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Universal Matsubara time decay of quantum autocorrelations for Boltzmann particles

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The general properties of time dependent autocorrelations in many-body quantum systems are here analyzed at thermodynamic equilibrium in the Boltzmann canonical ensemble at temperature T, by means of the exponential expansion theory (EET). It is shown that the Kubo-Martin-Schwinger (KMS) symmetry applied to the exponential expansion of the correlation leads to the existence of two different sets of decay modes (channels) here indicated as "Matsubara modes" and "system modes," respectively. The Matsubara modes are a series of pure decay channels with time constants representing a direct action of the thermostat upon the correlation, with a characteristic principal decay time $\tau_1 = \hbar/(2\pi k_B T)$, where $\hbar$ and k_B are the Planck and Boltzmann constants, and T is the temperature. Moreover, the KMS condition implies that the amplitudes pertaining to the even and odd contribution of the system modes to the quantum correlation are not independent. These two properties are quantum mechanical in nature and "universal," in the sense that they are present for any autocorrelation of a quantum system at equilibrium at a temperature T. The Matsubara modes' contribution to the time behavior of a quantum correlation is limited to times of the order of τ_1, which however can be comparable with some of the characteristic decay times of the system modes. In addition, since the parameters representing the overall time behavior of the quantum correlation can be given in terms of the parameters of its Kubo transform, the EET representation turns out to be useful in calculations exploiting the outputs of some widespread quantum simulation methods. A discussion of the properties of these relations is described in detail with numerical examples. The case of the velocity autocorrelation function of para hydrogen at low temperature is also reported as a final example for a real system.

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I. INTRODUCTION

The dynamical properties of a quantum mechanical many-body system at thermal equilibrium are predominantly determined by studying the time dependence of correlation functions of relevant variables. From the experimental side, information on some correlation functions is usually achieved by spectroscopic measurements in which the Fourier transform (FT) of the correlations is detected.

Correlation functions and their spectra can be analyzed referring to the exponential expansion theory (EET) [1–3], which allows one to determine the processes through which the correlation decays in time. The EET method has been applied successfully to various cases in order to discuss the nature of propagating and nonpropagating collective modes [4,5], as well as important single-particle properties of classical [6–8] and quantum [9,10] fluids. Nevertheless, the very general consequences of the Kubo-Martin-Schwinger (KMS) symmetry [11,12] within the EET of quantum correlation functions have not been discussed in detail previously. Here, we will show, in particular, that this symmetry leads to a peculiar set of decay channels of the correlation having a universal character.

Calculations of some correlation functions relevant to the microscopic dynamics of the system can be performed in weakly quantum fluids [13] by approximate molecular dynamics simulation methods like centroid molecular dynamics (CMD) [14,15] and ring polymer molecular dynamics (RPMD) [16–19], and those based on the Feynman-Kleinert approach [20,21]. However, in both the CMD and RPMD methods, the time behavior of the Kubo transform (KT) [12], and not that of the quantum correlation itself, is derived. Actually, this is not a drawback at all, since also the KT of a quantum correlation can be expanded in the EET framework, and it has been shown that it depends on a set of modes strictly related to the "system modes" of the quantum correlation, with a consequent great simplification of the data analysis. Of course, as a further step, it is important to have a general and direct functional connection between the quantum correlation and its KT in the time domain.

The first derivation was provided by Braams *et al.* using the convolution theorem [22], in order to invert the well-known relation between genuine quantum correlations and Kubo-transformed ones, once these are studied in Fourier space (a consequence of the fluctuation-dissipation theorem [12]). However, such an important step regarded the time behavior of the whole correlation function and the link with its KT, without focusing on the role that each single dynamical process (e.g., relaxations and propagating modes of density fluctuations) plays in the overall time decay of the quantum correlation.

Such a possibility was explored only rather recently by combining Braams *et al.*'s results for the total correlation [22] with its EET decomposition [23], the latter approach being able to give more insight about the contribution of individual decay mechanisms. In fact, the important achievement of Ref. [23] was to show that the quantum correlation can be written in terms of the parameters determining the exponential expansion of the KT. Reference [23] followed a different derivation from the one we illustrate in the present paper. The previous derivation leads to a compact, closed-form, expression which is indeed particularly suited for numerical calculations. However, it does not fully highlight some very general properties of the exponential expansion of quantum correlation functions, or the "universal" character of some of them.

Here we propose to discuss in detail the EET-based mode decomposition of a quantum correlation function with the aim of shedding light on some of its physical and fundamental properties. We also find it significant to better disclose the underlying physics and to outline some mathematical properties descending from the theory. This paper is also a completion of what done in Ref. [23] that might help reaching a deeper understanding of the, either universal or specifically system-dependent, modes that determine the time behavior of a quantum correlation at finite (nonzero) temperature. In the present description, the "structure" of both the universal and system-dependent components of the correlation can be deduced and compared in their trends as a function of time.

II. GENERAL PROPERTIES OF THE QUANTUM CORRELATION AND ITS KUBO TRANSFORM

Here we recall the symmetry properties and relations regarding the quantum correlation and its KT which are useful for the following development of the theory.

As mentioned, we refer to a quantum many-body system in thermodynamic equilibrium at a temperature T. The autocorrelation of a physical variable depending on real time t and represented by the Hermitian operator A is defined as the inner product

$$c(t) = (A(0), A(t)) = \langle A(0)A(t)\rangle = \mathrm{Tr}[Ae^{iHt/\hbar}Ae^{-iHt/\hbar}\rho], \tag{1}$$

where in the last member we used A in place of $A(0)$ and exploited the Heisenberg representation of $A(t)$, with H representing the Hamiltonian operator of the system and $\hbar$ the reduced Planck constant. The density operator is finally given by $\rho = \frac{e^{-\beta H}}{\mathrm{Tr}[e^{-\beta H}]}$, with $\beta = \frac{1}{k_B T}$, k_B being the Boltzmann constant.

The time reversal symmetry property of $c(t)$ descends from Eq. (1) as

$$c^*(t) = c(-t), \tag{2}$$

while the KMS relations [11,12], can be demonstrated to give

$$c(t) = c(-t + i\beta\hbar) \tag{3}$$

and

$$c^*(t) = c(t + i\beta\hbar). \tag{4}$$

The last two relations define a property of $c(t)$ in the complex plane and, similarly to what is done in thermal quantum field theory [24], by applying the Wick rotation $\tau = it$ to $c(t)$, the imaginary time representation $c(\tau)$ of $c(t)$ will be shown in the following to contain a periodic behavior with period equal to the "quantum thermal time" $\tau = \beta\hbar$ [25]. This periodicity can be decomposed in a Fourier series with contributions from all harmonics $\omega_n = n\omega_1$ of the principal frequency $\omega_1 = 2\pi/\tau = 2\pi/(\beta\hbar)$. As mentioned, the various harmonics ω_n are the so called Matsubara frequencies that have been introduced in the imaginary time description of the thermal quantum field [24].

In what follows we will discuss the properties of the quantum correlation $c(t)$ within the EET [1–3] taking into account the symmetry properties given in Eqs. (2), (3), and (4). Differently from what was done in Refs. [22,23], where Fourier transforms were used [26], we consider it more appropriate to work directly in the complex plane and to develop the theory with the use of the two-sided Laplace transform [27] (LT) indicated by $\mathcal{L}[\dots]$. In particular, such a transform, $\mathcal{L}[c(t), s]$, of $c(t)$ is defined as

$$\mathcal{L}[c(t), s] = C(s) = \int_{-\infty}^{\infty} dt\, e^{-st}\, c(t), \tag{5}$$

where s is complex. The transform of $c^*(t)$ is therefore given by

$$\mathcal{L}[c^*(t), s] = \int_{-\infty}^{\infty} dt\, e^{-st}\, c^*(t) = \left[\int_{-\infty}^{\infty} dt\, e^{-s^*t}\, c(t)\right]^* = C^*(s^*). \tag{6}$$

Moreover, the time symmetry of Eq. (2) implies that

$$C^*(s^*) = \int_{-\infty}^{\infty} dt\, e^{-st}\, c(-t) = \mathcal{L}[c(-t), s]. \tag{7}$$

Finally, by transforming both members of Eq. (4) we have

$$C(s) = e^{-i\beta\hbar s}C^*(s^*), \tag{8}$$

which represents the detailed balance condition for $C(s)$ in the complex plane. Usually, this property is given for the FT, $C(\omega)$, of $c(t)$ in the form $C(-\omega) = e^{-\beta\hbar\omega}C(\omega)$, and descends directly from the KMS relation.

It is useful to introduce the real and even part, $c_e(t)$, and the imaginary and odd part, $c_o(t)$ [with $c_o(t)$ real too], of the quantum correlation, so that $c(t) = c_e(t) + ic_o(t)$. Correspondingly, the LT can be written as $C(s) = C_S(s) + C_A(s)$, where the subscripts are meant to indicate the symmetric (S) and antisymmetric (A) parts of the transform, given, respectively, by

$$C_S(s) = \tfrac{1}{2}[C(s) + C^*(s^*)] = \tfrac{1}{2}[C(s) + e^{i\beta\hbar s}C(s)], \tag{9}$$

and

$$C_A(s) = \tfrac{1}{2}[C(s) - C^*(s^*)] = \tfrac{1}{2}[C(s) - e^{i\beta\hbar s}C(s)]. \tag{10}$$

The above equations also imply the relation

$$C_S(s) = \frac{1 + e^{i\beta\hbar s}}{1 - e^{i\beta\hbar s}}C_A(s) = -\coth(i\beta\hbar s/2)C_A(s), \tag{11}$$

which is meaningful only for $\beta > 0$, i.e., $T < +\infty$, where $T \to +\infty$ in Eqs. (9) and (10) represents the classical limit.

The time symmetries of $c_e(t)$ and $c_o(t)$ also imply that $C_S(s) = C_S^*(s^*)$ and $C_A(s) = -C_A^*(s^*)$.

The Kubo transform $z(t)$ of $c(t)$ is defined as [12]

$$z(t) = \frac{1}{\beta}\int_0^\beta d\lambda\, c(t+i\hbar\lambda) = \frac{1}{\beta}\int_0^\beta d\lambda\, (A(-i\hbar\lambda), A(t))$$
$$= \frac{1}{\beta}\int_0^\beta d\lambda\, \mathrm{Tr}[e^{\lambda H}Ae^{-\lambda H}e^{iHt/\hbar}Ae^{-iHt/\hbar}\rho]. \qquad (12)$$

Here $c(t)$ and $z(t)$ represent physical properties and therefore are supposed to be, in general, continuous, integrable, and differentiable functions, even though in practical applications the number of well defined useful derivatives is finite. It is also important to remember that by definition $z(t)$ has physical meaning only for $\beta \neq \infty$ and 0.

The time-reversal symmetry for $z(t)$ is

$$z(t) = z^*(t) = z(-t), \qquad (13)$$

that is, $z(t)$ is symmetric in time and real valued. The LT of $z(t)$ is

$$\mathcal{L}[z(t), s] = Z(s) = \int_{-\infty}^{\infty} dt\, e^{-st}\, z(t), \qquad (14)$$

and, due to Eq. (13), has the property $Z(s) = \mathcal{L}[z(t), s] = \mathcal{L}[z^*(t), s] = Z^*(s^*)$.

Using the definition of $z(t)$ given in the first row of Eq. (12), together with Eqs. (4) and (8), it is possible to write $Z(s)$ in terms of $C(s)$ as

$$Z(s) = \frac{1}{\beta}\int_0^\beta d\lambda\, e^{is\hbar\lambda}C(s) = \frac{e^{is\beta\hbar}-1}{is\beta\hbar}C(s). \qquad (15)$$

Therefore, we also have

$$C(s) = \frac{is\beta\hbar}{2}[\coth(is\beta\hbar/2) - 1]Z(s). \qquad (16)$$

By means of Eqs. (9) and (11), the relations between $Z(s)$ and, respectively, $C_{\mathrm{S}}(s)$ and $C_{\mathrm{A}}(s)$ are found to be

$$C_{\mathrm{S}}(s) = \frac{e^{is\beta\hbar}+1}{2}C(s) = \frac{is\beta\hbar}{2}\frac{e^{is\beta\hbar}+1}{e^{is\beta\hbar}-1}Z(s)$$
$$= \frac{is\beta\hbar}{2}\coth(is\beta\hbar/2)Z(s), \qquad (17)$$

for the symmetric part of $C(s)$, and

$$C_{\mathrm{A}}(s) = -\frac{is\beta\hbar}{2}Z(s), \qquad (18)$$

for the antisymmetric one.

The previous relations connecting the various LTs of the correlation functions in the complex plane, defined by the variable $s = \sigma + i\omega$, are generalizations of analogous relations for the FT of the correlation functions in the real variable ω (see, e.g., Sec. III of Ref. [28]). In particular, the various FTs (indicated by $\mathcal{F}[\dots]$) can be easily derived from Eqs. (16), (17), and (18) by remembering that

$$\mathcal{F}[c(t), \omega] = C(\omega) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} dt e^{-i\omega t}c(t)$$
$$= \frac{1}{2\pi}\mathcal{L}[c(t), s = i\omega]. \qquad (19)$$

Equations (17) and (18) can in principle be used to discuss the properties of $C_{\mathrm{S}}(s)$ and $C_{\mathrm{A}}(s)$ in the complex plane. The properties of $C_{\mathrm{S}}(s)$ could be deduced by studying the behavior of either the functions $\frac{is\beta\hbar}{2}\coth(is\beta\hbar/2)$ and $Z(s)$, or the functions $\frac{i\beta\hbar}{2}\coth(is\beta\hbar/2)$ and $sZ(s)$. However, in the first case, the function $s\coth(s)$ diverges for $s \to \infty$. In the second case, the function $\coth(s)$ equally has a pole at $s = 0$. This difficulty can be circumvented by rewriting $C_{\mathrm{S}}(s)$ in the different form

$$C_{\mathrm{S}}(s) = F(s)s^2Z(s) + Z(s) = \tilde{C}_{\mathrm{S}}(s) + Z(s), \qquad (20)$$

where we defined

$$F(s) = \frac{1}{s^2}\left[\frac{is\beta\hbar}{2}\frac{e^{is\beta\hbar}+1}{e^{is\beta\hbar}-1} - 1\right]$$
$$= \frac{1}{s^2}\left[\frac{is\beta\hbar}{2}\coth(is\beta\hbar/2) - 1\right] = \frac{\tilde{C}_{\mathrm{S}}(s)}{s^2Z(s)}. \qquad (21)$$

The limiting values of $F(s)$ for $s \to 0$ and ∞ are both finite and equal to $(i\beta\hbar)^2/12$ and 0, respectively. In addition, $F(s)$ has the property $F(s) = F^*(s^*)$.

In the following we will discuss the behavior of $\tilde{C}_{\mathrm{S}}(s)$ as determined by those of the two functions $F(s)$ and $s^2Z(s)$. In other words, we choose not to attribute s^2 to $F(s)$ because $s^2F(s)$ diverges at $\pm\infty$. Therefore, we will consider the properties of the above mentioned functions. Note that the LTs of the derivatives of a generic correlation $c(t)$ are given by

$$\mathcal{L}\left[\frac{d^kc(t)}{dt^k}, s\right] = s^kC(s) \quad k = 1, 2, \dots, \qquad (22)$$

so $s^2Z(s)$ is the LT of the second time derivative of $z(t)$.

From Eq. (21) it is seen that $F(s)$ has poles of the first order at the Matsubara frequencies $\pm\omega_n$ with $n = 1, 2, \dots$. Therefore, it can also be written in the form

$$F(s) = \sum_n \mathrm{Res}[F(s)]_{s\to+\omega_n}\frac{1}{s-\omega_n}$$
$$+ \sum_n \mathrm{Res}[F(s)]_{s\to-\omega_n}\frac{1}{s+\omega_n}, \qquad (23)$$

where the residues at the various poles are readily obtained considering the first definition of $F(s)$ in Eq. (21). In particular, it is found that

$$\mathrm{Res}[F(s)]_{s\to\pm\omega_n} = \lim_{s\to\pm\omega_n}[(s\mp\omega_n)F(s)] = \pm\frac{1}{\omega_n}, \qquad (24)$$

and Eq. (23) becomes

$$F(s) = \sum_n \frac{1}{\omega_n}\frac{1}{s-\omega_n} - \sum_n \frac{1}{\omega_n}\frac{1}{s+\omega_n} = \sum_n \frac{2}{s^2-\omega_n^2}. \qquad (25)$$

III. EXPONENTIAL EXPANSION OF QUANTUM CORRELATIONS

In this section we will discuss the properties of the exponential representation of $c(t)$. Then, we will give expressions for the parameters of $c(t)$ in terms of those of the exponential representation of the Kubo correlation $z(t)$. We remind the reader that, since $z(t)$ is defined only for $T \neq 0$ and ∞, the connection between $c(t)$ and $z(t)$ is valid only for $0 < \beta < \infty$.

First, let us recall that $c(t)$ and $z(t)$, and all their derivatives, are assumed to be continuous functions which, in general, can always be expanded in an infinite sum of exponentials: this is an intrinsic property of correlation functions of Hamiltonian dynamical systems at thermodynamic equilibrium [1–3]. In particular, we express $c(t)$ at $t \geqslant 0$ as

$$c(t) = c_{\rm e}(t) + ic_{\rm o}(t) = c(0)\sum_j c_j(t) = c(0)\sum_j J_j e^{w_j t} \quad (26)$$

with $c_e(t)$ and $c_o(t)$ both real. The set of (generally) complex amplitudes and frequencies $\{c(0)J_j, w_j\}$ must satisfy the condition $\mathrm{Re}\, w_j < 0$ [in order that $c(t) \to 0$ as $t \to \infty$], and the general sum rules leading to the condition for the spectral moments $C^{(k)}$:

$$C^{(k)} = \left[\frac{d^k}{dt^k}c(t)\right]_{t=0} = c(0)\sum_j J_j w_j^k, \quad (27)$$

which are supposed to be finite. Of course, the zeroth moment $C^{(0)} = c(0)$ leads to the condition $\sum_j J_j = 1$.

Here and in the following we will refer to the terms of the series in Eq. (26) as "modes" of the correlation, each mode being identified via the pair of generally complex parameters $c(0)J_j$ and w_j, both depending on the thermodynamic state and Hamiltonian dynamics of the system. The modes satisfying the KMS symmetry are either real, with J_j and w_j both real, or "complex," with $J_j \in \mathbb{C} \setminus \mathbb{R}$ (i.e., with a nonzero imaginary part), and w_j either belonging to $\mathbb{R}$ or to $\mathbb{C} \setminus \mathbb{R}$. We will carefully illustrate that, except for purely real modes, fulfillment of the symmetry condition leads to precise properties as far as the amplitudes are concerned.

Concerning the frequencies, it will be clearer in the following that when w_j is complex, i.e., belongs to $\mathbb{C} \setminus \mathbb{R}$, the frequencies w_j and w_j^* are both present in the series, and the physically significant contribution to Eq. (26) is expressed by the sum of the corresponding terms, i.e., by a pair of modes with complex conjugate frequencies.

The general expansion given in Eq. (26) can be specified in order to explicitly satisfy the symmetry properties of $c(t)$. The first of these is Eq. (2), which is equivalent to define the parity properties of $c_{\rm e}$ and $c_{\rm o}$, i.e.,

$$\begin{aligned} c_{\rm e}(t) &= c_{\rm e}(-t) = c(0)\sum_j c_{{\rm e}j}(t), \\ c_{\rm o}(t) &= -c_{\rm o}(-t) = c(0)\sum_j c_{{\rm o}j}(t). \end{aligned} \quad (28)$$

The complex amplitude J_j in Eq. (26) can thus be conveniently separated into two contributions: the first is $J_{{\rm e},j}$, which is generally complex, and contributes to that part of the single jth mode which is even in time, and can be written as $c(0)J_{{\rm e},j}e^{w_j|t|}$. Since $c_{{\rm e}j}(t)$ is a real quantity, the latter term and its complex conjugate of course add up to give the real and even result:

$$c_{{\rm e}j}(t) = c(0)(J_{{\rm e},j}e^{w_j|t|} + J_{{\rm e},j}^* e^{w_j^*|t|}). \quad (29)$$

The second contribution, $J_{{\rm o},j}$, determines that part of the single jth mode which is odd in time, and similarly to Eq. (29), leads to a real and odd result when summed up with its complex conjugate, according to

$$c_{{\rm o}j}(t) = c(0)\,\mathrm{sgn}(t)(J_{{\rm o},j}e^{w_j|t|} + J_{{\rm o},j}^* e^{w_j^*|t|}). \quad (30)$$

In Eq. (30), the function $\mathrm{sgn}(t)$ guarantees the odd character of $c_{{\rm o}j}(t)$.

With the above clarification on how complex-frequency modes appear in the series, Eq. (26) can be written in general as

$$c(t) = c(0)\sum_j [J_{{\rm e},j} + i\,\mathrm{sgn}(t)J_{{\rm o},j}]e^{w_j|t|} = c(0)\sum_j J_j e^{w_j|t|}, \quad (31)$$

with the identification

$$J_j = J_{{\rm e},j} + i\,\mathrm{sgn}(t)J_{{\rm o},j}, \quad (32)$$

for each individual mode. Thus, in Eq. (31) the sum runs over all $J_{{\rm e},j}$, $J_{{\rm o},j}$, w_j and their complex conjugates, when $w_j \in \mathbb{C} \setminus \mathbb{R}$. Given the form of Eq. (32), this means that in the last member of Eq. (31) the sum is over pairs of modes which have conjugate frequencies (w_j, w_j^*) but not conjugate amplitudes. In other words, complex conjugate pairs in the general expansion *do not* correspond to $J_j e^{w_j|t|} + J_j^* e^{w_j^*|t|}$, which would be a real-valued quantity in any case, but [see Eqs. (29) and (30)] to $[J_{{\rm e},j} + i\,\mathrm{sgn}(t)J_{{\rm o},j}]e^{w_j|t|} + [J_{{\rm e},j}^* + i\,\mathrm{sgn}(t)J_{{\rm o},j}^*]e^{w_j^*|t|}$.

Equation (31) must also satisfy the KMS condition expressed by Eq. (4). Since three different kinds of modes may contribute to $c(t)$, we carefully discuss in the following how this occurs for each set.

A. Pure real modes

Real modes, characterized by real values of both J_j and w_j in Eq. (26), represent pure exponential decays of $c(t)$, and only contribute to $c_{\rm e}(t)$, with $J_{{\rm o},j} = 0$ and $J_{{\rm e},j} \in \mathbb{R}$ in Eq. (32). Such purely real modes of $c(t)$ comply with the symmetry request of Eq. (4) if $e^{i\beta\hbar w_j} = 1$, which implies $w_j = -n\omega_1 = -\omega_n$, with $n = 1, 2, \ldots$. Note that such frequencies only depend on temperature, and will be present whatever the quantum system under consideration, and independently of the specifically investigated variable $A(t)$. Therefore, they can be seen as the fingerprint of the way in which any quantum system responds to a thermostat. How the specific system, and dynamical variable, couples with the thermostating bath will be clarified in what follows. We can anticipate, however, that the interaction between the thermostat and the system is contained in the amplitudes of the Matsubara modes, which will be shown to depend on the parameters describing the dynamical processes typical of a liquid.

With this purpose, we note that Eq. (31) can also be written, in general, in the form

$$\begin{aligned} c(t) &= c(0)\left\{\sum_n J_n^M e^{-\omega_n|t|} + \sum_i [J_{{\rm e},i} + i\,\mathrm{sgn}(t)J_{{\rm o},i}]e^{w_i|t|}\right\} \\ &= c(0)\left[\sum_n J_n^M e^{-\omega_n|t|} + \sum_i J_i^S e^{w_i|t|}\right], \end{aligned} \quad (33)$$

where we separated the real modes of real amplitudes J_n^M (the superscript meaning "Matsubara") and real damping $-\omega_n$, from the other modes, synthetically designated in the last row of Eq. (33) as J_i^S (the superscript meaning the system).

The previously described implications when dealing with real-valued amplitudes of the modes readily indicate that the other modes of the exponential expansion are characterized by complex amplitudes and enter both $c_e(t)$ and $c_o(t)$. In fact, the quantum character of the system dictates the existence of a nonzero imaginary part of the correlation, and this can happen only if the amplitudes of the other processes described by the exponential expansion take complex values.

B. Mixed modes

The system modes in Eq. (33) may have either real or complex (i.e., with a nonzero imaginary part) frequencies w_i. Here we define as "mixed" modes those having real frequencies (dampings). Physically, they represent the relaxation mechanisms of the system itself (like diffusive processes and structural relaxation), corresponding to simple exponential decays that contribute to both $c_e(t)$ and $c_o(t)$, with both $J_{e,i}$ and $J_{o,i}$ real. These modes, with real frequency, differ from the previous ones because, as mentioned, they originate from the system decay mechanisms such as those observed in classical systems.

For this set of modes one can also make the identification

$$J_{e,i} = \mathrm{Re} J_i^S,$$
$$J_{o,i} = \mathrm{Im} J_i^S, \tag{34}$$

so that Eq. (4) leads to the condition $\mathrm{Re}J_i^S - i\,\mathrm{Im}J_i^S = (\mathrm{Re}J_i^S + i\,\mathrm{Im}J_i^S)e^{iw_i\beta\hbar}$, which implies

$$\mathrm{Re}J_i^S = -\cot\left(\frac{w_i\beta\hbar}{2}\right)\mathrm{Im}J_i^S. \tag{35}$$

Equation (35) introduces divergences in $c(t)$ whenever w_i equals $-\omega_n$. However we will show (Appendix B) that these are removed by terms appearing in the amplitudes of the Matsubara modes.

C. Complex modes

Complex modes are those present in Eq. (26) when $w_i \in \mathbb{C} \setminus \mathbb{R}$ and amplitudes [see Eq. (32)] have complex $J_{e,i}$ and $J_{o,i}$. Consequently, the identification reported in Eq. (34) is no longer allowed. As explained before, the series contains these modes in pairs with complex conjugate frequencies (w_i, w_i^*) and amplitudes $(J_{e,i}, J_{e,i}^*$, and $J_{o,i}, J_{o,i}^*)$. As a consequence, in Eq. (33) the modes of one pair *do not have* conjugate amplitudes J_i^S, although they are conjugate in frequency. From a physical point of view, this set accounts for collective damped oscillatory processes occurring in the system, like longitudinal and transverse acoustic waves, each with damping $\mathrm{Re}w_i < 0$ and frequency $\mathrm{Im}w_i$.

It can be shown that relations similar to Eq. (35) are valid also in this case. In particular, Eq. (4) leads to

$$J_{e,i} = -\cot\left(\frac{w_i\beta\hbar}{2}\right)J_{o,i} \tag{36}$$

and

$$J_{e,i}^* = -\cot\left(\frac{w_i^*\beta\hbar}{2}\right)J_{o,i}^*, \tag{37}$$

and this is confirmed by the final expressions for J_i^S [Eqs. (46) and (47)] given in the following.

In summary, Eq. (33) shows that any quantum correlation can be expressed, in general, as a sum of exponentials, as anticipated in Eq. (26), where the set of modes $\{c(0)J_j, w_j\}$ is divided in two global sets. The first set, indexed by n, consists of the Matsubara modes (M modes) the existence of which is a necessary consequence of the KMS and EET properties of the correlation, and is mostly a direct and genuine manifestation of the quantum character of the system and of the temperature imposed by the thermostat, leading to the physical existence of a quantum thermodynamic time scale, $t_0 = \beta\hbar$, which also determines the time behavior of the system. Such a set is universal, in the sense that it is present with the same frequencies for any system and any correlation under consideration at a temperature T. How the specific system couples with the thermostating bath is instead reflected by the system-dependent amplitudes J_n^M, as we are going to illustrate. The second set, indexed by i, which includes both mixed and complex modes, is directly connected with the physical system, described by the Hamiltonian H, and the property $A(t)$ under investigation. We will refer to these modes as S modes. Note that also the property expressed by Eqs. (35) or (36) for the amplitudes of the S modes is universal.

We remark that Eqs. (31) and (33), derived from the general Eq. (26) by applying the discussed symmetry properties, are expressions of the exponential functionality of the correlation function. It is worth discussing here the mathematical implication of having $|t|$ and $\mathrm{sgn}(t)$, the former having a cusp, and the latter being discontinuous at $t = 0$. These facts introduce divergences in the derivatives of $c(t)$ at $t = 0$, in the form of a Dirac delta distribution $\delta(t)$, and of its derivatives. On the other hand, we have assumed $c(t)$ to be a continuous function, with all the derivatives: its continuity being guaranteed by the finite values of the moments $C^{(k)}$ in Eq. (27). Therefore, in the following we will neglect all the mathematical divergences caused by $|t|$ and $\mathrm{sgn}(t)$, since these have no physical significance for the present discussion. In particular, it has been shown [23] that the divergence at the level of the second derivative of $c(t)$ can be canceled, thanks to the first moment sum rule [see next Eq. (40)], when the properties of the KT $z(t)$ are considered.

The KT $z(t)$ associated with $c(t)$ can also be expanded for $t \geqslant 0$ as

$$z(t) = z(0)\sum_i I_i e^{z_i t}, \tag{38}$$

with the set $\{z(0)I_i, z_i\}$ satisfying the sum rules

$$Z^{(2k)} = \left[\frac{d^{2k}}{dt^{2k}}\right]_{t=0} = z(0)\sum_i I_i z_i^{2k}, \tag{39}$$

$$Z^{(2k+1)} = \left[\frac{d^{2k+1}}{dt^{2k+1}}\right]_{t=0} = z(0)\sum_i I_i z_i^{2k+1} = 0, \tag{40}$$

where the last equation descends from the symmetry of Eq. (13). The amplitudes $z(0)I_i$ and frequencies z_i characterize the modes (K modes) of the Kubo $z(t)$, with $\mathrm{Re}z_i < 0$. Again, the zeroth moment, $Z^{(0)} = z(0)$, implies $\sum_i I_i = 1$. As done previously for $c(t)$, the symmetry property of Eq. (13) allows us to write $z(t)$ on the whole time axis as

$$z(t) = z(0)\sum_i I_i e^{z_i|t|}. \tag{41}$$

TABLE I. Summary of the properties of the various sets of modes (see Secs. III A–III C) contributing to $c(t)$. For complex modes, representing damped propagating excitations, the prime (double prime) is used to synthetically indicate the real (imaginary) part of both amplitudes and frequencies.

Modes	Amplitude	Frequency/damping	Origin
Matsubara	$J_{\mathrm{e},j} \in \mathbb{R}, J_{\mathrm{o},j} = 0,$ $J_{\mathrm{e},j} = J_n^M$	$w_j \in \mathbb{R}$ $w_j = -\omega_n = -2\pi n/(\beta\hbar)$ $n = 1, 2, \ldots$	Existence of a quantum thermal time scale $t_0 = \beta\hbar$
Mixed	$J_{\mathrm{e},i}, J_{\mathrm{o},i} \in \mathbb{R}$ $J_{\mathrm{e},i} + iJ_{\mathrm{o},i} = J_i^S \in \mathbb{C} \setminus \mathbb{R}$	$w_i = z_i \in \mathbb{R}$	Diffusion and relaxation phenomena of the system
Complex	$J_{\mathrm{e},i}, J_{\mathrm{o},i} \in \mathbb{C} \setminus \mathbb{R}$ $(J'_{\mathrm{e},i} + iJ''_{\mathrm{e},i}) + \mathrm{sgn}(t)(-J''_{\mathrm{o},i} + iJ'_{\mathrm{o},i}) = J_i^S$ $(J'_{\mathrm{e},i} - iJ''_{\mathrm{e},i}) + \mathrm{sgn}(t)(J''_{\mathrm{o},i} + iJ'_{\mathrm{o},i}) \neq J_i^{S*}$	$w_i = z_i \in \mathbb{C} \setminus \mathbb{R}$ $z_i = z'_i + iz''_i$ $z_i^* = z'_i - iz''_i$	Collective excitations (pairs of modes)

The modes of $z(t)$ can have I_i and z_i either both real or both complex. As it happened before in the case of $J_{\mathrm{e},j}$ and $J_{\mathrm{o},j}$, the complex modes appear in the Kubo series in conjugate pairs [see, e.g., Eq. (29)].

It can be shown (see Appendix A) that $c_{\mathrm{e}}(t)$ and $c_{\mathrm{o}}(t)$ are expressed in terms of the Kubo and Matsubara modes by

$$\begin{aligned} c_{\mathrm{e}}(t) &= z(t) + \tilde{c}_{\mathrm{e}}(t) \\ &= z(t) + z(0)\sum_i \sum_n \left[\left(-\frac{1}{\omega_n} I_i z_i^2 \frac{2z_i}{\omega_n^2 - z_i^2}\right) e^{-\omega_n|t|} \right. \\ &\quad \left. + \left(I_i z_i^2 \frac{2}{z_i^2 - \omega_n^2}\right) e^{z_i|t|}\right], \end{aligned} \tag{42}$$

and

$$c_{\mathrm{o}}(t) = -\frac{\pi}{\omega_1} z(0) \sum_i I_i z_i \mathrm{sgn}(t) e^{z_i|t|}. \tag{43}$$

The total correlation was also written in Eq. (33) as

$$\begin{aligned} c(t) &= c_{\mathrm{e}}(t) + ic_{\mathrm{o}}(t) \\ &= c(0)\left[\sum_n J_n^M e^{-\omega_n|t|} + \sum_i J_i^S e^{w_i|t|}\right], \end{aligned} \tag{44}$$

so, one can readily make the identification $w_i = z_i$, i.e., the frequencies of the S modes of $c(t)$ coincide with those of the K modes of $z(t)$, implying that the physical processes characterizing the time behavior (regardless of the amplitudes) of the quantum system are grasped very well by the Kubo symmetric and real—and easy to handle—version of the correlation. Indeed, $c(t)$ and $z(t)$ are correlation functions of the same physical observable $A(t)$, so the characteristic frequencies of the physical system are bound to appear in both functions, although with different amplitudes.

Following the details given in Eqs. (A8)–(A11) regarding the various ways of expressing $c_{\mathrm{e}}(t)$, it is possible to make further identifications. In particular, one finds

$$J_n^M = \frac{z(0)}{c(0)} \sum_i \frac{I_i z_i}{\omega_1}\left[\varphi_n\left(-\frac{z_i}{\omega_1}\right) + \varphi_n\left(\frac{z_i}{\omega_1}\right)\right], \tag{45}$$

for the M modes, where φ_n is the fractional function $\varphi_n(s) = \frac{s}{n(n+s)}$. Note that the system-thermostat coupling is expressed by the dependence of J_n^M on the parameters of the S modes, while the Matsubara frequencies are system independent.

Regarding the amplitudes of the S modes, from the calculations reported in Appendix A it is found that

$$\begin{aligned} J_i^S = \frac{z(0)}{c(0)} \frac{I_i z_i}{\omega_1}\left[\frac{\omega_1}{z_i} + \psi\left(-\frac{z_i}{\omega_1} + 1\right) \right. \\ \left. - \psi\left(\frac{z_i}{\omega_1} + 1\right) - i\,\mathrm{sgn}(t)\pi\right], \end{aligned} \tag{46}$$

ψ being the digamma function. In particular, the real and imaginary parts in Eq. (46) can be verified to satisfy Eq. (36) thanks to the recurrence and reflection formulas (see 6.3.5 and 6.3.7 in Ref. [29]) for the digamma function, which lead to the relation $1/s + \psi(1-s) - \psi(1+s) = \pi\cot(\pi s)$. Therefore, one finally has

$$J_i^S = \frac{z(0)}{c(0)} \frac{I_i z_i}{\omega_1}\pi\left[\cot\left(\pi\frac{z_i}{\omega_1}\right) - i\,\mathrm{sgn}(t)\right]. \tag{47}$$

The previous results finally allow us to give in Table I a synoptic description of the properties of the sets of modes (introduced in Secs. III A–III C) which build up the quantum $c(t)$. Their main physical origin is also recalled. Note that, for a more compact notation, we use in Table I the prime and double prime in place of ReJ_e, ReJ_o and ImJ_e, ImJ_o, respectively.

IV. CHARACTERISTIC FEATURES OF $\tilde{c}_{\mathrm{e}}(t)$

In what follows, we are interested in analyzing in more detail the properties of $\tilde{c}_{\mathrm{e}}(t)$ of Eq. (42) as a function of T, via the variation of the quantity z_i/ω_1. In particular, by considering the structure of Eqs. (45) and (46), it is useful to distinguish four terms characterizing the time behavior of each mode of $\tilde{c}_{\mathrm{e}}(t)$:

$$\begin{aligned} \tilde{c}_{\mathrm{e}}(t) = z(0)\sum_i I_i\left\{\sum_n \left[M_{i,n}^{(-)}\left(\frac{z_i}{\omega_1}\right) + M_{i,n}^{(+)}\left(\frac{z_i}{\omega_1}\right)\right] e^{-\omega_n|t|} \right. \\ \left. + \left[S_i^{(-)}\left(\frac{z_i}{\omega_1}\right) + S_i^{(+)}\left(\frac{z_i}{\omega_1}\right)\right] e^{z_i|t|}\right\}, \end{aligned} \tag{48}$$

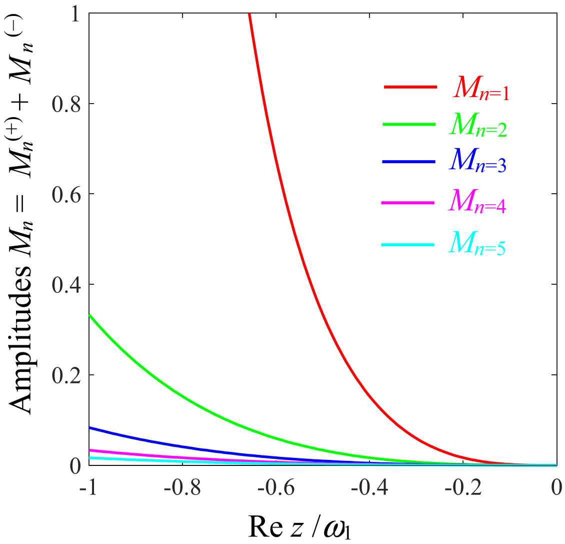

FIG. 1. First five terms, as a function of Rez/ω_1, for the overall amplitudes $M_n = M_n^{(+)} + M_n^{(-)}$ of the Matsubara series in Eq. (48). The color code is specified in the legend.

where, according to Eqs. (A9) and (A10), the four individual terms depending on z_i/ω_1 in Eq. (48) are given by

$$\begin{aligned} M_{i,n}^{(-)}\left(\frac{z_i}{\omega_1}\right) &= \frac{z_i}{\omega_1}\varphi_n\left(-\frac{z_i}{\omega_1}\right), \\ M_{i,n}^{(+)}\left(\frac{z_i}{\omega_1}\right) &= \frac{z_i}{\omega_1}\varphi_n\left(\frac{z_i}{\omega_1}\right), \\ S_i^{(-)}\left(\frac{z_i}{\omega_1}\right) &= \frac{z_i}{\omega_1}\psi\left(1-\frac{z_i}{\omega_1}\right), \\ S_i^{(+)}\left(\frac{z_i}{\omega_1}\right) &= -\frac{z_i}{\omega_1}\psi\left(1+\frac{z_i}{\omega_1}\right). \end{aligned} \tag{49}$$

Our analysis is aimed at understanding whether the above contributions play comparable roles or some of them dominate over the others with varying z/ω_1. Preliminarily, we show in Fig. 1 the global amplitude, $M_n = M_n^{(+)} + M_n^{(-)}$, for $n = 1, \ldots, 5$ of the, clearly converging, Matsubara series in Eq. (48) in the case of real z, with $-1 < z/\omega_1 < 0$. For the same case (real z), the dependence on z/ω_1 of the terms in Eq. (49) is reported in Fig. 2, for both an S mode and the leading term ($n = 1$) of an M mode. As expected from Eqs. (A9)–(A11), $S^{(+)}$ and $M_{n=1}^{(+)}$ show nearly opposite behaviors (both diverging at $z/\omega_1 = -1$), and leading to the eventual total cancellation of $S^{(+)}$ and $\sum_n M_n^{(+)}$ in $\tilde{c}_e(0)$. Figure 3 shows the same quantities of Fig. 2 in the case of complex z, with Re$z < 0$. Of course, the sum of complex conjugate terms provides real-valued S and M contributions that we plotted as a function of the real and imaginary parts of z/ω_1. Again, the competing behavior of $S^{(+)}$ and $M_{n=1}^{(+)}$ is evident also for complex pairs. By contrast, the amplitudes $S^{(-)}$ and $M_{n=1}^{(-)}$ give the dominant contribution of the S and M modes to $\tilde{c}_e(t)$.

The trends shown in Figs. 2 and 3 are not qualitatively modified by considering the role of the amplitudes I_i in Eq. (48), as we verified in a realistic case like, e.g., the one of a Kubo correlation function composed of a real mode and

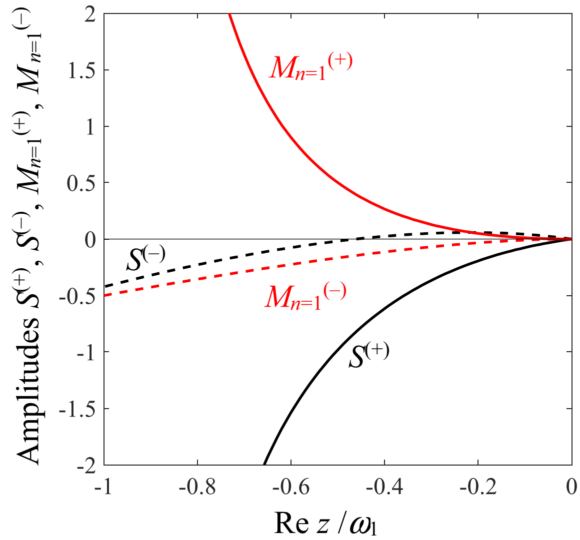

FIG. 2. Dependence on Rez/ω_1 of the individual terms contributing to the amplitude [see Eq. (49)] of an M mode and of an S mode in $\tilde{c}_e(t)$, for real z ($z < 0$) . For the M mode only the leading term ($n = 1$) is displayed (red curves). The two terms of the S mode are shown with black curves. Solid curves are used for $S^{(+)}$ and $M^{(+)}$, while dashed curves are used for $S^{(-)}$ and $M^{(-)}$.

a complex pair, satisfying both normalization $\sum_i I_i = 1$ and first moment sum rule [Eq. (40) for $k = 0$]. In the just mentioned case, it is more interesting to study the time behavior of the whole Matsubara part, $M(t) = \sum_i I_i \sum_n [M_{i,n}^{(-)}(\frac{z_i}{\omega_1}) + M_{i,n}^{(+)}(\frac{z_i}{\omega_1})]e^{-\omega_n|t|}$, and that of the system, $S(t) = \sum_i I_i[S_i^{(-)}(\frac{z_i}{\omega_1}) + S_i^{(+)}(\frac{z_i}{\omega_1})]e^{z_i|t|}$, in $\tilde{c}_e(t)$, for different values of z_i/ω_1. For instance, we considered the case in which the damping of the real mode (z_R) equals the one of the complex pair ($z'_C = \text{Re}z_C$), as well as the frequency of the oscillatory mode ($z''_C = \text{Im}z_C$). Figure 4 shows these parts of $\tilde{c}_e(t)$, along with their sum, in the three different situations indicated at

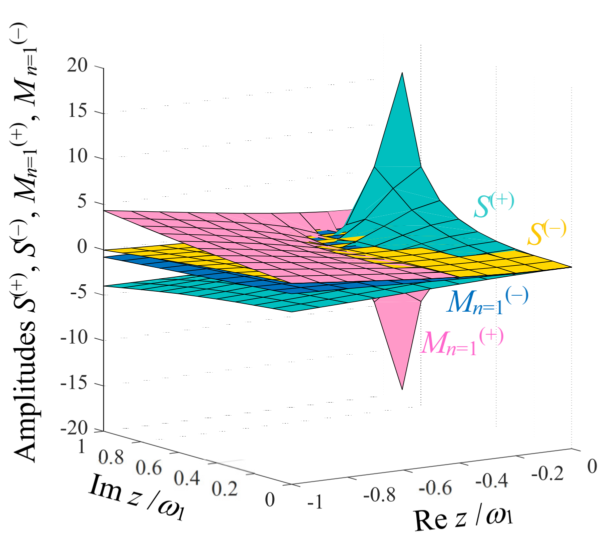

FIG. 3. As in Fig. 2, but for an M pair and an S pair with complex z (Re$z < 0$) in $\tilde{c}_e(t)$.

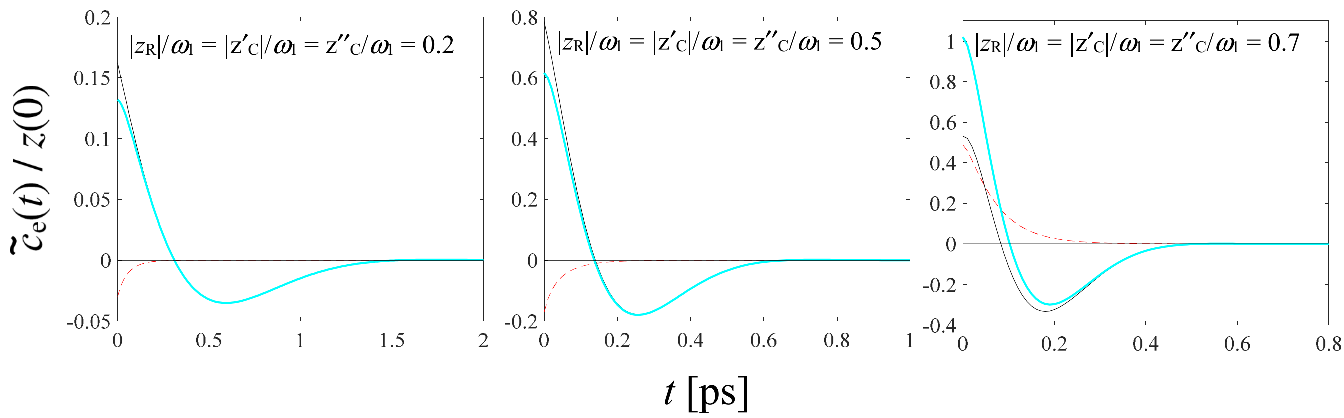

FIG. 4. $\tilde{c}_e(t)$ as a function of time (cyan thick curve) for a Kubo correlation characterized by one real mode and one complex pair, for different values of z/ω_1 (see text): 0.2 (left frame), 0.5 (central frame), and 0.7 (right frame). The global Matsubara (dashed red curve) and system (black thin curve) contributions are also shown separately.

the top of each frame. It is seen that the importance of the Matsubara term grows (in absolute value), and also changes sign, as ω_1 decreases, correctly witnessing the enhancement of quantum effects (and the growing "correction" role it plays) as the temperature is decreased. The last frame shows that there are conditions in which both the system and the Matsubara series almost equally contribute to $\tilde{c}_e(t)$ as $t \to 0$. Although the three frames of Fig. 4 necessarily cover different time ranges, it is also evident that the Matsubara part influences $\tilde{c}_e(t)$ over progressively larger time intervals as ω_1 (i.e., T) diminishes.

Finally, in Fig. 5 we compare the Matsubara and system parts for a real case. In particular, we show the real part of the velocity autocorrelation function of dense liquid para hydrogen at $T = 30$ K and density $n = 26.73$ nm^{-3}, as obtained by RPMD simulations [9], and via Eqs. (44)–(46) using the parameters of the exponential representation of the Kubo $z(t)$, fitted as described in Ref. [9]. Again the system and Matsubara parts are shown together with the total. At the chosen temperature, the principal Matsubara time constant is $\tau_1 = 0.04$ ps. The inset shows that, actually, the Matsubara series non-negligibly contributes only in such a limited time range, but its presence is crucial to obtain the correct behavior of the function as $t \to 0$.

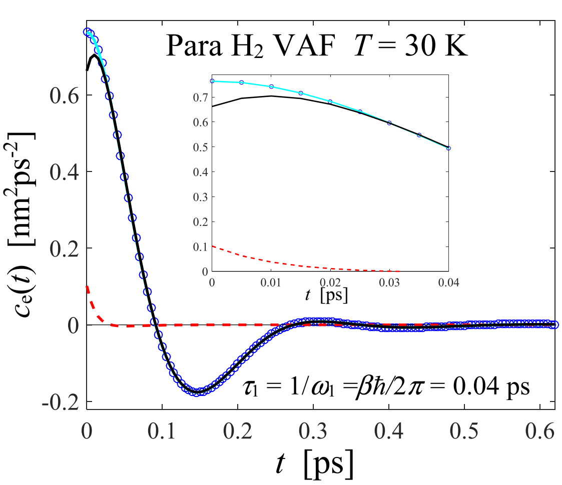

FIG. 5. Real part of the velocity autocorrelation function of liquid para H_2 at $T = 30$ K obtained by RPMD simulations [9] (blue circles) compared with the result of Eqs. (44)–(46) (cyan curve) using the parameters of the Kubo $z(t)$, fitted as described in Ref. [9]. As before, the global Matsubara (dashed red curve) and system (black curve) contributions are also shown separately. The inset is a zoom of the plot at short times, and extends up to the value of the Matsubara time constant τ_1 at the chosen temperature.

V. DISCUSSION AND CONCLUDING REMARKS

Equation (44) shows that the quantum correlation can be represented as an exponential series, in agreement with Eq. (26), where there are two sets of modes that characterize the time behavior. Both these sets are related to the parameters defining $z(t)$. As mentioned, the S modes characterized by the complex amplitudes $c(0)J_i^S$ and either real or complex frequencies z_i are those strictly related to the physical system and property A under investigation.

The second set of modes with real amplitudes $c(0)J_n^M$ and real frequencies ω_n represents pure decay channels (with characteristic times $\tau_n = 1/\omega_n$) which are directly connected with the KMS relations of Eqs. (3) and (4) and the EET representation.

At the present stage, it should be clear that the set of modes describing $c(t)$ is different from that describing $z(t)$, although strongly related. Indeed, the amplitudes J_n^M and J_i^S depend on the parameters of the K modes and on ω_1. The latter depends linearly on T and tends to zero as $T \to 0$. Therefore, the M modes increasingly contribute at longer times when the temperature is decreased towards zero. Of course, also the frequencies z_i can decrease with $T \to 0$, also contributing to $c(t)$ at longer times.

If the dependence on temperature of the dampings differs from the one of ω_1, there may be cases in which, at a given temperature, the damping of a real S mode equals $-\omega_n$, i.e., z_i coincides with one of the Matsubara frequencies $-\omega_n = -n\omega_1$ indicating a resonance between an S mode and an M mode. This means that in Eq. (A8) of Appendix A, and consequently in Eqs. (42) and (44) giving, respectively, $c_e(t)$

and $c(t)$, the fractional function $\varphi_n(t) = \frac{z_i/\omega_1}{n(n+z_i/\omega_1)}$ has a pole on the real axis for $z_i/\omega_1 = -n$. This pole of course affects the amplitudes J_i^M and J_i^S given in Eqs. (45) and (46), therefore the behavior of $c_e(t)$ and $c(t)$ needs to be analyzed with some care.

The existence of a possible pole in $c(t)$ is a direct consequence of the mathematical structure of $\tilde{C}_S(s)$ in Eq. (A6), which shows that the function has a pole for $z_i = -\omega_n$. The apparent divergence of $c(t)$ is however unphysical and should eventually disappear, as shown in Appendix B, where we find that the resonance between an S mode and an M mode leads to a different time behavior of the kind $|t|e^{-n\omega_1|t|}$, anyway decaying to zero at long times.

As mentioned in the Introduction, in the previous work based on the EET [23], the general exponential series of Eq. (31) was not given explicitly and the M modes of our Eqs. (33) and (45) were expressed via hypergeometric functions. Indeed, the equality between the previous and present expression for $c(t)$, that we omit for brevity, can be demonstrated without difficulties once the hypergeometric functions of Ref. [23] are expanded according to the Gaussian series defining them as $F(1, b; c; x) = \sum_n \frac{(b)_n}{(c)_n} x^n$, with the Pochhammer symbol meaning $(q)_n = q(q+1)(q+2)\dots(q+n-1)$. However, what we find more significant is that the present form allowed us to recognize and properly discuss also the case of possible resonances between S modes and M modes, differently from Ref. [23] where the analytic properties and convergence of the digamma and hypergeometric functions were not tackled in detail.

In conclusion, we can state that the EET exactly predicts the functionality of any classical, semiclassical, and quantum correlation function of many-body Hamiltonian systems in thermodynamic equilibrium. In particular, this paper shows that the correct symmetry properties of quantum correlations (KMS) applied within an exact theory like the EET lead to a remarkable result from the physical point of view: in the quantum case, correlations decay not only because we are dealing with an interacting many-body system governed by a certain Hamiltonian (like it happens in classical systems), but also because the interaction with the thermostat is highlighted by the existence of the nonzero time scale τ_1 entering the Matsubara part of the expansion.

Although other ways of expressing $c(t)$ can be preferred in numerical computations (within the EET [23]) we find that the one presented here can be more appropriate for understanding the role played by the Matsubara modes, which may affect substantially the time evolution of the correlation. As noticed, the M modes do contribute within times of the order of τ_1. The presence of these modes in the correlation also clarifies that the classical limit for $c(t)$ is not only represented by the fact that its imaginary part $c_o(t)$ tends to zero, but also by the assumption of disregarding any dynamical process with characteristic time $\tau_i \ll \tau_1$.

As a fact, the present form gives more physical insight about the properties of a quantum correlation, also elucidating the quantum coupling between the thermostat and the system. Such a coupling, embodied by the presence of (numerous) Matsubara modes, has growing importance with decreasing temperature, accordingly with a more and more marked quantum behavior of the system as T diminishes. By lowering the temperature, the M modes affect $c(t)$ in wider and wider time ranges: an effect that represents, in the time domain, the KMS symmetry, and which, together with the imaginary part of $c(t)$, translates into the well-known increasing asymmetry of the corresponding quantum spectra observed, for instance, by scattering techniques able to access some measurable quantum correlation function in the frequency domain, like, e.g., the dynamic structure factor of a quantum or semiquantum liquid. An example of the strong asymmetry of the measured (genuinely quantum) spectra can be found in Ref. [5], which regards a “weakly” quantum fluid as molecular deuterium. Here we give another example in Fig. 6, referring to the case analyzed in the last frame of Fig. 4 and showing the corresponding spectrum of $c(t)$ with all its components, the spectrum of the S modes [i.e., the FT of $c_e(t)$ plus the one of $c_o(t)$], and providing, on the whole, the strongly asymmetric total spectrum.

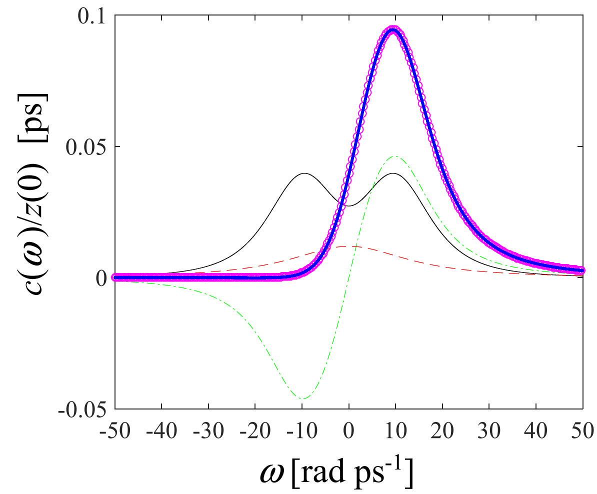

FIG. 6. Fourier transform of $c(t)/z(0) = [z(t) + \tilde{c}_e(t) + ic_o(t)]/z(0)$ in the same example case analyzed in the right frame of Fig. 4 for $\tilde{c}_e(t)/z(0)$. The total asymmetric spectrum (blue curve) is shown together with its components: the Matsubara part (red dashed curve), and the system symmetric (black thin curve) and antisymmetric (green dot-dashed curve) parts. The magenta circles correspond to the Kubo-asymmetrized spectrum of $z(\omega)/z(t=0)$, i.e., $\beta\hbar\omega/(1 - e^{-\beta\hbar\omega})z(\omega)/z(0)$, perfectly coinciding with the total asymmetric spectrum in blue. The magenta spectrum is simply Eq. (15) for real frequency.

Perspectives of this paper can be envisaged in the generalization of the present description also to space-dependent quantum correlations, and in the study of the Matsubara contribution to experimentally accessible correlation functions, like the intermediate scattering function of appropriate fluids. Indeed, it is expected, though not yet directly demonstrated to our knowledge, that the Matsubara role played in the overall fulfilment of the KMS symmetry of correlation functions of real dense systems grows in importance as smaller and smaller length scales are probed at fixed temperature. This should, in fact, be another route to observe enhanced quantum effects, in addition to the canonical ones of either increasing density or lowering the temperature (within obvious limits).

ACKNOWLEDGMENT

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APPENDIX A: DERIVATION OF EQS. (42) AND (43) AND EXPRESSIONS FOR $c_e(t)$

Following Eq. (41), with Re$z_i < 0$, the LT $Z(s)$ can be written in terms of the exponential mode parameters as

$$Z(s) = z(0)\sum_i I_i \frac{2z_i}{s^2 - z_i^2} = z(0)\sum_i I_i\left(\frac{1}{s - z_i} - \frac{1}{s + z_i}\right). \tag{A1}$$

By remembering Eq. (22), it follows that $sZ(s)$ and $s^2 Z(s)$ are, respectively, the transforms $\mathcal{L}[\frac{d}{dt}z(t), s] = \mathcal{L}[z(0)\sum_i I_i z_i \mathrm{sgn}(t) e^{z_i|t|}, s]$ and $\mathcal{L}[\frac{d^2}{dt^2}z(t), s] = \mathcal{L}[z(0)\sum_i I_i z_i^2 e^{z_i|t|}, s]$. As a consequence, with the aid of Eqs. (25) and (A1), we can express $\tilde{C}(s)$ of Eq. (20) in terms of $F(s)$ and of the parameters I_i and z_i of the modes of $z(t)$:

$$\tilde{C}_S(s) = z(0)\sum_n \frac{2}{s^2 - \omega_n^2}\sum_i I_i z_i^2 \frac{2z_i}{s^2 - z_i^2}. \tag{A2}$$

Equation (A2) shows that the poles of $\tilde{C}_S$ are at $s = \pm\omega_n$ and $\pm z_i$ with residues given by

$$\mathrm{Res}[\tilde{C}_S(s)]_{s\to\pm\omega_n} = \lim_{s\to\pm\omega_n}(s \mp \omega_n)\tilde{C}_S(s) = \pm\frac{z(0)}{\omega_n}\sum_i I_i z_i^2 \frac{2z_i}{\omega_n^2 - z_i^2}, \tag{A3}$$

$$\mathrm{Res}[\tilde{C}_S(s)]_{s\to\pm z_i} = \lim_{s\to\pm z_i}(s \mp z_i)\tilde{C}_S(s) = \pm z(0) I_i z_i^2 \sum_n \frac{2}{z_i^2 - \omega_n^2} \tag{A4}$$

where we made use of Eqs. (24) and (25). Consequently we can also write

$$\begin{aligned}\tilde{C}_S(s) = z(0)\sum_n\sum_i\Bigg[&\left(\frac{1}{\omega_n}I_i z_i^2\frac{2z_i}{\omega_n^2 - z_i^2}\right)\frac{1}{s-\omega_n} + \left(-\frac{1}{\omega_n}I_i z_i^2\frac{2z_i}{\omega_n^2 - z_i^2}\right)\frac{1}{s+\omega_n}\\ &+\left(I_i z_i^2\frac{2}{z_i^2-\omega_n^2}\right)\frac{1}{s - z_i} - \left(I_i z_i^2\frac{2}{z_i^2-\omega_n^2}\right)\frac{1}{s+z_i}\Bigg],\end{aligned} \tag{A5}$$

which can be recast in the form

$$\tilde{C}_S(s) = z(0)\sum_n\sum_i\left[\left(\frac{1}{\omega_n}I_i z_i^2\frac{2z_i}{\omega_n^2 - z_i^2}\right)\frac{2\omega_n}{s^2-\omega_n^2} + \left(I_i z_i^2\frac{2}{z_i^2-\omega_n^2}\right)\frac{2z_i}{s^2 - z_i^2}\right], \tag{A6}$$

while, following Eq. (18), for the antisymmetric function we have

$$C_A(s) = -\frac{i\beta\hbar}{2}z(0)\sum_i I_i z_i \mathrm{sgn}(t)\frac{2z_i}{s^2 - z_i^2}. \tag{A7}$$

By using Eqs. (20), (A8), and (A7), the inverse transforms $\mathcal{L}^{-1}[C_S(s), t] = c_e(t)$ and $\mathcal{L}^{-1}[C_A(s), t] = ic_o(t)$ are found to be those given in Eqs. (42) and (43).

The inverse Laplace transform $\mathcal{L}^{-1}[\tilde{C}_S(s), t] = \tilde{c}_e(t)$ is then

$$\begin{aligned}\tilde{c}_e(t) &= z(0)\sum_n\sum_i\left[\left(-\frac{1}{\omega_n}I_i z_i^2\frac{2z_i}{\omega_n^2 - z_i^2}\right)e^{-\omega_n|t|} + \left(I_i z_i^2\frac{2}{z_i^2-\omega_n^2}\right)e^{z_i|t|}\right]\\ &= z(0)\sum_n\sum_i\frac{I_i z_i}{\omega_1}\left\{\left[\frac{-z_i/\omega_1}{n(n - z_i/\omega_1)} + \frac{z_i/\omega_1}{n(n+z_i/\omega_1)}\right]e^{-\omega_n|t|} + \left[\frac{-z_i/\omega_1}{n(n - z_i/\omega_1)} - \frac{z_i/\omega_1}{n(n+z_i/\omega_1)}\right]e^{z_i|t|}\right\}.\end{aligned} \tag{A8}$$

Considering the inverse LT of Eq. (20) we thus obtain the real part of the correlation as

$$\begin{aligned}c_e(t) &= z(t) + \tilde{c}_e(t)\\ &= z(0)\sum_i I_i e^{z_i|t|} + z(0)\sum_i\frac{I_i z_i}{\omega_1}\left\{\sum_n\left[\varphi_n\left(-\frac{z_i}{\omega_1}\right) - \varphi_n\left(\frac{z_i}{\omega_1}\right)\right]e^{z_i|t|} + \sum_n\left[\varphi_n\left(-\frac{z_i}{\omega_1}\right) + \varphi_n\left(\frac{z_i}{\omega_1}\right)\right]e^{-\omega_n|t|}\right\},\end{aligned} \tag{A9}$$

where we introduced the fractional function $\varphi_n(s) = \frac{s}{n(n+s)}$ that enters the expansion (see 6.3.16 in Ref. [29]) of the digamma function $\psi(s+1)$, according to

$$\psi(s+1) = -\gamma + \sum_n \varphi_n(s), \quad s \neq -1, -2, -3, \dots \tag{A10}$$

where γ is the Euler-Mascheroni constant. Therefore, Eq. (A9) can equivalently be written as

$$c_e(t) = z(0)\sum_i I_i e^{z_i|t|} + z(0)\sum_i \frac{I_i z_i}{\omega_1}\left\{\left[\psi\left(-\frac{z_i}{\omega_1}+1\right) - \psi\left(\frac{z_i}{\omega_1}+1\right)\right]e^{z_i|t|} + \sum_n\left[\varphi_n\left(-\frac{z_i}{\omega_1}\right) + \varphi_n\left(\frac{z_i}{\omega_1}\right)\right]e^{-\omega_n|t|}\right\}. \tag{A11}$$

APPENDIX B: INVESTIGATING POSSIBLE RESONANCES IN $\tilde{c}_e(t)$

One can readily observe that Eq. (A8) contains resonances whenever $z_i/\omega_1 = -n$. In order to understand the role of these resonances, let us consider the case in which, for a particular i, the quantity z_i/ω_1 is very close to $-n$, i.e., $z_i/\omega_1 = -n - \Delta$ with $n \gg \Delta$. The interesting quantity in Eq. (A8) is then

$$\phi_i(t) = \left[\frac{z_i/\omega_1}{n(n+z_i/\omega_1)}\right]e^{-\omega_n|t|} - \left[\frac{z_i/\omega_1}{n(n+z_i/\omega_1)}\right]e^{z_i|t|}, \tag{B1}$$

which has two apparent poles leading to two divergences, opposite in sign, which can be discussed in the previously introduced approximation. When $z_i/\omega_1 = -n - \Delta$ with $n \gg \Delta$, Eq. (B1) becomes

$$\begin{aligned}\phi_i(t) &= \frac{n+\Delta}{n\Delta}e^{-n\omega_1|t|} - \frac{n+\Delta}{n\Delta}e^{-(n+\Delta)\omega_1|t|}\\ &\simeq \frac{1}{\Delta}e^{-n\omega_1|t|}(1-e^{-\omega_1\Delta|t|}) \to \omega_1|t|e^{-n\omega_1|t|},\end{aligned} \tag{B2}$$

where the last term corresponds to the limit for $\Delta \to 0$. Thus, the contribution to $\tilde{c}_e(t)$ of this pair of resonances is $\tilde{c}_i(t)$ given by

$$\tilde{c}_i(t) = z(0)\frac{I_i z_i}{\omega_1}\omega_1|t|e^{-n\omega_1|t|} = z(0)I_i z_i|t|e^{z_i|t|}, \tag{B3}$$

which shows that the two resonances are removed, leading to a different type of contribution to the correlation function, which can be of non-negligible intensity for times $t > 1/\omega_1$, compared to the others (without resonances) present in Eq. (A8). Finally, it is worth noting that the last equation implies that the pair of resonances contributes to $\tilde{C}(s)$ with $\mathcal{L}^{-1}[\tilde{c}_i(t), s] = z(0)I_i z_i\frac{2(z_i^2+s^2)}{(z_i^2-s^2)^2}$.

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