dynamics of acoustic modes can be viewed, at each Q, as that of a damped harmonic oscillator. This is defined by a characteristic frequency which depends on the detailed properties of the fluid, and is, in particular, affected by the microscopic relaxation parameters through a renormalization mechanism. The excitations propagate with an actual frequency related to the characteristic frequency of the system by the square-root relationship typical of damped oscillators, where the mode damping is also determined by the relaxation parameters such as thermal diffusion and viscosity. The same parameters also characterize the nonpropagating modes through the determination of the widths of the elastic lines. Thus, in the Q range relevant to sound propagation, a full, consistent account can be given of the role of thermal and transport properties of classical fluids in shaping the detailed features of the spectra of collective excitations.

(k) The formulation of models in terms of roots z_j and amplitudes I_j makes immediately evident which fit function is to be used when $F(Q,t)$ data are directly available, for example, as a result of molecular-dynamics simulation, without need of Fourier transformation to the frequency domain. The fit model is then simply given by $F(Q,t)/F(Q,0) = \Sigma_j I_j \exp(z_j|t|)$, where, again, the poles z_j and one of the amplitudes I_j play the role of fit parameters.

One of the advantages of the memory function approach is that with very simple hypotheses on the time dependence of $M(Q,t)$ it is possible to obtain a rather richly structured dynamical behavior, which is often able to account in detail for the observed correlations or spectra. However, the mechanisms that produce (second-order) memory effects in the time evolution of $F(Q,t)$ are not easily interpreted at the level of $F(Q,t)$ itself. For example, in the case of the viscoelastic model, the parameters $\tau(Q)$ and $\Gamma_T(Q)$ have an evident meaning as far as $M(Q,t)$ is concerned, but play a much less clear role in the explicit time dependence of the correlation function that we wish to describe. In fact, the time constants of $M(Q,t)$ determine both the three decay constants and the phase shift of the oscillating part of $F(Q,t)$. Conversely, it is the fitting of the parameters z_j that gives direct access to the time dependence of $F(Q,t)$.

ACKNOWLEDGMENTS

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APPENDIX A

The Cardano method for the solution of the cubic equation (31) $z^3+g_1z^2+g_2z+g_3=0$ requires the definition of the auxiliary coefficients $\xi=g_2-g_1^2/3$ and $\psi=(2/27)g_1^3-g_1g_2/3+g_3$, and the evaluation of the discriminant

$$\Delta=(\psi/2)^2+(\xi/3)^3. \tag{A1}$$

When $\Delta>0$, one finds one real (z_C) and two complex conjugated ($z'\pm iz''$) roots, with

$$z_C=u+v-\frac{g_1}{3},$$

$$z'=-\frac{u+v}{2}-\frac{g_1}{3},$$

$$z''=\frac{u-v}{2}\sqrt{3}, \tag{A2}$$

where

$$u=(-\psi/2+\sqrt{\Delta})^{1/3},\quad v=(-\psi/2-\sqrt{\Delta})^{1/3}. \tag{A3}$$

Being interested in the $Q\rightarrow 0$ behavior, we now use series expansions in powers of Q. Using the explicit Q dependence (30) of g_1, g_2, and g_3, one finds $\xi=c_s^2Q^2+O(Q^4)$, $\psi=[D_T-(\gamma_0D_T+\nu)/3]c_s^2Q^4+O(Q^6)$ and from (A1) $\Delta=c_s^6Q^6/27+O(Q^8)$, which is surely positive for low enough Q ($Q_{\max}$ being given by the lowest positive root of the equation $\Delta=0$). Through the series expansions of $(1+x)^{1/2}$ and $(1+x)^{1/3}$ for small x, one easily finds from (A3) and (A2) the results (43)–(45).

APPENDIX B

We investigate here the low-Q behavior of the viscoelastic model. In order to do so, the procedure of Appendix A is still applicable but requires the cumbersome explicit solution of the fourth-degree equation (62) by the Ferrari method. We follow here another approach. We first express the parameters of the memory function as generic power series of Q,

$$\gamma(Q)=\gamma^{(0)}+\gamma^{(1)}Q+\gamma^{(2)}Q^2+\cdots,$$

$$\Gamma_T(Q)=\Gamma_T^{(2)}Q^2+\Gamma_T^{(3)}Q^3+\Gamma_T^{(4)}Q^4+\cdots,$$

$$\langle\omega_Q^2\rangle=\langle\omega_Q^2\rangle^{(2)}Q^2+\langle\omega_Q^2\rangle^{(3)}Q^3+\langle\omega_Q^2\rangle^{(4)}Q^4+\cdots,$$

$$\omega_L^2(Q)=\omega_L^{(2)}Q^2+\omega_L^{(3)}Q^3+\omega_L^{(4)}Q^4+\cdots,$$

$$\tau(Q)=\tau^{(0)}+\tau^{(1)}Q+\tau^{(2)}Q^2+\cdots, \tag{B1}$$

where the lowest-order coefficients are known from hydrodynamics to be $\gamma^{(0)}=\gamma_0$, $\Gamma_T^{(2)}=\gamma_0D_T$, $\langle\omega_Q^2\rangle^{(2)}=c_s^2/\gamma_0$, $\tau^{(0)}=\tau_0$, and, as mentioned in Sec. IV C, $\omega_L^{(2)}=c_L^2=\nu/\tau_0+c_s^2$. Then, we solve the quartic equation (62) by the perturbative approach applied, for example, in Ref. [47] to Eq. (31). The method requires to write the generic root as $z=z^{(0)}+z^{(1)}Q+z^{(2)}Q^2+\cdots$, and substitute this into (62). By taking only the zeroth-order terms, one obtains $(z^{(0)})^4+(1/\tau_0)(z^{(0)})^3=0$, which has three coincident roots $z^{(0)}=0$ and the fourth root $z^{(0)}=-1/\tau_0$. The next step is to substitute each of the four zeroth-order roots back into the equation to be solved, take the first-order terms, and solve for the corresponding $z^{(1)}$. The procedure is then iterated until the desired order is reached in the solutions. With straightforward algebra the following results are obtained.

Two roots are real and their power expansions have lowest-order terms $z_C\sim -D_TQ^2$ and $z_D\sim -1/\tau_0$, and two are complex with $z'\sim -[(\gamma_0-1)D_T+\nu]Q^2/2$ and $z''\sim c_sQ$ for the real and imaginary parts, respectively. The four roots are all different. From (24) or (65)–(67), one also finds for the amplitudes $I_C\sim 1-1/\gamma_0$, $I'\sim 1/(2\gamma_0)$, $b\sim[3(\gamma_0-1)D_T+\nu]Q/(2c_s)$, and $I_D\sim \nu Q^2\langle\omega_0^2\rangle\tau_0^3$. Thus, for $Q\rightarrow 0$, three lines of the viscoelastic models coincide with the corresponding lines of the RB triplet, while the fourth one vanishes as Q^4. The power expansions of the widths of the central lines, with appropriate resummations, can be shown to give the following formulas, correct to within terms of order $O(Q^4)$,

$$z_h=\frac{\Gamma_T(Q)}{\gamma(Q)}+O(Q^4), \tag{B2}$$

$$z_2=\frac{1}{\tau(Q)}-\frac{\Delta_L^2(Q)}{1/\tau(Q)}+O(Q^4). \tag{B3}$$

All calculations reported in this Appendix can be as well performed for the generalized hydrodynamic model of Sec. IV A, starting again from the first three of Eqs. (B1) and including the power expansion of the memory-function parameter $B(Q)$. Apart from the obvious coincidence of the results with the RB triplet expression in the limit $Q\rightarrow 0$, it can be shown that (B2) is also valid for this model.

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