PHYSICAL REVIEW E **101**, 052110 (2020)

Time dependence of quantum correlation functions

Ubaldo Bafile,[1,*] Martin Neumann,[2] Daniele Colognesi,[1] and Eleonora Guarini[3]
[1]Consiglio Nazionale delle Ricerche, Istituto di Fisica Applicata "Nello Carrara", via Madonna del Piano 10, I-50019 Sesto Fiorentino, Italy
[2]Fakultät für Physik der Universität Wien, Strudlhofgasse 4, A-1090 Wien, Austria
[3]Dipartimento di Fisica e Astronomia, Università degli Studi di Firenze, via G. Sansone 1, I-50019 Sesto Fiorentino, Italy

(Received 21 January 2020; accepted 21 April 2020; published 12 May 2020)

In the past few years, the exponential expansion analysis of time autocorrelation functions has provided profound insight into the leading microscopic processes driving the atomic-scale dynamics and has made it possible to highlight the presence and the role of various relaxation channels through which the fundamental correlation functions decay with time. Here we apply this method to the determination of the full time dependence of a correlation function $c(t)$ in a quantum system at nonzero temperature, by making explicit its relationship with its Kubo transform $c_{\mathrm{K}}(t)$, which in some cases can be approximately computed with the presently available quantum simulation techniques. We obtain an exact expression for $c(t)$ in terms of the exponential modes that describe the time behavior of $c_{\mathrm{K}}(t)$. The relative importance of the various modes in determining the overall shape of $c(t)$ can then be studied in detail. This work extends to the full time domain the results of a previous paper [Guarini *et al.*, Phys. Rev. Lett. **123**, 135301 (2019)], in which we employed the same method to calculate the zero time value of the velocity autocorrelation function, to obtain a microscopic description of the quantum mean kinetic energy in a fluid. In particular, we show that the decay constants and the frequencies of the dominant microscopic modes of $c(t)$ are the same as those of $c_{\mathrm{K}}(t)$, but the dynamics of the quantum system also contains an additional term decaying on a time scale determined solely by temperature of the system.

DOI: 10.1103/PhysRevE.101.052110

I. INTRODUCTION

In recent years, the study of dynamical properties of condensed matter systems, with particular emphasis on the liquid state, has made significant progress through the application of the concept of an exponential mode expansion of time correlation functions. The theoretical basis of this approach consists in the proof, reported in Refs. [1–3], of a very general property of correlation functions in many-body Hamiltonian systems, which states that their exact time dependences can be expressed as an infinite series of exponential terms. In the theory, each of these terms, called "modes," corresponds to a relaxation process establishing a decay channel through which the autocorrelation gets weaker and, eventually, either vanishes or reaches a nonzero asymptotic value. (In the latter case, with which we will not be concerned here, the exponential functionality describes the decay to such a limit value.)

By investigating which modes are present in the exponential series of a given correlation function of a given system, one may gain deep insight into the underlying microscopic processes governing the dynamical behavior. The potential of such a method has been clearly demonstrated by showing, in the first case in which a thorough analysis has been carried out [4,5], that the time dependence of the velocity autocorrelation function (VAF) of a supercritical Lennard–Jones fluid is the result of an interplay of both diffusive and oscillatory motions. The latter exhibited the typical properties of collective propagating excitations such as longitudinal and, in a certain range of thermodynamic conditions, transverse acoustic waves. The former included also the very slow decay which is usually referred to as the so-called long time tail phenomenon [6–10]. However, one of the central results of the works reported in Refs. [4,5] was that a small subset of modes provided a consistent description of the VAF over the entire time range, and that the character of these modes was seen to change in a smooth way while varying the thermodynamic state of the fluid.

A further application of the exponential expansion is the analysis of relationships between the mode properties of autocorrelation functions of different dynamical variables of the same system. This is an exclusive achievement of the mode approach and highlights in a quantitative way the fact that the same dynamical processes shape the time behavior of inter-related correlation functions through different projections onto the respective dynamical variables. A representative example is the work reported in Ref. [11], where the modes describing the *self* part of the dynamic structure factor of a liquid metal have been used to determine the spectrum of the corresponding VAF, in perfect agreement with its direct evaluation through Fourier transformation of the VAF obtained from a molecular dynamics simulation [12]. The correspondence between the sets of modes involved in the description of the two mentioned dynamical quantities is based on the most common link between autocorrelation functions of interest in many-body systems, namely, the link between the autocorrelation of a dynamical variable and the autocorrelation of the time derivative of the same variable.

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[*] u.bafile@ifac.cnr.it

Such a case, given its relevance also for the problem addressed in this paper, will be treated in more detail in Sec. IV.

The exponential mode description is not limited to classical systems. For a quantum liquid, it has been proved [2,3] that an analogous expansion is also able to represent the entire time dependence of the Kubo transform [13] of an autocorrelation function of a Hermitian operator. Very recently, we have exploited this approach in the analysis of the mode expansion of the Kubo-transformed VAF in fluid parahydrogen, studied both as a function of temperature [14] and of density [15], using data obtained with the ring polymer molecular dynamics (RPMD) simulation technique [16,17].

The relationship between a true quantum autocorrelation function and its Kubo-transformed version is best expressed if one considers the respective frequency spectra, which are connected to each other by the detailed balance asymmetry. In the time domain, this asymmetry implies that, while the Kubo autocorrelation function is a real and even function of time, the standard autocorrelation of the relevant quantum operator is a complex function of time whose real and imaginary parts have specific and opposite parity properties.

So far, the question of how the decay processes governing the dynamical behavior determine the shape of a quantum autocorrelation function remains a fully unexplored problem. In view of the above considerations, it appears natural to investigate it by looking at the way the exponential modes forming the expansion of the Kubo autocorrelation function are modified to produce the time behavior of the corresponding quantum correlation. This paper presents the solution to this problem and provides an explicit and exact expression for the time dependence of the latter. This theoretical result is fully general, in that it is valid for the autocorrelation of any dynamical variable. We can then transfer to the quantum correlation function all the knowledge the mode expansion of its Kubo transform provides about the dynamical processes and the leading decay mechanisms acting in the system at the atomic scale.

The Kubo transform is a convenient tool not only theoretically, since it transforms the quantum dynamical information into a form that looks more like a classical correlation function, but also in the analysis of simulations, because there are computational approaches like centroid molecular dynamics (CMD) [18,19] or RPMD which yield approximations to the Kubo correlation as their primary output. However, there are simulation techniques such as forward-backward semiclassical dynamics [20,21] or the Feynman–Kleinert quasiclassical Wigner method [22,23], which produce the quantum correlation function (or its real part) directly. However, from the results presented in Sec. V it will appear that the mode expansion of the quantum correlation function is much more easily obtained through the expansion of its Kubo transform.

It is worth remarking that in this work we are not concerned with computational problems related to the calculation of Kubo correlation functions of quantum systems. Devising simulation techniques able to provide increasingly better numerical approximations continues to be an active research field [24]. However, to derive the properties of a quantum correlation function from the mode expansion of the respective Kubo transform we will simply assume that the latter is known. Thus, while the example reported in Sec. VI is, in fact, a case in which the Kubo correlation function is computable with a high degree of accuracy, the general result obtained here is valid independently of the quality of any numerical computations of correlation functions.

While the Kubo transform has originally been defined for systems at finite temperatures, it has recently been shown [25] that the concept can be suitably extended (although not by a simple $T \to 0$ limit) to describe also correlations at zero temperature, i.e., in the ground state. However, in this paper we will not consider the case of systems at temperature zero or very close to zero (e.g., superfluid helium).

II. EXPONENTIAL MODE EXPANSION

In this section we briefly recall the main concepts of the exponential mode analysis, as applied, for the sake of simplicity, to the classical autocorrelation function,

$$c(t) = \langle A(0)A(t)\rangle, \tag{1}$$

of a dynamical variable $A(t)$, where $\langle \cdots \rangle$ is a statistical average and we assume that in equilibrium $\langle A\rangle = 0$. The theory derived in Refs. [1–3] may be summarized by the statement that the exact solution of the generalized Langevin equation governing the time dependence of $c(t)$ may be written in the form of an infinite sum of (generally complex) exponential functions, i.e.,

$$c(t) = \sum_{j=1}^{\infty} c_j(t) = c(0) \sum_{j=1}^{\infty} I_j \exp(z_j|t|), \tag{2}$$

with $\mathrm{Re}\, z_j < 0$ and $\sum_{j=1}^{\infty} I_j = 1$. Each term $c_j(t)$ represents a characteristic decay mode of $c(t)$ having I_j and z_j as its parameters. Equation (2) accounts for two types of decay processes: when I_j and z_j are real quantities, the jth mode is an exponentially decaying relaxation; other processes contribute to $c(t)$ with an exponentially damped, oscillating behavior, represented by pairs of terms in the sum having complex conjugate values of I_j and z_j. The two conjugate modes add up to a real quantity, and, in the classical case, the total $c(t)$ is also real. The condition $\mathrm{Re}\, z_j < 0$ incorporates the physical requirement that the total correlation function, as well as each of its modes, must decay to zero in the limit of infinite time. Moreover, each mode is an even function of time.

The spectrum of $c(t)$ is given by its Fourier transform,

$$\tilde{c}(\omega) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} dt\, e^{-i\omega t} c(t) = \sum_{j=1}^{\infty} \tilde{c}_j(\omega)$$
$$= \frac{c(0)}{\pi} \sum_{j=1}^{\infty} \frac{-I_j z_j}{\omega^2 + z_j^2}. \tag{3}$$

For a real mode, $\tilde{c}_j(\omega)$ is a Lorentzian line with half-width $-z_j$. For a complex mode Eq. (3) yields a more complicated expression which includes an imaginary part but, when taken together with its conjugate, produces a spectral shape made up of a doublet of two real, noncentral, asymmetric quasi-Lorentzian lines. For the sake of conciseness, we will refer to $\tilde{c}_j(\omega)$ as a "Lorentzian" line in both cases throughout this paper [26]. Analogously, we will generally call z_j the "frequency" of the jth mode, even though for real modes $-z_j$

actually represents a damping constant, while for complex modes $-\mathrm{Re}\, z_j$ is the damping and $\mathrm{Im}\, z_j$ is the true oscillation frequency.

Although Eq. (2) gives the formally exact expression of $c(t)$ as an infinite sum, any actual set of data, derived from either experiments or simulations, always consists of a finite number of values collected over a finite time domain and with a limited degree of accuracy. The data, therefore, never allow for an exact determination of an infinite number of modes, so that the actual description of the time behavior of $c(t)$ must be obtained from a suitable truncation of the series in Eq. (2). This is a standard procedure in dynamics studies, for instance when the generalized Langevin equation is written in the form of a truncated continued fraction [6–8,27]. In Ref. [1] we have shown that the approximation introduced by the truncation consists in the neglect of higher-order derivatives of the dynamical variable $A(t)$. The exponential expansion is thus implemented by determining, through a fitting procedure, the parameters of a suitable number of exponential modes representing the dominant decay channels of the correlation function under consideration. As discussed in Refs. [4,5], there is no arbitrariness in the composition of the fit function, if the set of exponential terms retained in the truncated series is the smallest one which yields an accurate fitting, depending on the extent and accuracy of available data. In this way, no unjustified overparametrization of the fit model is allowed for. With respect to this point we also note that the application of Bayesian inference methods can prove very effective in the determination of the number of modes to be included in the sum in Eq. (2) by exploiting the information content of the analyzed data together with any available prior information [28,29].

In a system of particles interacting via a continuous potential it is assumed that a physically meaningful autocorrelation function of a dynamical variable is smooth and well-behaved. In particular, its time derivatives of any order are assumed to exist and to be finite. This condition is surely satisfied by the expansion in Eq. (2), but some attention must be paid to what happens at $t = 0$. For an even function of time such as $c(t)$, one requires that its first derivative vanishes at the time origin, which implies that the second derivative is finite; likewise, a vanishing third derivative at $t = 0$ leads to a finite fourth derivative, and so on, so that, provided the complete expansion is used, that function has a valid Taylor expansion around time zero. Thus, the above physical requirement of a well-behaved correlation function translates into a set of mathematical conditions called "sum rules," namely,

$$\sum_{j=1}^{\infty} I_j z_j^k = 0, \tag{4}$$

for all odd values of k. However, when only a finite number of terms is retained in the exponential series, it is not possible to satisfy the whole set of sum rules. This is an intrinsic feature of the approximation entailed by the truncation of the series or of the corresponding continued fraction [3]. In the following, we will consider sums of exponentials consisting of an unspecified, finite number of terms, constrained by an equal, or smaller, number of sum rules. Both numbers are chosen so as to obtain the best fit model according to the criteria explained above. The sum rules so enforced in the fitting, together with the obviously necessary condition $\sum_j I_j = 1$, act as constraints for the determination of the amplitudes I_j, effectively reducing the number of free parameters to be fitted. In any case, we will assume that the first sum rule,

$$\sum_j I_j z_j = 0, \tag{5}$$

is always obeyed. Note that $\mathrm{Re}\, I_j$ is not required to be positive for all j. This is evident, for example, when only real modes are present, as Eq. (5) implies that at least one of them must have a negative amplitude. In the general case, it can well happen that $\mathrm{Re}\, I_j < 0$ for more than one mode.

In the following, as in Eq. (5), all sums over modes will be assumed to extend over a finite number of terms, leaving the range of the index j unspecified.

III. CORRELATION FUNCTIONS IN A QUANTUM SYSTEM

The standard autocorrelation function of an operator $A(t)$ in a quantum system at temperature T has the general form

$$c(t) = \langle A(0)A(t)\rangle = \frac{\mathrm{Tr}[e^{-\beta H} A(0) e^{iHt/\hbar} A(0) e^{-iHt/\hbar}]}{\mathrm{Tr}[e^{-\beta H}]}, \tag{6}$$

where the angular brackets now denote the quantum statistical average performed with the canonical partition function $\mathrm{Tr}[e^{-\beta H}]$, H is the Hamiltonian operator of the system, depending on the positions and momenta of all particles, $\beta = (k_\mathrm{B}T)^{-1}$, and k_B is the Boltzmann constant.

The corresponding Kubo-transformed correlation function is [13]

$$\begin{aligned} c_\mathrm{K}(t) &= \frac{1}{\beta}\int_0^\beta d\lambda\, \langle e^{\lambda H} A(0) e^{-\lambda H} A(t)\rangle \\ &= \frac{1}{\beta}\int_0^\beta d\lambda\, \langle A(-i\hbar\lambda) A(t)\rangle. \end{aligned} \tag{7}$$

As anticipated in the Introduction, $c(t)$ is a complex-valued function, whose real and imaginary parts are even and odd functions of time, respectively, while $c(t)$ itself obeys the equation $c(-t) = c^*(t) = c(t + i\hbar\beta)$, with the asterisk denoting complex conjugation. The latter property expresses the detailed balance principle in the time domain. By contrast, $c_\mathrm{K}(t)$ is a real and even function which, although it contains information on the quantum dynamics, does so in a form more similar to a classical correlation function, for which all the properties discussed in Sec. II, including the exponential mode expansion, hold true. However, some features of $c_\mathrm{K}(t)$ can be markedly different from their true quantum properties, as exemplified by the case of the VAF, where $Mc_\mathrm{K}(0)/2 = 3/(2\beta)$ (with M the molecular mass), as dictated by the classical equipartition theorem, whereas the quantum mechanical mean translational kinetic energy is generally substantially higher than its classical counterpart. One advantage of using $c_\mathrm{K}(t)$ is the fact that, for a certain class of autocorrelation functions, some of the available quantum simulation techniques provide quite reasonable approximations to their Kubo transform, while $c(t)$ remains problematic. Here too, the VAF is a good example, since it has been observed that methods such as RPMD or CMD are able to reproduce the Kubo VAF surprisingly well, at least in liquid hydrogen and deuterium [30], as confirmed by comparison with neutron scattering cross section data [31,32] and inelastic neutron scattering experiments on H_2-D_2 mixtures [33].

By Fourier transformation of $c(t)$ and $c_K(t)$ the respective frequency spectra $\tilde{c}(\omega)$ and $\tilde{c}_K(\omega)$ are obtained. Both functions are real and, while $\tilde{c}_K(\omega)$ is even, $\tilde{c}(\omega)$ can be decomposed into its symmetric and antisymmetric parts, $\tilde{c}(\omega) = \tilde{c}_s(\omega) + \tilde{c}_a(\omega)$, which are the Fourier transforms of $\mathrm{Re}\, c(t)$ and $i\,\mathrm{Im}\, c(t)$, respectively.

The three quantities just defined are all related to each other by the detailed balance requirement, $\tilde{c}(-\omega) = \exp(-\beta\hbar\omega)\tilde{c}(\omega)$, and the following relationships hold:

$$\tilde{c}(\omega) = \frac{\beta\hbar\omega}{1-\exp(-\beta\hbar\omega)}\tilde{c}_K(\omega), \tag{8}$$

$$\tilde{c}_s(\omega) = (\beta\hbar\omega/2)\coth(\beta\hbar\omega/2)\tilde{c}_K(\omega), \tag{9}$$

$$\tilde{c}_a(\omega) = (\beta\hbar\omega/2)\tilde{c}_K(\omega). \tag{10}$$

The problem of calculating $c(t)$ from the knowledge of $c_K(t)$ in the time domain has already been elegantly solved in Ref. [34], but here, exploiting some results of that work, we want to obtain an explicit expression for $c(t)$, starting from the exponential expansion of its Kubo transform. It will be convenient to first discuss the problem in the frequency domain, where the above equations for the various spectral functions will be used.

IV. MODE EXPANSION OF QUANTUM SPECTRA

As a preliminary step, we first need to consider the relationship between the mode expansion of a generic time correlation function and that of its second derivative with respect to time. The relevance of this problem for the determination of a quantum correlation function will be apparent soon. For our purposes it is sufficient to consider the classical autocorrelation function of Eq. (1). It is well known [7] that, with overdots denoting time derivatives,

$$\ddot{c}(t) = -\langle \dot{A}(0)\dot{A}(t)\rangle, \tag{11}$$

which is an autocorrelation function as well. Then, given the expansion of $c(t)$ in exponential terms [see Eq. (2)], we seek the corresponding expansion of $\ddot{c}(t)$. We first establish the connection between the expansions in sums of Lorentzian lines of the respective frequency spectra $\tilde{c}(\omega)$ and $\tilde{c}^{(2)}(\omega)$, related by

$$\tilde{c}^{(2)}(\omega) = -\omega^2\tilde{c}(\omega). \tag{12}$$

It is clear from the outset that the Lorentzian modes of $\tilde{c}^{(2)}(\omega)$ cannot be the same as those of $\tilde{c}(\omega)$, since the latter, upon multiplication by ω^2, would display a nondecaying, nonintegrable, behavior. Indeed, using Eq. (3) and rewriting the Lorentzian as two terms, we have

$$\begin{aligned}\tilde{c}^{(2)}(\omega) &= -\omega^2\frac{c(0)}{\pi}\sum_j \frac{-I_j z_j}{\omega^2+z_j^2}\\ &= \frac{c(0)}{\pi}\sum_j\left(I_j z_j + \frac{-I_j z_j^3}{\omega^2+z_j^2}\right).\end{aligned} \tag{13}$$

Equation (13) shows that, in the frequency domain, each exponential mode of $c(t)$ gives rise to a Lorentzian line with half-width $-z_j$ and amplitude $c(0)I_j z_j^2$, to which the nonzero constant $c(0)I_j z_j/\pi$ is added. Since the constant prevents the jth spectral mode from decaying to zero at large frequency and causes its integral to diverge, this extra term makes Eq. (13) an invalid expression for the mode expansion of the spectrum of the autocorrelation function $\ddot{c}(t)$, which we require to comply with the form of Eq. (3).

However, the constant term may be eliminated if the condition Eq. (5) is applied. In fact, the first time derivative of the generic mode of $c(t)$, given by

$$\dot{c}_j(t) = c(0)I_j z_j \exp(z_j|t|)\,\mathrm{sign}(t) \tag{14}$$

for $t \neq 0$, is discontinuous at $t = 0$ because its left and right limits for $t \to 0$ are $-c(0)I_j z_j$ and $c(0)I_j z_j$, respectively, and are in general different from zero. Accordingly, the second time derivative of $c_j(t)$ is

$$\ddot{c}_j(t) = c(0)I_j z_j^2 \exp(z_j|t|) + 2c(0)I_j z_j\delta(t), \tag{15}$$

where the term containing $\delta(t)$ comes from the step discontinuity of $\dot{c}_j(t)$ at the origin and its Fourier transform is just $c(0)I_j z_j/\pi$. Thus, it appears that removing the ω-independent part of Eq. (13) amounts exactly to ignoring the singularity in the second time derivative of $c_j(t)$. A few comments are in order here:

(i) As mentioned in Sec. II, the sum rule of Eq. (5) is enforced to ensure that the total $c(t)$, when approximated by a finite number of terms, has a continuous first derivative that vanishes at $t = 0$, i.e., it has no step there, and that the second derivative is finite everywhere. It is no surprise that such a constraint is required whenever a physical property of the system involves the second time derivative of the given autocorrelation function. Nevertheless, it is a peculiarity of the expansion in exponentials that, taken individually, the second derivatives of the modes have a singularity at the origin.

(ii) To ensure that $\ddot{c}(t)$ and $\tilde{c}^{(2)}(\omega)$ can still be described by a proper exponential (or, respectively, Lorentzian) mode expansion, $\ddot{c}_j(t)$ must be made continuous at $t = 0$, just as $c_j(t)$ has to be continuous to represent the zero-time value of $c(t)$. This is obtained by exploiting the sum rule Eq. (5) to remove the singularity in Eq. (15). The application of this constraint, required for the reasons just explained, is sufficient to ensure that no divergences occur in $\ddot{c}_j(t)$ and in the frequency integrals of $\tilde{c}_j^{(2)}(\omega)$.

(iii) In this way we are actually redefining the exponential modes of $\ddot{c}(t)$ at $t = 0$ and the corresponding Lorentzian modes $\tilde{c}_j^{(2)}(\omega)$. However, with such a proviso and for the sake of clarity, we maintain the same notation and, assuming that the constraint Eq. (5) has been enforced in the determination of the parameters (I_j, z_j), we replace Eqs. (15) and (13) with

$$\ddot{c}_j(t) = c(0) I_j z_j^2 \exp(z_j|t|) \tag{16}$$

and

$$\tilde{c}^{(2)}(\omega) = \frac{c(0)}{\pi} \sum_j \frac{-I_j z_j^3}{\omega^2 + z_j^2}, \tag{17}$$

respectively. However, it is worth stressing that these redefinitions concern the individual modes only, while the total $\ddot{c}(t)$ and $\tilde{c}^{(2)}(\omega)$ remain unchanged.

Although not of interest here, it is clear that the procedure could be repeated if correlations of higher-order derivatives of $A(t)$ were considered, and that in such cases higher-order sum rules of the type Eq. (4) must be enforced as well.

The important physical meaning of Eq. (17) is that the autocorrelation function of the variable $A(t)$ has the same decay channels as that of its time derivatives, determined by the dampings $-\mathrm{Re}\, z_j$ and frequencies $\mathrm{Im}\, z_j$, which completely characterize the microscopic processes driving the global dynamics of the system. What changes in passing to autocorrelation functions of time derivatives of increasing order are the amplitudes of the various modes, which get multiplied each time by z_j^2, so that the faster a mode decays or oscillates, the stronger is its contribution to the higher order correlation functions.

A relationship involving an autocorrelation function and its second derivative is found in the case of some important quantities relevant for the description of the dynamics of disordered systems. Besides the example mentioned in the Introduction and dealt with in Ref. [11], an important quantity in the theory of liquid state, namely the longitudinal current autocorrelation function, is proportional to the second time derivative of the intermediate scattering function, i.e. of the van Hove autocorrelation function of density fluctuations [7].

The reason why such a kind of relationship has been analyzed in detail is that it is exactly of the form of the connection between the quantum spectrum $\tilde{c}(\omega)$ and the corresponding Kubo spectrum $\tilde{c}_{\mathrm{K}}(\omega)$ [see Eq. (19) below]. Therefore, it plays a relevant role in the problem we are dealing with here, that is to derive the former from the mode expansion of the latter.

We will first consider the symmetric part $\tilde{c}_{\mathrm{s}}(\omega)$, i.e., the Fourier transform of the real part of $c(t)$. In place of Eq. (12) we have now Eq. (9), which we rewrite as

$$\tilde{c}_{\mathrm{s}}(\omega) = B(\omega)\tilde{c}_{\mathrm{K}}(\omega), \tag{18}$$

and in this case too the spectral modes of $\tilde{c}_{\mathrm{s}}(\omega)$ must differ from those of the Kubo spectrum. However, since $B(\omega) = (\beta\hbar\omega/2)\coth(\beta\hbar\omega/2)$ grows only as $|\omega|$ for $|\omega| \to \infty$, the divergence problem upon multiplication by $B(\omega)$ is milder than that of Eq. (12) where, instead, a factor ω^2 is involved. We first rewrite Eq. (18) as

$$\tilde{c}_{\mathrm{s}}(\omega) = \frac{B(\omega) - 1}{\omega^2}[\omega^2 \tilde{c}_{\mathrm{K}}(\omega)] + \tilde{c}_{\mathrm{K}}(\omega), \tag{19}$$

where no singularity is introduced by the ω^2 factor in the denominator, as the limiting behavior of $B(\omega)$ for $\omega \to 0$ is given by $1 + (\beta^2\hbar^2/12)\omega^2 + O(\omega^4)$. The transformation of Eq. (18) into the form of Eq. (19) has already been used in Ref. [34], but here we apply it to the expansions in Lorentzians, taking into account the results Eqs. (3) and (13), and we obtain

$$\tilde{c}_{\mathrm{s}}(\omega) = -\left(\frac{B(\omega)-1}{\omega^2}\right)\frac{c_{\mathrm{K}}(0)}{\pi}\sum_j \left(I_j z_j + \frac{-I_j z_j^3}{\omega^2 + z_j^2}\right) + \frac{c_{\mathrm{K}}(0)}{\pi}\sum_j \frac{-I_j z_j}{\omega^2 + z_j^2}. \tag{20}$$

Due to the presence of the prefactor $[B(\omega) - 1]/\omega^2$, the constant terms in the first sum are now forced to decay to zero as $1/|\omega|$ at large frequency, but they still remain not integrable. Then, for the same physical requirement as in the case of Eq. (13), we again use Eq. (5) to remove the divergence. Thus, we finally obtain

$$\tilde{c}_{\mathrm{s}}(\omega) = -\left(\frac{B(\omega)-1}{\omega^2}\right)\frac{c_{\mathrm{K}}(0)}{\pi}\sum_j \frac{-I_j z_j^3}{\omega^2 + z_j^2} + \frac{c_{\mathrm{K}}(0)}{\pi}\sum_j \frac{-I_j z_j}{\omega^2 + z_j^2}, \tag{21}$$

where $\tilde{c}_{\mathrm{s}}(\omega)$ is seen to consist of two sums: the second one is simply the Lorentzian expansion of the Kubo spectrum, while the first is a sum of Lorentzian lines with the same half-widths $-z_j$ but different amplitudes $I_j z_j^2$, multiplied by a quantity solely related to the detailed balance factor.

V. TIME DEPENDENCE OF THE QUANTUM CORRELATION FUNCTION

The real part of the autocorrelation function $c(t)$ is the inverse Fourier transform of Eq. (21), but a direct calculation of the Fourier integral is not straightforward due to the presence of the prefactor to the first sum. [The second term simply gives $c_{\mathrm{K}}(t)$.] In Ref. [34] the problem was solved by applying the convolution theorem after evaluation of the inverse Fourier transform of the function $[B(\omega) - 1]/\omega^2$, which was shown [34] to be $-2\pi k_1(t)$, where

$$k_1(t) = \tau\ \log[1 - \exp(-|t|/\tau)] \tag{22}$$

and

$$\tau = \frac{\beta\hbar}{2\pi} \tag{23}$$

is a time constant depending on the system temperature only. Then, the convolution theorem allows one to obtain, from Eq. (20),

$$\mathrm{Re}\, c(t) = c_{\mathrm{K}}(t) + \int_{-\infty}^{\infty} dt'\, k_1(t')\, \ddot{c}_{\mathrm{K}}(t - t'). \tag{24}$$

(Analogous methods have also been applied in a somewhat broader context in Ref. [35].) It has to be noted that $k_1(t)$ has a singularity at $t \to 0$, but the divergence is of the logarithmic type and therefore an integrable one. In Ref. [34] Eq. (24) was only used to obtain the value of an arbitrary autocorrelation function at time zero, but with $\ddot{c}_{\mathrm{K}}(t)$ written as a sum of modes of the form Eq. (16) the above convolution integral can be calculated explicitly for any value of t value to give

$$\begin{aligned}\mathrm{Re}\, c(t) = c_{\mathrm{K}}(t) + c_{\mathrm{K}}(0) \sum_j I_j z_j \tau\{[\psi(1 - z_j\tau) \\ - \psi(1 + z_j\tau)]e^{z_j|t|} - [f(z_j\tau, e^{-|t|/\tau}) \\ + f(-z_j\tau, e^{-|t|/\tau})]e^{-|t|/\tau}\}. \qquad (25)\end{aligned}$$

Here $\psi(z)$ is the digamma function [36] and, for a complex parameter s, we have defined the function

$$f(s, x) = \frac{F(1, 1 + s; 2 + s; x)}{1 + s} - F(1, 1; 2; x), \qquad (26)$$

where $F(a, b; c; x) = {}_2F_1(a, b; c; x)$ is the Gaussian hypergeometric function [36]. Equation (25), whose derivation is outlined in Appendix A, can be conveniently rewritten in a different form by using the property of the digamma function $\psi(1 - z) - \psi(1 + z) = \pi \cot(\pi z) - 1/z$ [37]. In this way one obtains

$$\begin{aligned}\mathrm{Re}\, c(t) = c_{\mathrm{K}}(0) \sum_j I_j z_j \tau\{\pi \cot(z_j\tau\pi)e^{z_j|t|} \\ - [f(z_j\tau, e^{-|t|/\tau}) + f(-z_j\tau, e^{-|t|/\tau})]e^{-|t|/\tau}\}. \qquad (27)\end{aligned}$$

As far as the imaginary part of $c(t)$ is concerned, we make use of the well-known result

$$\mathrm{Im}\, c(t) = -\frac{\beta\hbar}{2}\dot{c}_{\mathrm{K}}(t). \qquad (28)$$

This relationship can be obtained by taking the time derivative of the definition Eq. (7) and noting that $\langle A(-i\hbar\lambda)\dot{A}(t)\rangle = -\langle \dot{A}(-i\hbar\lambda)A(t)\rangle$, which follows from the cyclic invariance of the trace. Utilizing Eq. (5.20) of Ref. [13],

$$\begin{aligned}\dot{c}_{\mathrm{K}}(t) &= -\frac{1}{\beta}\int_0^\beta d\lambda\, \langle e^{\lambda H}\dot{A}(0)e^{-\lambda H}A(t)\rangle \\ &= -\frac{1}{i\beta\hbar}\langle [A(0), A(t)]\rangle, \qquad (29)\end{aligned}$$

where $[\cdots, \cdots]$ is a commutator, Eq. (28) now follows from $\langle [A(0), A(t)]\rangle = \langle A(0)A(t)\rangle - \langle A(t)A(0)\rangle = 2i\, \mathrm{Im}\, c(t)$. The same result can also been obtained through a different route starting from Eq. (10), as done in Ref. [34]. The imaginary part of $c(t)$ is an odd function of time that vanishes at $t = 0$, so that $c(0)$ is real. By expressing $\dot{c}_{\mathrm{K}}(t)$ through a sum of modes of the form Eq. (14) and adding $i\, \mathrm{Im}\, c(t)$ to the real part given by Eq. (27), one eventually finds

$$\begin{aligned}c(t) = c_{\mathrm{K}}(0) \sum_j I_j z_j \tau\pi[\cot(z_j\tau\pi) - i\, \mathrm{sign}(t)]e^{z_j|t|} \\ - c_{\mathrm{K}}(0) \sum_j I_j z_j \tau[f(z_j\tau, e^{-|t|/\tau}) \\ + f(-z_j\tau, e^{-|t|/\tau})]e^{-|t|/\tau}. \qquad (30)\end{aligned}$$

For ease of reference we label the two parts of the right-hand-side as $c_{\mathrm{A}}(t)$ and $c_{\mathrm{B}}(t)$, respectively, and write $c(t) = c_{\mathrm{A}}(t) + c_{\mathrm{B}}(t)$.

From Eq. (30) it is evident that $c_{\mathrm{A}}(t)$ is an exponential expansion with the same mode frequencies z_j as in the expansion of $c_{\mathrm{K}}(t)$, meaning that the same relaxation processes determine the decays of both correlation functions. Although this may seem intuitive, it is not at all obvious, and proving it is one of the central tasks of the present work. The mode intensities are different from, though written in terms of, those pertaining to $c_{\mathrm{K}}(t)$, and contain an imaginary part to account for the complex nature of $c(t)$. The overall time dependence of $c_{\mathrm{B}}(t)$ is determined by the exponential term $\exp(-|t|/\tau)$, both as an explicit factor and through the argument of the functions f. To $c_{\mathrm{B}}(t)$, each mode of $c_{\mathrm{K}}(t)$ contributes with a weight proportional to its own intensity, but its frequency also determines the specific arguments of the functions f. We will show in Sec. VI that $c_{\mathrm{B}}(t)$ provides a small but essential correction to the time dependence of $c_{\mathrm{A}}(t)$ to ensure the correct short-time behavior of $\mathrm{Re}\, c(t)$, and, in particular, that this correction is only effective in a time range of the order of τ.

Equation (30) also shows that, apart from the mode exponentials $\exp(z_j|t|)$, in all other occurrences the reduced frequencies $z_j\tau$ appear. This means that in a quantum system $1/\tau$ plays an essential role as a frequency unit in determining the jth amplitude in both $c_{\mathrm{A}}(t)$ and $c_{\mathrm{B}}(t)$.

As shown in detail in Appendix A, $c(t)$ has the following expected properties: (a) in the limit as $\hbar \to 0$ or $\beta \to 0$, i.e., in the classical limit, it reduces to $c_{\mathrm{K}}(t)$ (which in turn reduces to the classical correlation function); (b) it obeys the condition $c^*(t) = c(t + i\hbar\beta)$; and (c) its value at $t = 0$ is given by

$$c(0) = \mathrm{Re}\, c(0) = c_{\mathrm{K}}(0)\left\{1 + 2\sum_j I_j z_j \tau[\psi(1 - z_j\tau) + \gamma]\right\}, \qquad (31)$$

where γ is the Euler–Mascheroni constant. Equation (31) has very recently been applied [14] to the determination of the contributions of the modes of the Kubo VAF to the translational mean kinetic energy per molecule $\langle K\rangle$ in dense fluid parahydrogen at a density above that of the triple point and at four temperatures decreasing from a slightly supercritical value to that of a cold liquid state. In fact, if $c(t)$ represents the VAF, then one has $\langle K\rangle = c(0)M/2$, i.e., a value known to exceed the one given by the classical equipartition theorem, $3/(2\beta) = c_{\mathrm{K}}(0)M/2$, by an amount which increases substantially when T is decreased and the quantum character of the fluid becomes more pronounced. The study in Ref. [14] has been carried out on the basis of RPMD simulation data, which will be used in Sec. VI as an example case for the discussion of the present results. In a similar study [15], Eq. (31) was used to follow the increase of $\langle K\rangle$ over the classical value when the density is increased from near-critical to close-to-melting values, at a slight supercritical temperature.

Another application of Eq. (31) is obtained if $c(t)$ is identified with the intermediate scattering function $F(Q, t)$, i.e., the autocorrelation function of density fluctuations at a fixed wave vector Q. Its value at $t = 0$ gives the static structure factor $S(Q)$, which it is often common, but incorrect, practice to identify with the zero time value of the Kubo transform, that is, with the frequency integral of the spectrum symmetrized by removing the detailed balance asymmetry.

It can also be shown that Eq. (31) reproduces the well-known result for the temperature dependence of the quantum mechanical mean kinetic energy of a single undamped

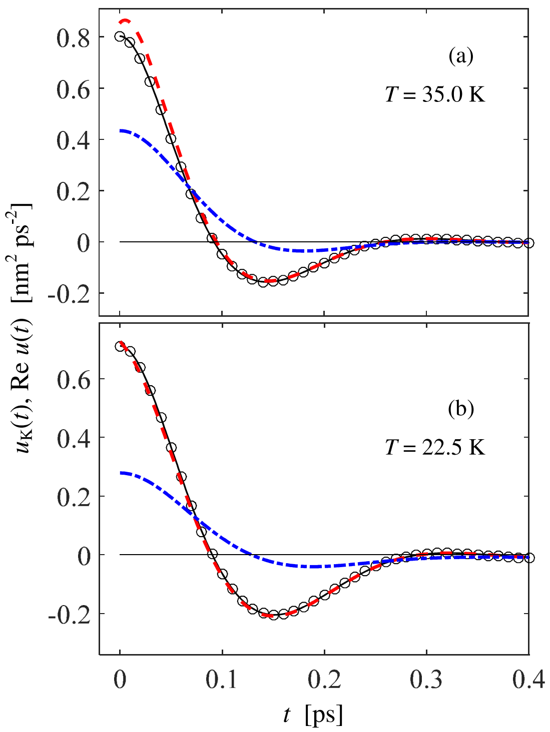

FIG. 1. Real part of the quantum VAF (black circles) $u(t)$ of fluid parahydrogen at density $n = 26.73$ nm^{-3} (from Ref. [14]) computed through a forward/inverse Fourier transform and Eq. (18) from the Kubo VAF $u_K(t)$ (blue dash-dotted line) obtained from RPMD simulations. The black solid line is the result of the mode expansion, Eq. (27). The red dashed line displays the real part of $u_A(t)$ alone. Each frame refers to the temperature indicated.

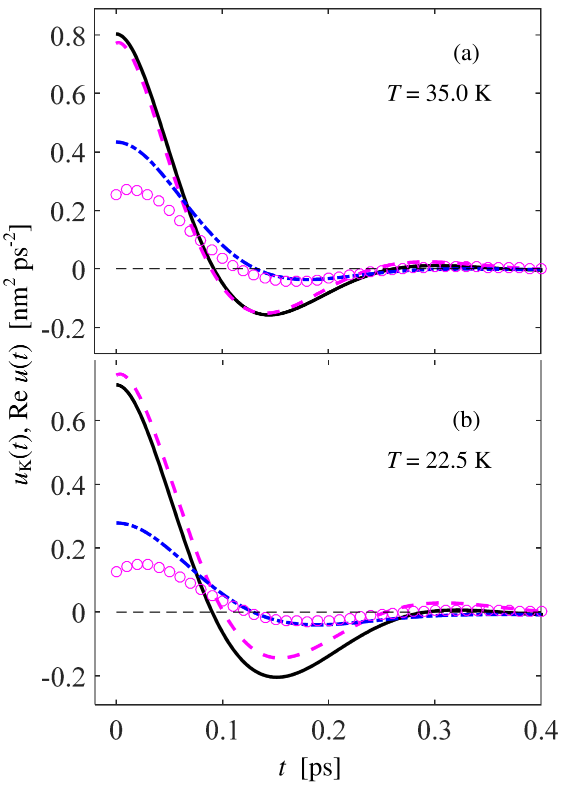

FIG. 2. The Kubo VAF obtained from parahydrogen simulations [14] (blue dash-dotted line) and the real part of the quantum VAF obtained from Eq. (27) (black solid line) are compared with the respective contributions provided by the mode pair C2 alone (magenta circles and dashes, respectively). Each frame refers to the temperature indicated.

harmonic oscillator. Although to describe the behavior of such an ideal model we have to relax the initial assumption Re $z_j < 0$, it is still possible to use the concept of exponential modes, as described in Appendix B.

VI. RESULTS IN AN EXAMPLE CASE

We illustrate the representation of Re $c(t)$ by Eq. (27) in the case where $c(t) = u(t) = (1/N)\sum_{k=1}^{N}\langle \mathbf{v}_k(0)\cdot\mathbf{v}_k(t)\rangle$ is the center-of-mass VAF of a system of N particles, and $u_K(t)$ is its Kubo transform. The latter was obtained from an RPMD simulation of fluid parahydrogen with $N = 864$ molecules interacting through the Silvera-Goldman potential [38] at a molecular number density $n = 26.73$ nm^{-3} and at the highest ($T = 35$ K) and lowest ($T = 22.5$ K) temperature of the four states investigated in Ref. [14]. The Kubo VAF was numerically Fourier transformed to provide the spectrum $\tilde{u}_K(\omega)$, and, after applying Eq. (18), an inverse Fourier transformation was performed to give the real part of the quantum correlation $u(t)$, which we treat as reference data to be compared with the results of Eq. (27). The values of τ are 0.0347 ps at $T = 35$ K and 0.0540 ps at $T = 22.5$ K.

In the case considered here, the time dependence of $u_K(t)$ was very accurately described by the sum of a set of exponential modes including (i) two pairs of complex conjugate modes, identified with the propagating excitations related to longitudinal and transverse collective motions [4,5,11,14,15] and labeled as C2 and C3 for consistency with previous papers; and (ii) a very fast decaying real mode (R1) with a very small amplitude. An even weaker, slowly decaying real mode (R4), accounting for the long time tail, is just visible at the higher temperature but remains below the detectability threshold at the lower one, and has not been included in the fit model for the latter case. The quality of all fits to $u_K(t)$ is excellent, as was shown in Fig. 1 of Ref. [14].

We show in Fig. 1 that Eq. (27) reproduces the Fourier transformed data very well in the whole time range, and therefore provides a correct and effective representation of Re $u(t)$. We also note that Re $u(t)$ differs substantially from $u_K(t)$, signaling the presence of considerable quantum effects in the dynamics of the system, and that most of this difference is accounted for by the real part of $u_A(t)$ alone. However, the contribution of $u_B(t)$ is seen to be essential for reproducing the correct behavior of the correlation function at short times, in particular, the horizontal tangent of Re $u(t)$ at $t = 0$.

In Fig. 2, together with $u_K(t)$ and Re $u(t)$, we display the respective contributions (including the "A" as well as "B" parts) provided by the C2 pair alone. While for the Kubo VAF the contribution of C2 is substantial, it becomes truly dominant in the case of Re $u(t)$. This result is related to the fact that quantum effects on the spectra grow in importance with increasing frequency, due to the growth of $B(\omega)$. Therefore, modes with larger $|z_j|$, having broader frequency

TABLE I. Values of z_j and I_j for the modes fitted to the Kubo VAF $u_K(t)$ data on liquid parahydrogen of Ref. [14].

	$T = 35$ K		$T = 22.5$ K	
Mode(s)	z_j [ps^{-1}]	I_j	z_j [ps^{-1}]	I_j
R1	-52.254	0.0610	-95.808	0.0044
R4	-0.944	0.0050	–	–
C2	$-12.153 \pm 20.723\,i$	$0.2921 \mp 0.3189\,i$	$-10.606 \pm 20.355\,i$	$0.2264 \mp 0.3139\,i$
C3	$-8.547 \pm 8.415\,i$	$0.1748 \mp 0.0039\,i$	$-7.838 \pm 4.437\,i$	$0.2714 \pm 0.3716\,i$

distributions, will contribute more to the quantum correlation function, and their importance will increase in passing from the Kubo to the full quantum correlation function. That C2 is responsible for most of the excess of $u(0)$ and of the related mean kinetic energy per molecule over their classical counterparts, has already been thoroughly discussed in Refs. [14,15] where we have proposed a physical interpretation in terms of the Heisenberg uncertainty principle. To better appreciate the frequencies involved by each decay mode, we list the values of the respective parameters I_j and z_j in Table I. The prominent role played by the C2 pair in the quantum dynamics is evident if one considers that, although R1 has a much larger decay constant (and thus a broader spectral distribution), it provides an intrinsically weak contribution. Moreover, Fig. 2 also shows that at the lower temperature C2 is larger than the total Re $u(t)$, in agreement with the fact that other modes can have a negative amplitude, as noted at the end of Sec. II.

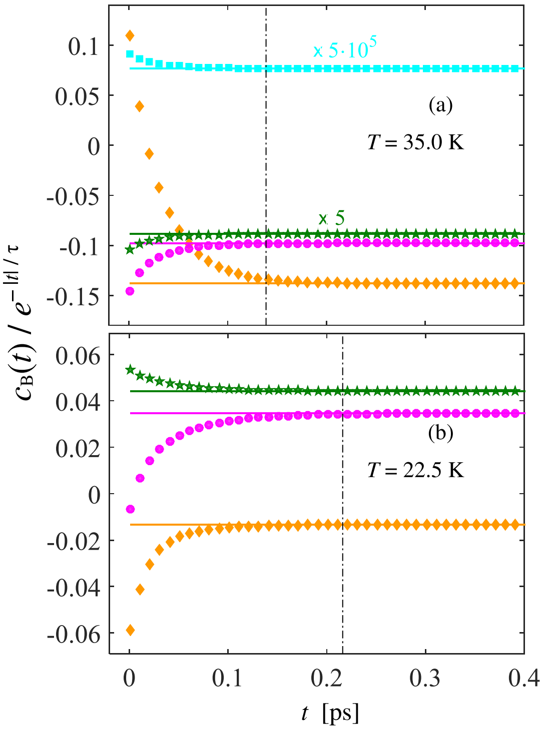

FIG. 3. Time dependence of the contributions of the modes of the exponential expansion of the Kubo VAF of parahydrogen, [14] to $c_B(t)/e^{-|t|/\tau}$ according to the following color legend: R1 (orange diamonds), R4 (cyan squares), C2 (magenta circles), and C3 (green stars). For each complex pair C2 and C3, the sum of the two modes of the pair is displayed. The lines with the same colors are the respective infinite-time asymptotes. The vertical dash-dot black line marks the value of $t = 4\tau$. In frame (a) the R4 term has so weak an intensity that to make its time decay visible it has been multiplied by 5×10^5. This term is absent at the lower temperature [frame (b)]. Also, for the same reason, in frame (a) the contribution of the C3 pair is multiplied by 5.

As already pointed out, the parameter τ sets a temperature-dependent quantum mechanical time scale. In Fig. 3 we plot the time dependence of the contributions of each mode or pair of modes to the quantity $c_B(t)/e^{-|t|/\tau}$, together with their respective asymptotic long-time limits. It is clearly seen that in all cases the decay time to the asymptotic value is of the order of τ, which is also the time scale on which $c_B(t)$ itself decays to zero. Therefore, because τ depends on the system temperature only, for any system and whatever dynamical variable is considered, it is tempting to interpret this second term as the manifestation of a pure quantum property of correlation functions related to the detailed balance asymmetry.

VII. CONCLUSIONS

In the past few years, the exponential mode expansion has proven to be a very effective tool for the identification of physical processes which determine the dynamic behavior as expressed by autocorrelation functions of fundamental dynamical variables. In our previous investigations we have shown how the existence of certain decay mechanisms connected to specific atomic motions, be they single-particle or collective ones, can be identified in different correlation functions, and we have made explicit the quantitative relationships between their sets of exponential modes (and between the sets of Lorentzian modes of their respective spectra). This work extends the range of applications of these concepts to quantum systems at nonzero temperature by expressing a quantum correlation function in terms of the dynamical modes of its Kubo-transformed counterpart through an explicit and exact expression. In doing so, we are able to demonstrate that the quantum nature of a system, which forces it to obey a fundamental property of fully general character such as the quantum asymmetry of spectral distributions, plays an essential role in shaping the high-frequency spectral tail and, correspondingly, ensuring the correct short-time behavior of the correlation function in the range of the "quantum correlation time" $\tau = \beta\hbar/(2\pi)$. At times long compared to τ, the set of modes required for the Kubo correlation function is also sufficient (although with modified amplitudes) to provide an excellent representation of the real part of the full quantum correlation function. For the imaginary part of $c(t)$ this holds trivially true at all times as, apart from a prefactor, $\mathrm{Im}\, c(t)$ is just the first time derivative of $c_{\mathrm{K}}(t)$.

The results of the present work are to be viewed as a tool applicable to a much wider area than simply that of semiquantum fluids such as liquid parahydrogen, here used only as an appropriate example. To support this statement of generality, we mention the following two points.

(1) The expansion in exponential modes is an approach fully complementary to the usual Taylor-based short-time expansion of correlation functions [3], as the former in general converges at long times faster than at short ones, so that a truncation that retains a small number of exponential terms provides a better approximation to the long-time, or low-frequency, dynamics. This makes it particularly suitable for the study of phenomena in which the slowing down of microscopic dynamics plays a key role such as, for example, supercooling, freezing processes, glass or sol-gel transitions. In particular, recent works have made clear that in various examples of the mentioned processes (e.g., those involving water molecules) quantum effects are not negligible even at room temperature [39]. Our results could also lead to a deeper understanding of the dynamical effects of the hydrogen bond, where the exponential mode expansion already proved very effective in a classical treatment [40].

The capability of the method of rigorously incorporating the quantum properties of a system through the expansion in exponential modes of its Kubo correlation functions is also very important according to some recent trends in condensed matter science. Actually, with increasing evidence [41] the key role of the zero-point energy (a quantity of a purely quantum nature) is revealed by a series of macroscopic thermodynamic properties in systems of interest for physical chemistry and biophysics. Moroever, various spectral properties (essentially of pseudophononic nature) are frequently used [42] as a very stringent test for the validity of semiempirical potentials and ab initio methods in various systems, e.g., hydrogen bonded materials.

ACKNOWLEDGMENTS

We thank Fabrizio Barocchi for many stimulating discussions on the subject. This research was funded by Ente Cassa di Risparmio Firenze (2016-0866) and by Ministero dell'Istruzione dell'Università e della Ricerca Italiano (PRIN2017-2017Z55KCW).

APPENDIX A: DERIVATION OF EQ. (25) AND PROPERTIES OF $c(t)$

Given the even parity of $\mathrm{Re}\, c(t)$ we can restrict its calculation to positive values of t. With Eq. (16),

$$\ddot{c}_{\mathrm{K}}(t) = c_{\mathrm{K}}(0) \sum_j I_j z_j^2 \exp(z_j |t|), \tag{A1}$$

k_1 given by Eq. (22), and τ defined as in Eq. (23), the convolution integral of Eq. (24) is split into the sum of three terms:

$$\mathrm{Re}\, c(t) = c_{\mathrm{K}}(t) + c_{\mathrm{K}}(0)\tau \sum_j I_j z_j^2 \bigg[e^{z_j t} \int_{-\infty}^{0} dt' \, \log(1 - e^{t'/\tau}) e^{-z_j t'} + e^{z_j t} \int_0^t dt' \, \log(1 - e^{-t'/\tau}) e^{-z_j t'} + e^{-z_j t} \int_t^{\infty} dt' \, \log(1 - e^{-t'/\tau}) e^{z_j t'} \bigg], \tag{A2}$$

or, introducing a new variable $x = e^{t'/\tau}$ in the first integral and $x = e^{-t'/\tau}$ in the other ones,

$$\mathrm{Re}\, c(t) = c_{\mathrm{K}}(t) + c_{\mathrm{K}}(0) \sum_j I_j (z_j \tau)^2 \bigg[e^{z_j t} \int_0^1 dx \, \log(1 - x) x^{-1 - z_j \tau} + e^{z_j t} \int_{e^{-t/\tau}}^1 dx \, \log(1 - x) x^{-1 + z_j \tau} + e^{-z_j t} \int_0^{e^{-t/\tau}} dx \, \log(1 - x) x^{-1 - z_j \tau} \bigg]. \tag{A3}$$

The integrals are evaluated by means of [43]

$$\int dx \, \log(1 - x) x^{-1+s} = \frac{x^{1+s}}{s} \bigg[\frac{F(1, 1 + s; 2 + s; x)}{1 + s} - F(1, 1; 2; x) \bigg], \tag{A4}$$

where both hypergeometric functions are of the type $F(1, b; b + 1; x)$. Since for $x \to 1$ one has [43]

$$F(1, b; b + 1; x) \approx -b[\log(1 - x) + \psi(b) + \gamma], \tag{A5}$$

both terms in Eq. (A4) have the same logarithmic divergence for $x \to 1$ which cancels out when their difference is taken. Then the auxiliary function $f(s, x)$ defined in Eq. (26) is everywhere finite, Eq. (A4) becomes

$$\int dx \, \log(1 - x) x^{-1+s} = \frac{x^{1+s}}{s} f(s, x), \tag{A6}$$

and Eq. (A3) can be rewritten as

$$\operatorname{Re} c(t) = c_{\mathrm{K}}(t) + c_{\mathrm{K}}(0)\sum_j I_j (z_j\tau)^2 \left\{ e^{z_j t}\left[\frac{x^{1-z_j\tau}}{-z_j\tau} f(-z_j\tau, x)\right]_0^1 + e^{z_j t}\left[\frac{x^{1+z_j\tau}}{z_j\tau} f(z_j\tau, x)\right]_{e^{-t/\tau}}^1 + e^{-z_j t}\left[\frac{x^{1-z_j\tau}}{-z_j\tau} f(-z_j\tau, x)\right]_0^{e^{-t/\tau}} \right\}. \tag{A7}$$

The evaluation at $x = 0$ is carried out by noting that $F(a, b; c; 0) = 1$ for all a, b and c, which implies $f(-z_j\tau, 0) = z_j\tau/(1 - z_j\tau)$, and that $x^{1-z_j\tau}$ vanishes for $x = 0$ due to the condition $\operatorname{Re}(1 - z_j\tau) > 0$ valid for all modes. For the case $x = 1$, we use Eq. (A5) and the property $\psi(1) = -\gamma$ to obtain

$$f(\pm z_j\tau, 1) = -\psi(1 \pm z_j\tau) - \gamma. \tag{A8}$$

Putting together these results and rearranging terms, Eq. (25) is readily obtained and, proceeding as in Sec. V, one arrives at the formulation of $c(t)$ given by Eq. (30).

The classical limit of $c(t)$ is recovered immediately by letting $\tau \to 0$. Then both $c_{\mathrm{B}}(t)$ and the imaginary part of $c_{\mathrm{A}}(t)$ vanish, while $z_j\tau\pi \cot(z_j\tau\pi) \to 1$ and $c(t)$ reduces to $\sum_j c_{\mathrm{K}}(0)\exp(z_j|t|)$, i.e., to $c_{\mathrm{K}}(t)$.

Next, we verify that $c^*(t) = c(t + i\hbar\beta)$ at $t \geqslant 0$. For $c_{\mathrm{B}}(t)$, which is a real quantity depending on time through $\exp(-t/\tau)$ only, such a condition is satisfied because $\exp[(-t + i\hbar\beta)/\tau] = \exp(-t/\tau)$. Moreover, evaluating

$$c_{\mathrm{A}}^*(t) = c_{\mathrm{K}}(0)\left\{\sum_j I_j z_j\tau\pi[\cot(z_j\tau\pi) + i]e^{z_j t}\right\} \tag{A9}$$

and

$$c_{\mathrm{A}}(t + i\hbar\beta) = c_{\mathrm{K}}(0)\left\{\sum_j I_j z_j\tau\pi[\cot(z_j\tau\pi) - i]e^{z_j t}e^{i2\pi s_j}\right\} \tag{A10}$$

and taking the difference of the last two expressions, one has

$$c_{\mathrm{A}}^*(t) - c_{\mathrm{A}}(t + i\hbar\beta) = c_{\mathrm{K}}(0)\left\{\sum_j I_j z_j\tau\pi[\cot(z_j\tau\pi)(1 - e^{i2z_j\tau\pi}) + i(1 + e^{i2z_j\tau\pi})]e^{z_j t}\right\}. \tag{A11}$$

The terms in square brackets of Eq. (A11) can be written as

$$-2i[\cot(z_j\tau\pi)\sin(z_j\tau\pi) - \cos(z_j\tau\pi)]e^{iz_j\tau\pi} = 0. \tag{A12}$$

An analogous derivation leads to the same result for $t < 0$.

Finally, remembering that $\operatorname{Im} u(0) = 0$, one can calculate $c(0)$ from the $t = 0$ value of Eq. (25). It is immediately seen that

$$c_{\mathrm{A}}(0) = c_{\mathrm{K}}(0)\left\{1 + \sum_j I_j z_j\tau[\psi(1 - z_j\tau) - \psi(1 + z_j\tau)]\right\}, \tag{A13}$$

while from Eq. (A8) one finds

$$c_{\mathrm{B}}(0) = c_{\mathrm{K}}(0)\sum_j I_j z_j\tau[\psi(1 + z_j\tau) + \psi(1 - z_j\tau) + 2\gamma], \tag{A14}$$

and, adding the two formulas, Eq. (31) is obtained.

APPENDIX B: THE QUANTUM MECHANICAL UNDAMPED HARMONIC OSCILLATOR

For treating the idealized case of a three-dimensional isotropic harmonic oscillator with frequency ω_0 and zero damping, we consider a Kubo-transformed VAF $u_{\mathrm{K}}(t)$ composed of two modes with $I_1 = I_2 = 1/2$ and $z_1 = i\omega_0$ and $z_2 = -i\omega_0$. For this system, $\tilde{u}_{\mathrm{K}}(\omega)$ is a spectrum consisting of two δ functions at positions $\omega = \pm\omega_0$ with equal amplitudes $1/2$. Inserting the mode parameters in Eq. (31) leads to

$$u(0) = u_{\mathrm{K}}(0)\{1 + i\omega_0\tau[\psi(1 - i\omega_0\tau) - \psi(1 + i\omega_0\tau)]\}, \tag{B1}$$

which, using again $\psi(1 - z) - \psi(1 + z) = \pi\cot(\pi z) - 1/z$ together with $\cot(ix) = -i\coth(x)$, reduces to

$$u(0) = u_{\mathrm{K}}(0)\pi\omega_0\tau\coth(\pi\omega_0\tau). \tag{B2}$$

With $\langle K\rangle = (M/2)u(0)$ and $u_{\mathrm{K}}(0) = 3/(M\beta)$ this gives for the mean kinetic energy

$$\langle K\rangle = \frac{3}{4}\hbar\omega_0 \coth\left(\frac{\beta\hbar\omega_0}{2}\right), \tag{B3}$$

in agreement with the result reported in Refs. [44,45]. Equation (B2) is the zero time value of the full $u(t)$, which can also be obtained by inserting the above values of I_j and z_j into Eq. (30). One sees immediately that the term containing the f functions vanishes, leaving

$$u(t) = u_{\mathrm{K}}(0)\frac{\beta\hbar\omega_0}{2}\left[\coth\left(\frac{\beta\hbar\omega_0}{2}\right)\cos\omega_0 t - i\sin\omega_0 t\right]. \tag{B4}$$

This expression was given in Ref. [46] as one of the cases in which the so-called "Gaussian approximation" for the *self* dynamics is exactly valid.

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