Expansion in Lorentzian functions of spectra of quantum autocorrelations

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(Received 13 March 2013; published 24 June 2013)

We show that in a quantum mechanical many-body system of Boltzmann particles having space inversion symmetry the spectrum of the autocorrelation function of a local observable can always be given, similarly to the classical case [Phys. Rev. E **85**, 022102 (2012)], in terms of a series of Lorentzian functions multiplied by the proper quantum detailed balance factor. This is done by transforming the continued fraction representation, which is derived via recurrent relations and without the use of the generalized Langevin equation hierarchy, into a series expansion. In this way characteristic frequencies can be defined, also in quantum mechanics, which refer to the particular autocorrelation. These are the frequencies of the eigenmodes of the relaxation function connected to the observable. We also show that in practical cases of interest in experimental spectroscopy, and particularly in inelastic neutron and x-ray scattering, the use of a finite number of Lorentzian shapes for an approximate description of the data is related to a reduction of the number of the relevant dynamical variables taken into account, equivalent to the lowering of the dimensionality of the orthogonalized space onto which the dynamic of the system is projected. Examples of application are given for the spectrum of the velocity autocorrelation function of liquid parahydrogen, calculated with a quantum simulation algorithm (path-integral centroid molecular dynamics), and for the molecular center-of mass dynamic structure factor in liquid carbon dioxide as computed by means of classical molecular dynamics simulation.

DOI: 10.1103/PhysRevE.87.062133 PACS number(s): 05.30.−d, 05.20.Jj, 61.20.Lc

I. INTRODUCTION

The time dependence of correlation functions is of primary interest for the discussion of the dynamical properties of many-particle systems, together with the complementary frequency dependences of the respective spectra, which usually are directly connected to experimental results. A large number of spectroscopic methods are based on the use, as a probe, of an external field weakly coupled to the system under study, so that only the linear dependence of the response to the perturbation is of interest. This fact gives the possibility of studying the properties of the unperturbed system itself. The use of photons, neutrons, charged particles, and phonons as spectroscopic probes in a very broad range of energies is now very common in order to study various types of dynamical behavior in solids, liquids, and gases.

The most general framework in which the theory of the linear response to an external perturbation has been developed for both classical and quantum many-body systems was set up in fundamental papers by Kubo, Mori, and Zwanzig [1–5]. Applications of this theory have been discussed in a number of review papers [6–8] and books [9–11], particularly for the study of properties of fluids and other disordered systems.

The generalized Langevin equation (GLE) is derived by Mori and Zwanzig (MZ) [1,2,5] as the equation governing the behavior of correlation functions of observables of the system. The introduction of the concepts of fluctuating forces and memory functions leads to a hierarchy of GLE equations, which is formally solved via Laplace transformations to give, as a final result, the well-known continued fraction representation of spectra of correlation functions.

This representation, however, is rather formal and not easily endowed with physical meaning as far as higher-order memory functions are involved, leading to a difficult interpretation of the GLE hierarchy. The lack of knowledge about the precise time dependence to be assigned to memory functions and the difficulty of interpreting the truncation of the continued fraction have led sometimes to improper applications of the MZ method.

An alternative approach to the dynamics of many-body systems was developed some time ago by Lee [12–14]. This method is based on a projection procedure in a Hilbert space which does not require the introduction of memory functions and provides a clearer connection to physical properties via the derivation of particular recurrence relations, though leading to the continued-fraction representation of spectra similar to what is obtained in MZ theory. The correspondence of the MZ and Lee approaches has been pointed out, for example, in Ref. [15]. We note, however, that in Lee's works the method of recurrence relations is only applied to the case of Hermitian operators, leading to correlation functions which naturally possess the time inversion symmetry, and therefore is less general than the MZ theory, which does not have any restriction.

In a recent paper [16] we have exploited the Lee approach to the description of the dynamics of classical systems, showing that it leads to a very general formulation where correlation functions display an exponential functionality (EF). More precisely, it was shown that the time-dependent autocorrelation function of a dynamical variable can be written as an infinite sum of (complex) exponential functions, which play the role of eigenmodes of the dynamical property under consideration, and that in practical cases this is approximated by retaining a small number of modes. In full analogy, the frequency spectrum of the given correlation function is shown to have a Lorentzian functionality (LF).

Here, we generalize the above results to the case of a quantum-mechanical many-body system of Boltzmann particles. For the very broad class of autocorrelation functions of the spatial Fourier components of local operators in a system

with space inversion symmetry, we show that the spectra can be written as products of the detailed balance factor times a spectral function which possesses an LF, corresponding to the existence of a set of characteristic frequencies which in the following we refer to as eigenfrequencies of the given autocorrelation. This result is obtained by exploiting the connection between the autocorrelation function of a variable and the corresponding relaxation function, as defined by Kubo in the context of linear response theory [4]. In fact, we show that an EF and an LF can be given for the relaxation functions in time and frequency domain, respectively, and the same holds for the whole hierarchy of memory functions.

Approximations for the frequency dependence of spectra and the time behavior of the relaxation functions can be directly related to the contraction of the dimensionality of the assumed Hilbert space in which the dynamics of the system is represented. This gives to possible practical approximations of the LF of the spectra a precise meaning which provides a guide for physical interpretations better founded than assuming an *ad hoc* time dependence of the memory function at an arbitrarily chosen truncation level.

A few years ago we reviewed [17] the theoretical models most commonly employed as spectral functions to be fitted to the experimental or simulated dynamic structure factor $S(k,\omega)$ for the analysis of spectra of density fluctuations in classical fluids. All the models there considered are based on a common scheme that assumes for the second-order memory function a time dependence in the form of a combination of a δ function and/or exponential terms. We showed that this assumption implies spectra composed of a number of Lorentzian lines, which varies according to the chosen model, i.e., to the type of truncation of the continued fraction, although this general property has often gone unnoticed in most of the literature on the subject. Thus, our previous work [16] and the present one also provide a rigorous theoretical justification for the use of such fit models. Moreover, although the models considered in Ref. [17] referred to classical systems, the present work demonstrates that essentially the same approach can be extended to quantum systems if an analogous modeling is applied to the spectrum of the relaxation function.

A large number of published works report on analyses of spectra of correlation functions relevant to fluids dynamics, and in some of them the observation of an LF is explicitly made [18–20]. Here, as examples of spectra which can be represented by a finite number of Lorentzian shapes, we present the cases of the velocity autocorrelation function of liquid parahydrogen [21] and of the center-of-mass dynamic structure factor of the molecular liquid CO_2, representing the collective translational dynamics [22]. The first example refers to a system displaying a non-negligible quantum behavior, while the second pertains to an essentially classical case.

In Sec. II we recall the general theory for the Lee derivation of the EF behavior of an inner product in a Hilbert space, which is valid for any properly defined time-dependent inner product possessing the time inversion symmetry property, but is applied here to the specific case in which the inner product is identified with a Kubo transform. In Sec. III we report definitions and symmetry properties of correlation functions and their spectra relevant for our discussion. Section IV is devoted to applying our findings to the time autocorrelation of the spatial Fourier components of local operators in many-body systems. In Sec. V we briefly discuss the two abovementioned examples of how the concepts exposed in this paper apply to the analysis of spectral data, while the conclusions are summarized in Sec. VI.

II. GENERAL THEORY

Let us consider an N-body system at thermodynamic equilibrium with total Hamiltonian H and denote by A the operator which represents the property under consideration, while $A^\dagger$ is its adjoint.

The time evolution of both A and $A^\dagger$ is governed by the Liouville equation

$$\frac{d}{dt}A(t) = iLA(t), \tag{1}$$

where $L = (1/\hbar)[H,\ldots]$ and $[\ldots,\ldots]$ denotes the commutator. A formal solution for Eq. (1) can be given in an exponential operator form and as a series expansion, i.e.,

$$A(t) = \exp(iLt)A = \sum_{\nu=0}^{\infty}(t^\nu/\nu!)A^{(\nu)}, \tag{2}$$

where $A^{(\nu)} = (iL)^\nu A = [d^\nu A(t)/dt^\nu]_{t=0}$ and $A^{(0)} \equiv A$, and similarly for $A^\dagger(t)$.

The study of the time behavior of the observables of the N-body system, and in particular of A, can be carried out with reference to an appropriate autocorrelation function defined in a Hilbert space S, where Eq. (1) is a linear transformation which determines the time evolution of any operator in S. This study requires for two operators A and B of the system the assumption of a specific form for their inner product (A,B), and consequently the normalization and the metric of the space.

Here we define the inner product as the Kubo transform

$$\begin{aligned}(A,B) &\equiv \int_0^\beta d\mu\langle Ae^{-\mu H}B^\dagger e^{\mu H}\rangle \\ &= \int_0^\beta d\mu \mathrm{Tr}(Ae^{-\mu H}B^\dagger e^{\mu H}\rho_0),\end{aligned} \tag{3}$$

where $\langle\cdots\rangle = \mathrm{Tr}(\cdots\rho_0)$ denotes a quantum mechanical average at thermodynamic equilibrium performed by means of the statistical operator $\rho_0 = \exp(-\beta H)$ with $\beta = 1/(k_\mathrm{B}T)$, where k_B is the Boltzmann constant and T is the temperature. For convenience, for now on we assume that $\langle A\rangle = \langle B\rangle = 0$, which is always possible if one looks at the fluctuations of the variables of the system. The correlation given in Eq. (3) is the relaxation function, which is introduced in the linear response theory [4], as discussed in Sec. III.

By definition of inner product, $(A,A(t)) = (A,A(-t))^*$. Here, however, we consider only the particular case, even though relevant for our purposes, in which the inner product is actually symmetric under time reversal, that is, $(A,A(t)) = (A,A(-t))$, which implies the reality of $(A,A(t))$. This property is true, for example, when the operator A is Hermitian, as can be easily demonstrated and is assumed in Ref. [12]. However, this is not a necessary condition and in Sec. IV we consider a specific non-Hermitian case.

The solution (2) gives $A(t)$ in terms of the complete set $\{A^{(\nu)}\}$ of S, which is not orthogonal. Once an inner product is defined in S, the Gram-Schmidt process (GS) permits,

however, construction of an orthogonal set $\{f_\nu\}$ starting from $\{A^{(\nu)}\}$. Since in the process one of the $\{f_\nu\}$ can be chosen arbitrarily, we make the choice $f_0 = A$. Following the procedure of construction of the set $\{f_\nu\}$ and using the symmetry under time reversal of $(A, A(t))$ it is easy to show that a differential recurrent relation holds for the $\{f_\nu\}$ [12], i.e.,

$$f_{\nu+1} = \dot{f}_\nu + \Delta_\nu f_{\nu-1}, \tag{4}$$

which is valid for all $\nu \geqslant 0$ with the definition $f_{-1} \equiv 0$. Here, $\dot{f}_\nu = iLf_\nu$ and $\Delta_\nu = (f_\nu, f_\nu)/(f_{\nu-1}, f_{\nu-1})$, with $\Delta_0 \equiv 1$. Equation (4) can be used to successively derive at all orders the explicit expression of

$$f_\nu = f_\nu(A, A^{(1)}, A^{(2)}, \ldots, A^{(\nu)}; \Delta_1, \Delta_2, \ldots, \Delta_{\nu-1}). \tag{5}$$

We can now rewrite $A(t)$ in terms of the orthogonal set $\{f_\nu\}$ as

$$A(t) = \sum_{\nu=0}^{\infty} a_\nu^*(t) f_\nu, \tag{6}$$

where $a_\nu(t) = (f_\nu, A(t))/(f_\nu, f_\nu)$ and in particular $a_0(t) = (A, A(t))/(A, A)$, with $a_\nu(0) = \delta_{\nu 0}$ and $a_\nu(t) \longrightarrow 0$ for $t \longrightarrow \infty$. Moreover, from the definition property of the inner product for the complex conjugate of $a_\nu(t)$, we have $a_\nu^*(t) = (A(t), f_\nu)/(f_\nu, f_\nu)$.

The substitution of Eq. (6) into the Liouville equation (1) and the use of the recurrence relation (4) permits us to derive a differential recurrence relation also for the correlations $a_\nu(t)$, which are the coefficients of the expansion (6), i.e.,

$$a_{\nu-1}(t) = \dot{a}_\nu + \Delta_{\nu+1} a_{\nu+1}(t), \tag{7}$$

with $\dot{a}_\nu = da_\nu(t)/dt$ and $a_{-1} \equiv 0$. Denoting with a tilde the Laplace transform of a function of time, such as $\tilde{a}_\nu(z) = \mathcal{L}[a_\nu(t)]$, the transformation of Eq. (7) gives

$$1 = z\tilde{a}_0(z) + \Delta_1 \tilde{a}_1(z), \tag{8a}$$

$$\tilde{a}_{\nu-1}(z) = z\tilde{a}_\nu(z) + \Delta_{\nu+1}\tilde{a}_{\nu+1}(z), \tag{8b}$$

for $\nu \geqslant 1$, which can be rewritten in the form

$$\tilde{K}_\nu(z) = \Delta_\nu [z + \tilde{K}_{\nu+1}(z)]^{-1}, \tag{9}$$

with $\tilde{K}_0(z) = \tilde{a}_0(z)$ and $\tilde{K}_\nu(z) = \Delta_\nu[\tilde{a}_\nu(z)/\tilde{a}_{\nu-1}(z)]$ for $\nu \geqslant 1$.

The Laplace antitransformation of Eq. (9) into the time domain gives

$$\dot{K}_\nu(t) + \int_0^t dt' K_{\nu+1}(t-t') K_\nu(t') = 0, \tag{10}$$

with $K_\nu(0) = \Delta_\nu$. This is the hierarchy of GLE equations identifying $\{K_\nu(t)\}$ as the set of quantum-mechanical memory functions of $a_0(t) = K_0(t)$. The GLE hierarchy is here derived as a direct consequence of the Liouville equation via the projection in the manifold $\{f_\nu\}$ and the recurrent relation (7). Mori and Zwanzig have demonstrated that $\{K_\nu(t)\}$ are correlation functions of variables of the many-body system, which can be properly defined and denoted as "fluctuating forces" [2,5]. In particular it can be shown that these "forces" are directly related to the $\{f_\nu\}$ [13].

Moreover, from Eq. (10) we see that when $K_0(t)$ is an even function of time, so are all the $\{K_\nu(t)\}$, while from Eq. (7) the $\{a_\nu(t)\}$ have the same parity as the index ν.

From the definition of $\tilde{K}_\nu(z)$ for $\nu \geqslant 1$ we also have

$$\begin{aligned} a_\nu(t) &= 1/\Delta_\nu \int_0^t dt' K_\nu(t-t') a_{\nu-1}(t') \\ &= \left(\prod_{i=1}^{\nu} \frac{1}{\Delta_i}\right) \int_0^t dt_\nu \int_0^{t_\nu} dt_{\nu-1} \ldots \int_0^{t_2} dt_1 \\ &\quad \times K_\nu(t-t_\nu) K_{\nu-1}(t_\nu - t_{\nu-1}) \ldots K_1(t_2 - t_1) a_0(t_1), \end{aligned} \tag{11}$$

indicating that the $\{a_\nu(t)\}$ components of $A(t)$ for $\nu \geqslant 1$ in the manifold $\{f_\nu\}$ are successively generated starting from $a_0(t_1)$ for $t > t_\nu > t_{\nu-1} > \cdots > t_2 > t_1 > 0$ via convolutions with the memory functions $K_\lambda(t - t_\lambda)$, $1 \leqslant \lambda \leqslant \nu$. In other words, since the norm $\|A(t)\| = (A(t), A(t))/(A, A) = 1$, the dynamics of the vector $A(t)$ in the Hilbert space S is a rotation which successively in time acquires components $a_\nu(t)$, which are driven by a memory function correlation with the previous one $a_{\nu-1}(t')$ for $t > t'$. These considerations clarify that Eq. (6) is a possible way of building up $A(t)$ in S starting from its autocorrelation at $t = 0$ and then summing, in a sequential process, correlations of $A(t)$ itself with increasing-order derivatives at $t = 0$, which are brought in particular combinations up to $A^{(\nu)}$ by the f_ν.

The hierarchy (9) can be combined to give the continued fraction representation of $\tilde{a}_0(z)$ and $\tilde{K}_\nu(z)$, which is also the result of the MZ theory, i.e.,

$$\tilde{K}_\nu(z) = \cfrac{\Delta_\nu}{z + \cfrac{\Delta_{\nu+1}}{z + \cfrac{\Delta_{\nu+2}}{z + \cdots}}}. \tag{12}$$

Here we also see that $\tilde{K}_\nu(z)$ is defined with respect to the subspace $S_\nu \subset S$, which is also a Hilbert space, spanned, however, by f_ν, $f_{\nu+1}$,..., f_∞. Both Δ_ν and $\tilde{K}_\nu(0) = \int_0^\infty dt\, K_\nu(t)$ are positive quantities.

The continued fractions (12) can be expressed as ratios of polynomials in z as it follows, since the first ν terms constitute the νth convergent [12,23], that

$$\tilde{K}_\nu(z) = \lim_{\lambda\to\infty} \Delta_\nu \frac{\det \mathbf{D}^{(\lambda,\nu+1)}(z)}{\det \mathbf{D}^{(\lambda,\nu)}(z)}, \tag{13}$$

where $\mathbf{D}^{(\lambda,\nu)}(z)$ is a $(\lambda - \nu)$-dimensional tridiagonal symmetric matrix whose elements are $D_{\alpha\alpha}^{(\lambda,\nu)} = z$, $D_{\alpha\beta}^{(\lambda,\nu)} = i\Delta_{\alpha+\nu}^{1/2}\delta_{\alpha,\beta-1}$, where $1 \leqslant \alpha < \beta \leqslant \lambda - \nu$.

If we denote by $\{z_j^{(\lambda,\nu)}\} = \{z_1^{(\lambda,\nu)}, z_2^{(\lambda,\nu)}, \ldots, z_{\lambda-\nu}^{(\lambda,\nu)}\}$ the set of zeros of the polynomial $\det \mathbf{D}^{(\lambda,\nu)}(z)$, which can be derived explicitly by diagonalizing the matrix $\mathbf{D}^{(\lambda,\nu)}(z)$ itself, expressions (13) can also be written as

$$\tilde{K}_0(z) = \tilde{a}_0(z) = \lim_{\lambda\to\infty} \sum_{j=1}^{\lambda} \frac{I_j^{(\lambda,0)}}{z - z_j^{(\lambda,0)}}, \tag{14a}$$

$$\tilde{K}_\nu(z) = \lim_{\lambda\to\infty} \sum_{j=1}^{\lambda-\nu} \frac{I_j^{(\lambda,\nu)}}{z - z_j^{(\lambda,\nu)}}, \tag{14b}$$

where the residues $I_j^{(\lambda,\nu)}$ are

$$I_j^{(\lambda,\nu)} = \lim_{z\to z_j^{(\lambda,\nu)}} \left(z - z_j^{(\lambda,\nu)}\right) K_\nu(z). \tag{15}$$

From Eqs. (14), by Laplace antitransformation we can now write

$$a_0(t) = \frac{(A, A(t))}{(A,A)} = \sum_{j=1}^{\infty} I_j^{(0)} \exp\left(z_j^{(0)}|t|\right), \tag{16a}$$

$$K_\nu(t) = \sum_{j=1}^{\infty} I_j^{(\nu)} \exp\left(z_j^{(\nu)}|t|\right), \tag{16b}$$

with $\mathrm{Re} z_j^{(\nu)} < 0$, where we have also dropped the superscript λ having taken the limit to infinity. Here $I_j^{(\nu)}$ and $z_j^{(\nu)}$ appear as amplitudes and characteristic frequencies of a normal-mode representation of $a_0(t)$ and $K_\nu(t)$ and may be in general either real or pairs of complex conjugate values in agreement with our assumption of reality of these functions. We indicate expression (16a) as the EF solutions of the dynamics of the many-body system.

Moreover, it can be shown from the GS construction of the f_ν and the definition of the $\{\Delta_\nu\} = \{\Delta_1, \Delta_2, \ldots, \Delta_\nu\}$, all the three sets $\{\Delta_\nu\}$, $\{I_j^{(0)}\}$, and $\{z_j^{(0)}\}$ may be expressed in terms of the normalized spectral moments $\{\langle\omega^{(\nu)}\rangle\} = \{\omega^{(\nu)}/\omega^{(0)}\}$. In particular, from Eq. (16a) and the relationship between the normalized moments and the zero-time derivatives of the correlation function, we see that $\{I_j^{(0)}\}$ and $\{z_j^{(0)}\}$ satisfy a set of relations of the form

$$\sum_{j=1}^{\infty} I_j^{(0)} \left(z_j^{(0)}\right)^k = i^k \langle\omega^k\rangle \tag{17}$$

for $0 < k < \infty$. Similar considerations can also be given for all the memory functions $K_\nu(t)$ of Eq. (16b).

The expansion (16a) of the quantum mechanical relaxation function (normalized to its initial-time value) $a_0(t)$ of the variable A is given in terms of an infinite set of exponential functions and is a general form for the solution of the GLE (10), which appears as a reorganization of, and an alternative to, the usual power expansion

$$a_0(t) = \sum_{n=0}^{\infty} \frac{i^n \langle\omega^n\rangle}{n!} t^n. \tag{18}$$

The expressions (16a) and (18) of the time behavior of the correlation function $a_0(t)$ are both exact but in some sense complementary to each other since, when taken in an approximated form with partial summation, Eq. (18) is useful in describing the behavior at short times, while Eq. (16a) is useful at longer times. In fact, approximations of (18) mean to retain a few power terms, while to approximate Eq. (16a) means to retain a few exponential functions, which is the same as truncating the continued fraction (12) at a convenient low level. Obviously both approximations violate, at some level, the physical request that all frequency moments of $(A, A(t))$ must be determined and finite, limiting the number of relations (17) that can be practically used.

From the previous considerations it is clear that the general result given in Eqs. (14a) and (16a) can be derived, in the present framework, without introducing the GLE and the concept of memory function. We have, however, rederived the GLE and introduced here the definition of memory functions in order to match the theoretical derivations conventionally adopted following the MZ approach. Once the concept of memory function is introduced, Eq. (16b) shows that an EF can also be given for the $\{K_\nu(t)\}$ for any value of ν.

III. SYMMETRY PROPERTIES OF AUTOCORRELATIONS AND SPECTRA

In order to apply the results of Sec. II to time autocorrelation functions relevant to the study of many-body quantum mechanical systems, we need to consider their symmetry properties and those of the related spectra. For this, we refer to and recall a few basic results of the linear response theory [4,6,24], assuming that we are interested in the time evolution of the autocorrelation of a variable A, expressed as

$$f_{AA^\dagger}(t) = \langle A A^\dagger(t)\rangle. \tag{19}$$

We consider a system in which initially ($t = -\infty$) is in thermodynamic equilibrium, for which a small perturbation $H_1 = -A\xi(t)$ is added adiabatically to the equilibrium Hamiltonian H. The effect of the perturbation is to produce an explicit time dependence of the average value of the variable associated to the operator $A^\dagger$, given by

$$\overline{A^\dagger(t)} = \int_{-\infty}^{t} dt' \frac{i}{\hbar} \phi_{A^\dagger A}(t - t')\xi(t'), \tag{20}$$

where we used the previous assumption that $\langle A^\dagger\rangle = 0$ and where

$$\phi_{A^\dagger A}(t) = \langle [A^\dagger(t), A]\rangle = f_{A^\dagger A}(-t) - f_{AA^\dagger}(t). \tag{21}$$

For convenience, we use in the following $\phi_{A^\dagger A}(t)$ instead of the exact linear response function defined in the literature as $(i/\hbar)\phi_{A^\dagger A}(t)$.

For our purposes, as will become clear later, a more interesting function is the Kubo relaxation function

$$R_{A^\dagger A}(t) = \int_0^\beta d\mu \langle A e^{-\mu H} A^\dagger(t) e^{\mu H}\rangle, \tag{22}$$

which is related to the response function through

$$R_{A^\dagger A}(t) = \frac{i}{\hbar} \int_t^\infty dt' \phi_{A^\dagger A}(t') \tag{23}$$

and describes the time behavior of the relaxation of the system. In fact, the change in $\overline{A^\dagger(t)}$ after that the perturbation $\xi(t)$ is switched off at $t = 0$ is, from Eq. (20)

$$\overline{A^\dagger(t)} = \int_t^\infty dt' \frac{i}{\hbar} \phi_{A^\dagger A}(t')\xi(t - t'), \tag{24}$$

showing that $R_{A^\dagger A}(t)$ is a property of the system independent of the form of the perturbation, which in particular closely resembles the evolution of $\overline{A^\dagger(t)}$ after the switching off of a static perturbation.

From the general property of the autocorrelation (19)

$$f_{AA^\dagger}(-t) = f^*_{AA^\dagger}(t) \tag{25}$$

and Eq. (21) it follows that

$$\phi_{A^\dagger A}(-t) = \phi^*_{A^\dagger A}(t), \tag{26}$$

while from the definition (22) one also has

$$R_{A^\dagger A}(-t) = R^*_{A^\dagger A}(t). \tag{27}$$

Moreover, it is easy to show that

$$f_{AA^\dagger}(-t) = f_{A^\dagger A}(t + i\hbar\beta), \tag{28}$$

$$\phi_{A^\dagger A}(-t) = -\phi_{AA^\dagger}(t), \tag{29}$$

and

$$R_{A^\dagger A}(-t) = R_{AA^\dagger}(t). \tag{30}$$

The latter two equations display the opposite behavior of $\phi_{A^\dagger A}(t)$ and $R_{A^\dagger A}(t)$ with respect to the time inversion under exchange of the involved operators, in agreement with (23) or with its equivalent

$$\frac{i}{\hbar}\phi_{A^\dagger A}(t) = -\frac{dR_{A^\dagger A}}{dt}(t). \tag{31}$$

Let us now discuss the properties of the power spectrum of the various correlation functions defined above. If we denote by $\hat{F}(\omega)$ the Fourier transform of a generic function of time $F(t)$ we have

$$\begin{aligned}\hat{F}(\omega) &= \frac{1}{2\pi}\int_{-\infty}^{+\infty} dt\, \exp(-i\omega t)F(t) \\ &= \frac{1}{2\pi}\mathcal{L}[F(t), z = i\omega] + \frac{1}{2\pi}\mathcal{L}[F(-t), z = -i\omega],\end{aligned} \tag{32}$$

but if $F(-t) = F^*(t)$ the last term equals $(1/2\pi)\mathcal{L}[F^*(t), z = -i\omega]$ so that

$$\hat{F}(\omega) = \frac{1}{\pi}\mathrm{Re}\tilde{F}(i\omega) \tag{33}$$

and the spectrum $\hat{F}(\omega)$ is real. Equations (25)–(27) show that the above condition is satisfied by all the correlation functions of interest here.

Under Fourier transformation the relationships (28)–(30) translate into

$$\hat{f}_{AA^\dagger}(-\omega) = \exp(-\beta\hbar\omega)\hat{f}_{A^\dagger A}(\omega), \tag{34}$$

$$\hat{\phi}_{A^\dagger A}(-\omega) = -\hat{\phi}_{AA^\dagger}(\omega), \tag{35}$$

and

$$\hat{R}_{A^\dagger A}(-\omega) = \hat{R}_{AA^\dagger}(\omega), \tag{36}$$

while from Eq. (31) the spectra of $R_{A^\dagger A}(t)$ and $\phi_{A^\dagger A}(t)$ are related by

$$\hat{\phi}_{A^\dagger A}(\omega) = -\hbar\omega\hat{R}_{A^\dagger A}(\omega). \tag{37}$$

Using Eqs. (21), (34), and (37) we finally find

$$\begin{aligned}\hat{f}_{AA^\dagger}(\omega) &= -[1 + n(\omega)]\hat{\phi}_{A^\dagger A}(\omega) \\ &= \hbar\omega[1 + n(\omega)]\hat{R}_{A^\dagger A}(\omega)\end{aligned} \tag{38}$$

with $1 + n(\omega) = [1 - \exp(-\beta\hbar\omega)]^{-1}$, where $n(\omega)$ is the occupation number in the Bose-Einstein statistics.

It is seen that the spectra $\hat{f}_{AA^\dagger}(\omega)$, $\hat{R}_{A^\dagger A}(\omega)$, $\hat{\phi}_{A^\dagger A}(\omega)$ are all related to one another by means of simple expressions and the knowledge of one is sufficient to know all of them. They also possess simple symmetry relations with respect to ω inversion and operator exchange.

The key formula in this section is Eq. (30), because we have used the Kubo relaxation function for the definition of the inner product (3) in order to demonstrate the LF of spectra from the continued fraction representation. However, we already noted that the Lee method requires the inner product to be an even function of time. Equation (30) evidently satisfies this condition when A is a Hermitian operator, but in the next section we show that the same is also true for correlations of large interest in spectroscopic techniques, in which non-Hermitian operators are involved.

IV. HERMITIAN LOCAL OPERATORS

Let us now consider the relevant particular case of a Hermitian operator $A(\mathbf{r})$ representing a local variable and therefore explicitly depending on the coordinate $\mathbf{r}$ of a generic point in the N-body system. We write

$$A(\mathbf{r}) = \sum_{\ell=1}^{N} A_\ell \delta(\mathbf{r} - \mathbf{R}_\ell), \tag{39}$$

where $\mathbf{R}_\ell$ is the position operator of the ℓth particle while A_ℓ is the operator corresponding to the one-particle dynamical variable. The spatial Fourier components of $A(\mathbf{r})$,

$$A_\mathbf{k} = \sum_{\ell=1}^{N} A_\ell \exp(i\mathbf{k}\cdot\mathbf{R}_\ell), \tag{40}$$

are not Hermitian and, in fact, $A_\mathbf{k} = A^\dagger_{-\mathbf{k}}$.

We are interested in the space-time autocorrelation of $A(\mathbf{r})$ defined in general as $\langle A(\mathbf{r})A(\mathbf{r}',t)\rangle$. However, it is customary to remove the dependence on the choice of the space origin by integrating on the whole space, and consider the quantity

$$f_{AA}(\mathbf{r},t) = \left\langle \frac{1}{N}\int d\mathbf{r}' A(\mathbf{r}' - \mathbf{r})A(\mathbf{r}',t)\right\rangle, \tag{41}$$

where now $\mathbf{r}$ denotes the distance between the two points. With $A_\ell = 1$ this is, for example, the standard definition of the pair correlation function $G(\mathbf{r},t)$ introduced by van Hove [25] in order to describe the dynamics of the autocorrelation of density fluctuations. It can be easily shown [24] that

$$f_{AA}(\mathbf{r},t) = \frac{1}{(2\pi)^3}\int d\mathbf{k} F_{A^\dagger_\mathbf{k}A_\mathbf{k}}(\mathbf{k},t)\exp(-i\mathbf{k}\cdot\mathbf{r}), \tag{42}$$

where we have introduced the so-called intermediate correlation function

$$F_{A^\dagger_\mathbf{k}A_\mathbf{k}}(\mathbf{k},t) = \frac{1}{N}\langle A^\dagger_\mathbf{k}A_\mathbf{k}(t)\rangle. \tag{43}$$

We now apply the results of previous sections to the time autocorrelation (43) and to its spectrum

$$\hat{f}_{A^\dagger_\mathbf{k}A_\mathbf{k}}(\mathbf{k},\omega) = \frac{N}{2\pi}\int_{-\infty}^{+\infty} dt\exp(-i\omega t)F_{A^\dagger_\mathbf{k}A_\mathbf{k}}(\mathbf{k},t), \tag{44}$$

which is the space and time Fourier transform of $f_{AA}(\mathbf{r},t)$. Equations (34) and (38) prescribe that

$$\begin{aligned}\hat{f}_{A^\dagger_\mathbf{k}A_\mathbf{k}}(\mathbf{k},\omega) &= \exp(-\beta\hbar\omega)\hat{f}_{A_\mathbf{k}A^\dagger_\mathbf{k}}(\mathbf{k},\omega) \\ &= \hbar\omega[1 + n(\omega)]\hat{R}_{A_\mathbf{k}A^\dagger_\mathbf{k}}(\mathbf{k},\omega).\end{aligned} \tag{45}$$

If the system possesses space inversion symmetry, namely, $f_{AA}(\mathbf{r},t) = f_{AA}(-\mathbf{r},t)$, it is immediately found from Eq. (42) that all the time correlations of the $A_{\mathbf{k}}$ are symmetric with respect to the $\mathbf{k}$ inversion, which amounts to interchange the subscripts $A_{\mathbf{k}}$ and $A_{\mathbf{k}}^{\dagger}$. Then

$$R_{A_{\mathbf{k}}^{\dagger}A_{\mathbf{k}}}(\mathbf{k},t) = R_{A_{\mathbf{k}}A_{\mathbf{k}}^{\dagger}}(\mathbf{k},t). \tag{46}$$

Since from Eq. (30) we also have $R_{A_{\mathbf{k}}^{\dagger}A_{\mathbf{k}}}(\mathbf{k},t) = R_{A_{\mathbf{k}}A_{\mathbf{k}}^{\dagger}}(\mathbf{k},-t)$, we find

$$R_{A_{\mathbf{k}}^{\dagger}A_{\mathbf{k}}}(\mathbf{k},t) = R_{A_{\mathbf{k}}^{\dagger}A_{\mathbf{k}}}(\mathbf{k},-t). \tag{47}$$

Together with Eq. (27), this shows that $R_{A_{\mathbf{k}}^{\dagger}A_{\mathbf{k}}}(\mathbf{k},t)$ is a real, even function of time and, correspondingly, its spectrum obeys

$$\hat{R}_{A_{\mathbf{k}}^{\dagger}A_{\mathbf{k}}}(\mathbf{k},\omega) = \hat{R}_{A_{\mathbf{k}}^{\dagger}A_{\mathbf{k}}}(\mathbf{k},-\omega), \tag{48}$$

i.e., it is an even function of ω.

Equations (47) or (48) ensure the applicability of the results of Sec. II for the development of the LF representation of $\hat{f}_{A_{\mathbf{k}}^{\dagger}A_{\mathbf{k}}}(\mathbf{k},\omega)$ through the one relative to $\hat{R}_{A_{\mathbf{k}}^{\dagger}A_{\mathbf{k}}}(\mathbf{k},\omega)$. We start by writing $R_{A_{\mathbf{k}}^{\dagger}A_{\mathbf{k}}}(\mathbf{k},t)$ and its Laplace transform using Eq. (16) as

$$R_{A_{\mathbf{k}}^{\dagger}A_{\mathbf{k}}}(\mathbf{k},t) = R_{A_{\mathbf{k}}^{\dagger}A_{\mathbf{k}}}(\mathbf{k},0)\sum_{j=1}^{\infty} I_j^{(R)}(\mathbf{k})\exp\left(z_j^{(R)}(\mathbf{k})|t|\right), \tag{49}$$

$$\tilde{R}_{A_{\mathbf{k}}^{\dagger}A_{\mathbf{k}}}(\mathbf{k},z) = R_{A_{\mathbf{k}}^{\dagger}A_{\mathbf{k}}}(\mathbf{k},0)\sum_{j=1}^{\infty}\frac{I_j^{(R)}(\mathbf{k})}{z - z_j^{(R)}(\mathbf{k})}, \tag{50}$$

where $I_j^{(R)}(\mathbf{k})$ and $z_j^{(R)}(\mathbf{k})$, similarly to the general case (16), are functions of the reduced moments $\{\langle\omega^{\nu}(\mathbf{k})\rangle\}$ of $\hat{R}_{A_{\mathbf{k}}^{\dagger}A_{\mathbf{k}}}(\mathbf{k},\omega)$ and may only be either real or pairs of complex conjugate values because in this case we are dealing with a relaxation function which is real and symmetric under time reversal. $I_j^{(R)}(\mathbf{k})$ and $z_j^{(R)}(\mathbf{k})$ appear as the amplitudes and the eigenfrequencies, respectively, of a normal mode representation of $R_{A_{\mathbf{k}}^{\dagger}A_{\mathbf{k}}}(\mathbf{k},t)$, with $\mathrm{Re}z_j^{(R)}(\mathbf{k}) < 0$ since $R_{A_{\mathbf{k}}^{\dagger}A_{\mathbf{k}}}(\mathbf{k},t) \to 0$ for $t \to \infty$.

Expression (49) is a solution of the dynamical equation for $R_{A_{\mathbf{k}}^{\dagger}A_{\mathbf{k}}}(\mathbf{k},t)$ given in terms of an expansion with respect to a set of exponential functions, and also in this case is alternative to the usual expansion in powers of the time

$$\frac{R_{A_{\mathbf{k}}^{\dagger}A_{\mathbf{k}}}(\mathbf{k},t)}{R_{A_{\mathbf{k}}^{\dagger}A_{\mathbf{k}}}(\mathbf{k},0)} = \frac{(A_{\mathbf{k}},A_{\mathbf{k}}(t))}{(A_{\mathbf{k}},A_{\mathbf{k}})} = \sum_{j=0}^{\infty}\frac{t^j}{j!}\langle\omega^j(\mathbf{k})\rangle, \tag{51}$$

where $i^j\langle\omega^j(\mathbf{k})\rangle = (A_{\mathbf{k}},A_{\mathbf{k}}^{(j)})/(A_{\mathbf{k}},A_{\mathbf{k}})$, while the parity of $R_{A_{\mathbf{k}}^{\dagger}A_{\mathbf{k}}}(\mathbf{k},t)$ implies that $\langle\omega^j(\mathbf{k})\rangle = 0$ for all odd j.

The spectrum $\hat{R}_{A_{\mathbf{k}}^{\dagger}A_{\mathbf{k}}}(\mathbf{k},\omega)$ assumes the LF form [26]:

$$\begin{aligned}\hat{R}_{A_{\mathbf{k}}^{\dagger}A_{\mathbf{k}}}(\mathbf{k},\omega) &= \frac{1}{\pi}R_{A_{\mathbf{k}}^{\dagger}A_{\mathbf{k}}}(\mathbf{k},0)\mathrm{Re}\left[\tilde{R}_{A_{\mathbf{k}}^{\dagger}A_{\mathbf{k}}}(\mathbf{k},i\omega)\right]\\ &= \frac{1}{\pi}R_{A_{\mathbf{k}}^{\dagger}A_{\mathbf{k}}}(\mathbf{k},0)\left[\sum_r\frac{-I_r(\mathbf{k})z_r(\mathbf{k})}{z_r^2(\mathbf{k})+\omega^2} + \sum_c\left(\frac{-I_c'(\mathbf{k})z_c'(\mathbf{k}) + I_c''(\omega - z_c''(\mathbf{k}))}{(z_c'(\mathbf{k}))^2 + (\omega - z_c''(\mathbf{k}))^2} + \frac{-I_c'(\mathbf{k})z_c'(\mathbf{k}) - I_c''(\omega + z_c''(\mathbf{k}))}{(z_c'(\mathbf{k}))^2 + (\omega + z_c''(\mathbf{k}))^2}\right)\right],\end{aligned} \tag{52}$$

where we have dropped the superscript (R) and where r labels the real $\{z_j(\mathbf{k}), I_j(\mathbf{k})\}$, while c refers to pairs of complex conjugate $\{z_j(\mathbf{k}), I_j(\mathbf{k})\}$ with mode frequencies $z_c(\mathbf{k}) = z_c'(\mathbf{k}) \pm i z_c''(\mathbf{k})$ and respective amplitudes $I_c(\mathbf{k}) = I_c'(\mathbf{k}) \pm i I_c''(\mathbf{k})$.

The final expression in LF form of the spectrum of the autocorrelation function is then

$$\begin{aligned}\hat{f}_{A_{\mathbf{k}}^{\dagger}A_{\mathbf{k}}}(\mathbf{k},\omega) = \frac{1}{\pi}\hbar\omega[1+n(\omega)]R_{A_{\mathbf{k}}^{\dagger}A_{\mathbf{k}}}(\mathbf{k},0)&\left[\sum_r\frac{-I_r(\mathbf{k})z_r(\mathbf{k})}{z_r^2(\mathbf{k})+\omega^2}\right.\\ &\left.+\sum_c\left(\frac{-I_c'(\mathbf{k})z_c'(\mathbf{k}) + I_c''(\omega - z_c''(\mathbf{k}))}{(z_c'(\mathbf{k}))^2 + (\omega - z_c''(\mathbf{k}))^2} + \frac{-I_c'(\mathbf{k})z_c'(\mathbf{k}) - I_c''(\omega + z_c''(\mathbf{k}))}{(z_c'(\mathbf{k}))^2 + (\omega + z_c''(\mathbf{k}))^2}\right)\right].\end{aligned} \tag{53}$$

In full analogy with the results (47) and (48), one also obtains that $\phi_{A_{\mathbf{k}}^{\dagger}A_{\mathbf{k}}}(\mathbf{k},t)$ is an imaginary and odd function of time, while $\hat{\phi}_{A_{\mathbf{k}}^{\dagger}A_{\mathbf{k}}}(\mathbf{k},\omega)$ is a real and odd function of frequency. Using Eq. (31) it is then possible to write $\phi_{A_{\mathbf{k}}^{\dagger}A_{\mathbf{k}}}(\mathbf{k},t)$ in the form

$$\begin{aligned}\phi_{A_{\mathbf{k}}^{\dagger}A_{\mathbf{k}}}(\mathbf{k},t) = i\hbar\,\mathrm{sgn}(t)&R_{A_{\mathbf{k}}^{\dagger}A_{\mathbf{k}}}(\mathbf{k},0)\\ &\times\sum_{j=1}^{\infty}I_j^{(R)}(\mathbf{k})z_j^{(R)}(\mathbf{k})\exp\left(z_j^{(R)}(\mathbf{k})|t|\right),\end{aligned} \tag{54}$$

where $\mathrm{sgn}(t) = t/|t|$ accounts for the odd time parity property of $\phi_{A_{\mathbf{k}}^{\dagger}A_{\mathbf{k}}}(\mathbf{k},t)$. Also, using Eq. (37), the spectrum of the response function $\hat{\phi}_{A_{\mathbf{k}}^{\dagger}A_{\mathbf{k}}}(\mathbf{k},\omega)$ is immediately obtained from Eq. (52) in terms of the same set of eigenfrequencies which characterize the time or frequency behavior of the relaxation function.

V. APPLICATIONS

We now consider two cases of practical application of the results of the general theory to spectra of many-body correlation functions in fluids, showing that they can be represented with Lorentzian functions. In both cases, the relevant quantities are not directly accessible with spectroscopic techniques. Therefore, we analyze spectra obtained by molecular dynamics simulations, which usually present the further advantage of being calculated in broad frequency ranges. However, the

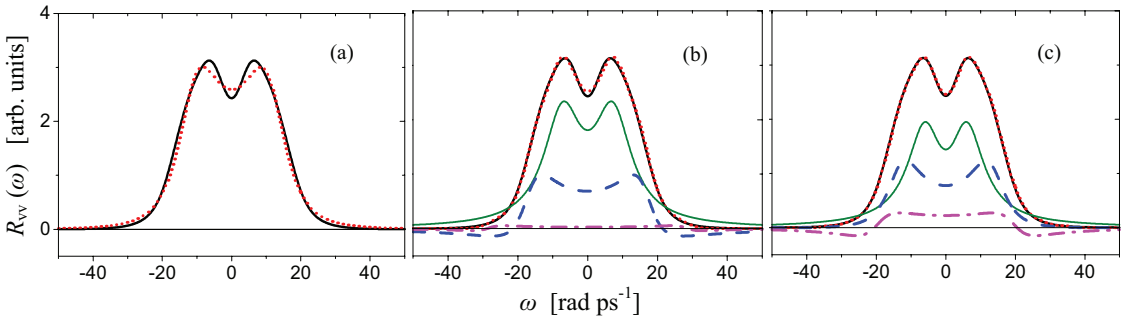

FIG. 1. (Color online) Spectrum of the relaxation function of the velocity autocorrelation function of liquid parahydrogen computed from PICMD simulation [21] (thick black curve) and best fits (red [gray] dots) obtained with the sum of 2, 6, and 10 Lorentzian lines in panels (a)–(c) respectively. In panels (b) and (c), besides the total fit, the contributions to the total of the most intense pairs of Lorentzian lines are also shown by the solid (green online), dashed (blue online), and dash-dotted (magenta online) curves.

compatibility of simulations with available experimental data has been demonstrated [21,22] as a preliminary, mandatory task to be carried out before confidently resorting to simulated data.

A. The velocity autocorrelation function of liquid hydrogen

The normalized velocity autocorrelation function is defined as

$$f_{\mathbf{vv}}(t) = \frac{\langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle}{\langle \mathbf{v}(0) \cdot \mathbf{v}(0) \rangle}, \tag{55}$$

where $\mathbf{v}(t)$ is the Hermitian operator representing the velocity of a single particle at time t and the dot denotes the scalar product. When quantum-mechanical properties are relevant it is convenient to refer to the normalized velocity relaxation function $R_{\mathbf{vv}}(t)$

$$R_{\mathbf{vv}}(t) = \frac{\int_0^\beta d\mu \langle \mathbf{v} e^{-\mu H} \cdot \mathbf{v}(t) e^{\mu H} \rangle}{\int_0^\beta d\mu \langle \mathbf{v} e^{-\mu H} \cdot \mathbf{v}(0) e^{\mu H} \rangle}. \tag{56}$$

Much work has been devoted in recent years to the development of algorithms for the simulation of the dynamics of quantum mechanical fluids of Boltzmann particles. We use here the results obtained recently from the application of the path-integral centroid molecular dynamics (PICMD) technique to the case of liquid parahydrogen [21], and we analyze the spectrum $\hat{R}_{\mathbf{vv}}(\omega)$ by fitting to the data the sum of an increasing number of Lorentzian lines. It turns out that the quality of the fit significantly improves when new lines are added in pairs, corresponding to the introduction of pairs of complex conjugate frequencies $z_j^{(R)}$, and we have used 2, 4, 6, 8, and 10 lines.

The results are shown in Fig. 1 for the cases of 2, 6, and 10 lines. The contributions of the most intense pairs are shown together with the total fitted spectrum, which can hardly be distinguished from the data in the second fit and shows a perfect agreement in the third one. The dramatic improvement of the fit quality with increasing the number of complex Lorentzian lines is evident in Fig. 2, which shows an exponential reduction of sum of squares of residuals $\Delta^2 = \sum_i (S_i - S_{i,\mathrm{fit}})^2$, where S_i and $S_{i,\mathrm{fit}}$ are the simulated and fitted spectral intensities, respectively, and the index i runs over the data points.

B. The dynamic structure factor of liquid CO_2

The dynamic structure factor of a monatomic fluid is the spectrum (44) of the autocorrelation function (43) of the local operator $A_{\mathbf{k}}$ given by Eq. (40) when $A_\ell = 1$, thus

$$S(\mathbf{k},\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt \exp(-i\omega t) \times \left\langle \frac{1}{N} \sum_{\ell,\ell'=1}^{N} \exp(-i\mathbf{k} \cdot \mathbf{R}_\ell) \exp(i\mathbf{k} \cdot \mathbf{R}_{\ell'}(t)) \right\rangle. \tag{57}$$

(In order to comply with the standard notation we do not put a hat over the symbol S.) In the case of a molecular fluid, being interested in the translational dynamics, we identify the position $\mathbf{R}_\ell$ as that of the center of mass of the ℓth molecule, as discussed in Ref. [22] where a neutron scattering experimental validation of molecular dynamics simulations of liquid carbon dioxide allowed for a detailed analysis of the partial carbon-carbon dynamic structure factor. CO_2 can be considered as a classical fluid, so that the expansion in Lorentzian functions can be applied directly to the structure factor, which for a homogeneous and isotropic fluid depends only on the magnitude k of the wave vector $\mathbf{k}$.

In Ref. [22] it was shown that the spectrum is well described if the continued fraction is truncated at the level of the second-order memory function and a viscoelastic modeling

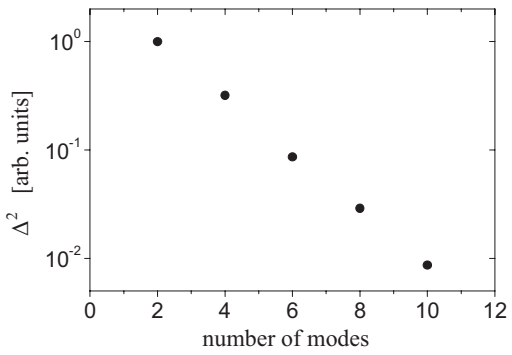

FIG. 2. Values of the sum of squares of residuals in the fit of sum of Lorentzian lines to the data shown in Fig. 1, as a function of the number of lines, arbitrarily normalized to the value obtained with two Lorentzians.

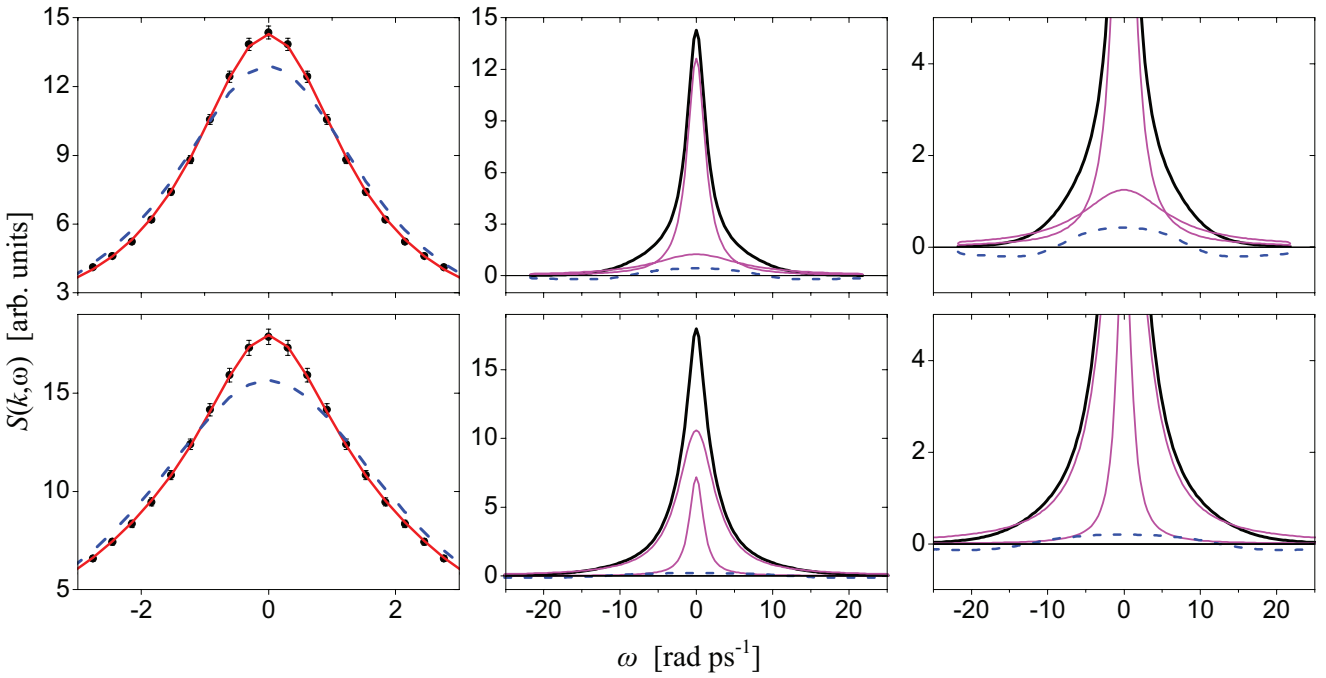

FIG. 3. (Color online) Left panels: simulated center-of-mass $S(k,\omega)$ of liquid CO_2 (dots) and best fits obtained with the four-line viscoelastic model (solid [red online] curve through the data points) and the three-line generalized-hydrodynamics model (dashes [blue online]). Only the peak region is displayed. Central panels: for the viscoelastic fit only, the total curve (black solid curve) is shown together with the separate contributions of each central Lorentzian line (thin solid [magenta online] curves) and of the pair of inelastic sound modes (dashes [blue online]). Right panels: The low-intensity parts of the plots in the central frames are magnified for a clearer display of the inelastic mode contributions. The upper panels refer to $k = 6$ nm^{-1}, and the lower panels refer to $k = 9$ nm^{-1}.

for the latter is assumed, which is known to give rise to a four-Lorentzian spectrum [17]. In the whole k range, with the exception of an interval around the position of the main peak of the static structure factor $S(k)$, two of the four lines are characterized by complex eigenfrequencies and correspond to the excitation of acoustic modes. Here we compare the result of such a viscoelastic fit with the one based on the simpler function provided by the generalization of the well-known three-line hydrodynamic lineshape, where only one central Lorentzian is added to the pair of inelastic lines describing the acoustic modes.

Figure 3 shows, for two values of k, how the four-Lorentzian approximation reveals itself superior, mainly in the description of the shape of the quasielastic central peak. For the two values of k considered in the figure, the reduced χ^2 of the fit is smaller by factors of 5.5 and 1.8, respectively, than that obtained with the generalized-hydrodynamics fit model. It is worth noting that the same result was obtained in the analysis of liquid CD_4 as well [19]. The two central components and the sum of the two inelastic lines of the viscoelastic spectrum are also displayed in Fig. 3.

As already recalled in Sec. I, this kind of analysis has been carried out on a large variety of experimental datasets obtained from neutron and x-ray inelastic scattering studies on fluids by modeling the second-order memory function in various ways, which can all be shown to lead to a spectrum composed of a sum of an appropriate number of Lorentzian lines [17], although in many cases this universal property of the line shapes was not recognized.

VI. CONCLUSIONS

We have here applied the recurrent relation approach to the solution of the dynamical problem in a many-body quantum mechanical system of Boltzmann particles at thermodynamic equilibrium. We have demonstrated the following:

(a) The relaxation function of a single operator defined by the Kubo transform can be written in terms of an infinite sum of exponential functions when either the operator is Hermitian or it is the spatial Fourier component of a local variable in a system with space inversion symmetry. As a consequence, the spectum of the relaxation function can be given as an infinite sum of Lorentzian functions.

(b) The previous results lead to the possibility of defining eigenfrequencies in a normal-mode representation of the relaxation function. These are the complex frequencies emerging from the diagonalization procedure of the continued-fraction Laplace transform of the relaxation itself.

(c) Exploiting directly the relation between the spectrum of the relaxation function and that of the autocorrelation function of a dynamical variable, we also give an LF for the latter, which is the quantity usually connected to experimental results and also properly takes into account the detailed balance property.

(d) Similar to the classical case, also in the general quantum case the solution of the dynamical problem in terms of the EF of the relaxation function as well as the LF representation of its spectrum does not require the introduction of the GLE hierarchy and the concept of memory function, although these may be useful in some cases.

(e) In practical cases, experimental or calculated spectra of autocorrelations must be approximated with a finite number of Lorentzian functions, and the related relaxation function must be approximated with a finite number of exponential functions. This amounts to performing a "long-time" representation which will not be able to account in detail for all the higher-order time derivatives at $t = 0$, corresponding to the impossibility of having finite values for the higher-order frequency moments of the spectrum.

(f) From a practical point of view, the few-mode approximation is equivalent to the truncation of the continued fraction at an appropriate level. However, it is directly linked to the concept of retaining an appropriate number of normal modes in the description of the correlation which is not evident at all in the continued fraction alone. This truncation can be carried out by exploiting the Markovian approximation to model the memory function at the corresponding level as a δ function of time.

(g) The few-mode approximation, as well as the truncation of the continued fraction at a given level ν_0, has the same effect as the contraction of the general Hilbert space S down to ν_0 dimensions. This is equivalent to considering for the reconstruction of $a_0(t)$ only the manifold $\{f_1, f_2, \ldots, f_{\nu_0}\}$, corresponding to the well-defined physical fact of taking into account, in the time evolution of $a_0(t)$, only correlations of $A(t)$ with $A^{(\nu)}$ up to $\nu = \nu_0$.

What we call here eigenmodes of the correlation functions or of the respective spectra reflect the existence of many (in theory, infinite) decay channels for the correlation under consideration. These may differ to a great extent depending on the dynamical variable of which one takes the autocorrelation, the system, and its macroscopic state. For example, physical intuition suggests that the eigenmodes of correlation functions related to single-particle dynamics in fluids may clearly differ in meaning and behavior when passing from a dilute gas to a dense liquid, reflecting the difference between situations dominated, respectively, either by free streaming or by slow diffusion hindered by oscillatory motions related to cage effects, as in the case considered. The results of the theory presented in this paper are very general in nature and, as such, we do not expect them to have a prescriptive character in detail.

The two examples reported in this work illustrate the general properties summarized here. While the analysis of collective dynamics spectra is traditionally performed by means of fit models that can be reduced to application of the LF property, the interpretation of the velocity autocorrelation spectrum in terms of Lorentzian lines has not been presented so far in the literature.

ACKNOWLEDGMENT

We are grateful to Martin Neumann for providing the simulation data of the velocity autocorrelation spectrum of liquid hydrogen.

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[26] Equation (52) is equivalent to formula (20) in Ref. [16], where, unfortunately, the second of the two terms relative to a pair of complex conjugate modes was missing. We apologize for the mistake.