Exact exponential function solution of the generalized Langevin equation for autocorrelation functions of many-body systems

Fabrizio Barocchi,[1] Ubaldo Bafile,[2] and Marco Sampoli[1]
[1]*Dipartimento di Fisica e Astronomia, Università di Firenze, via G. Sansone 1, I-50019 Sesto Fiorentino, Italy*
[2]*Consiglio Nazionale delle Ricerche, Istituto dei Sistemi Complessi, via Madonna del Piano 10, I-50019 Sesto Fiorentino, Italy*
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We show that an exact solution of the generalized Langevin equation (GLE) for the autocorrelations of a many-body classical system can be given in an exponential functionality (EF) form. As a consequence, the power spectrum of the correlation has a Lorentzian functionality, i.e., is represented by an infinite sum of Lorentzian functions corresponding to the eigenmodes of the considered correlation. By means of the simple derivation of the GLE by M. H. Lee [Phys. Rev. B **26**, 2547 (1982)], we also show that, in practical cases of interest to experimental spectroscopies, possible approximations of the EF are related to a reduction of the relevant dynamical variables via a restriction of the dimensions of the orthogonalized space onto which the dynamics of the system is projected.

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The study of the time behavior of properties of many-particle systems and of the corresponding frequency spectra has been done mostly with reference to the framework of the generalized Langevin equation (GLE), derived by Mori and Zwanzig (MZ) a long time ago [1–3]. The GLE is at the same time the equation governing the dynamic behavior of correlation functions of observables of the many-body system and the place where the useful concepts of fluctuating forces and memory functions are defined and introduced. This theory has often been applied to study transport and the spectroscopic properties of fluids [4].

The memory function approach leads to a hierarchy of GLE equations which is solved through Laplace transformation and gives the well-known continued fraction representation of the spectra of correlation functions. However, this general result is not cast in an easily tractable expression and is so formal that it may appear physically empty, although the definition of the related projection operators and memory functions is clear enough. The difficulty of physically interpreting the GLE hierarchy, which is related to the precise time dependence of memory functions, together with the difficulty of physically interpreting the truncation of the continued fraction spectra at a certain level, has led sometimes to improper applications and to incorrect approximations of the memory function expressions.

Lee [5–7] has presented a method of solution of the dynamic many-body problem with the derivation of recurrence relations and continued fraction spectra, based on an orthogonalization procedure in the Hilbert space that provides a clearer connection to physical concepts, though arriving at a description of the spectra analogous to that of the MZ theory.

Here, starting from the Lee derivation and going few steps further, we will show that a general "Lorentzian functionality" (LF) of spectra and "exponential functionality" (EF) of correlation functions can be given, and that approximations for the frequency and time behaviors, respectively, can be directly related to the contraction of the dimensionality of the assumed Hilbert space in which the dynamics of the system is represented. This gives a precise physical meaning to possible practical approximations of the EF of correlations and LF of spectra.

We are interested in the behavior of a classical many-body system and therefore classical correlation functions and spectra. Similarly to Lee [5], let us start considering a dynamical Hermitian variable A of an N-body system at thermodynamic equilibrium. The time evolution of A is governed by the Liouville equation

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

where L is the Liouville operator, $LA = i\{H,A\}$, $\{\ldots,\ldots\}$ denotes a Poisson bracket, and H is the total Hamiltonian. Equation (1) can be formally solved as

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

where $A^{(\nu)} = (iL)^\nu A = [d^\nu A(t)/dt^\nu]_{t=0}$ are the initial-time derivatives of $A(t)$ and $A^{(0)} \equiv A$.

An inner product (A,B) is defined as the correlation function of A and B, $(A,B) \equiv \langle A^* B\rangle$, where $\langle\ldots\rangle$ denotes a classical statistical average at thermodynamic equilibrium and for convenience we make the choice $\langle A\rangle = 0$. Equations (1) and (2), together with the above definition of the inner product, define a Hilbert space S, where however the complete set $\{A^{(\nu)}\}$ describing the dynamics of A is not orthogonal.

The Gram-Schmidt (GS) process permits us to construct an orthogonal set $\{f_\nu\}$ out of $\{A^{(\nu)}\}$ with the starting choice $f_0 = A$ and then to rewrite $A(t)$ as

$$A(t) = \sum_{\nu=0}^{\infty} a_\nu(t) f_\nu, \tag{3}$$

with $(f_\nu, f_\mu) = \delta_{\nu\mu} M_\nu$, $a_\nu(t) = (f_\nu, A(t))/M_\nu$ and, in particular, $a_0(t) = (A, A(t))/(A,A)$. The initial-time values are $a_\nu(0) = \delta_{\nu 0}$. The following recurrence relation is found to hold [5]:

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

for $\nu \geqslant 1$, with $\dot{f}_\nu = iLf_\nu$ and $\Delta_\nu = M_\nu/M_{\nu-1} = (f_\nu, f_\nu)/(f_{\nu-1}, f_{\nu-1})$. Equation (4) can be used to successively derive the explicit expression of

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

starting from $f_0 = A$ with $f_{-1} = 0$ and $\Delta_0 \equiv 1$.

The substitution of Eq. (2) into the Liouville equation (1) and the use of the recurrence relation (4) yields a recurrence relation for the correlations $a_\nu(t)$ [5]; i.e.,

$$a_{\nu-1}(t) = \dot{a}_\nu + \Delta_{\nu+1} a_{\nu+1}(t) \tag{6}$$

for $\nu \geqslant 1$ and $\dot{a}_\nu = da_\nu(t)/dt$ with $a_{-1} = 0$. Because of (6), the Laplace transforms $a_\nu(z) = \mathcal{L}[a_\nu(t)]$ are such that

$$1 = z a_0(z) + \Delta_1 a_1(z), \tag{7a}$$

$$a_{\nu-1}(z) = z a_\nu(z) + \Delta_{\nu+1} a_{\nu+1}(z), \tag{7b}$$

which can also be written

$$a_0(z) = \left[z + \frac{\Delta_1 a_1(z)}{a_0(z)} \right]^{-1}, \tag{8a}$$

$$\frac{a_\nu(z)}{a_{\nu-1}(z)} = \left[z + \frac{\Delta_{\nu+1} a_{\nu+1}(z)}{a_\nu(z)} \right]^{-1}, \tag{8b}$$

with $\nu \geqslant 1$. If we now define

$$K_0(z) = a_0(z), \tag{9a}$$

$$K_\nu(z) = \Delta_\nu \frac{a_\nu(z)}{a_{\nu-1}(z)}, \tag{9b}$$

from Eqs. (8) it follows that

$$K_0(z) = [z + K_1(z)]^{-1}, \tag{10a}$$

$$K_\nu(z) = \Delta_\nu [z + K_{\nu+1}(z)]^{-1}, \tag{10b}$$

which in the time domain correspond to

$$\dot{K}_0(t) + \int_0^t dt' K_1(t - t') K_0(t') = 0, \tag{11a}$$

$$\dot{K}_\nu(t) + \int_0^t dt' K_{\nu+1}(t - t') K_\nu(t') = 0, \tag{11b}$$

with $\nu \geqslant 1$ and $K_0(t = 0) = 1$, $K_\nu(t = 0) = \Delta_\nu$. This is the hierarchy of GLE equations identifying $\{K_\nu(t)\}$ as the set of memory functions of $a_0(t) = K_0(t)$. MZ have demonstrated that $\{K_\nu(t)\}$ are correlation functions of variables of the many-body system which can be properly defined and denoted as "fluctuating forces" [1,3]. In particular it can be shown that these "forces" are directly related to the $\{f_\nu\}$ [6]. From the definition (9b) of $K_\nu(z)$ we also have

$$\begin{aligned} a_\nu(t) &= 1/\Delta_\nu \int_0^t dt' K_\nu(t - t') a_{\nu-1}(t') \\ &= \left(\prod_{i=1}^{\nu} \frac{1}{\Delta_i} \right) \int_0^t dt_\nu \int_0^{t_\nu} dt_{\nu-1} \cdots \int_0^{t_2} dt_1 \\ &\quad \times K_\nu(t - t_\nu) K_{\nu-1}(t_\nu - t_{\nu-1}) \ldots K_1(t_2 - t_1) a_0(t_1), \end{aligned} \tag{12}$$

indicating that the $\{a_\nu(t)\}$ components of $A(t)$ in the manifold $\{f_\nu\}$ are successively generated starting from $a_0(t_1)$ for $t > t_\nu > t_{\nu-1} > \ldots > t_2 > t_1 > 0$ via convolutions with the memory functions $K_\mu(t - t_\mu)$ where $\mu \leqslant \nu$. In other words, since the norm $\|A(t)\| = (A(t), A(t))/(A, A) = 1$, the dynamic of the vector $A(t)$ in the Hilbert space S is a rotation which successively in time acquires components $a_\nu(t)$ which are driven by a memory function correlation with the previous one $a_{\nu-1}(t')$ for $t > t'$. These considerations clarify that Eq. (3) is a possible way of building up $A(t)$ in S starting from its autocorrelation and then summing, in a sequential process, correlations of $A(t)$ itself with increasing-order derivatives at $t = 0$, which are brought in particular combinations up to $A^{(\nu)}$ by the f_ν.

Equations (9) can be combined to give the continued fraction representation of $a_0(z)$ and $K_\nu(z)$ which is also the result of the MZ theory; i.e.,

$$a_0(z) = \cfrac{1}{z + \cfrac{\Delta_1}{z + \cfrac{\Delta_2}{z + \ldots}}}, \tag{13a}$$

$$K_\nu(z) = \cfrac{\Delta_\nu}{z + \cfrac{\Delta_{\nu+1}}{z + \cfrac{\Delta_{\nu+2}}{z + \ldots}}}, \tag{13b}$$

with $\nu \geqslant 1$. Equation (13b) clarifies that $K_\nu(z)$ is defined with respect to the subspace $\mathrm{S}_\nu \subset \mathrm{S}$, which is also a Hilbert space spanned by $f_\nu, f_{\nu+1}, \ldots$.

The continued fractions (13) can be expressed as ratios of polynomials in z [8]:

$$a_0(z) = \lim_{\lambda \to \infty} \frac{\det \mathbf{D}^{(\lambda,1)}(z)}{\det \mathbf{D}^{(\lambda,0)}(z)}, \tag{14a}$$

$$K_\nu(z) = \lim_{\lambda \to \infty} \Delta_\nu \frac{\det \mathbf{D}^{(\lambda,\nu+1)}(z)}{\det \mathbf{D}^{(\lambda,\nu)}(z)}, \tag{14b}$$

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

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

$$a_0(z) = \lim_{\lambda \to \infty} \sum_{j=1}^{\lambda} \frac{I_j^{(\lambda,0)}}{z - z_j^{(\lambda,0)}}, \tag{15a}$$

$$K_\nu(z) = \lim_{\lambda \to \infty} \sum_{j=1}^{\lambda-\nu} \frac{I_j^{(\lambda,\nu)}}{z - z_j^{(\lambda,\nu)}}, \tag{15b}$$

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

$$I_j^{(\lambda,\nu)} = \lim_{z \to z_j^{(\lambda,\nu)}} \left(z - z_j^{(\lambda,\nu)} \right) K_\nu(z), \tag{16}$$

which also holds for $\nu = 0$, i.e., for $K_0(z) = a_0(z)$.

From Eqs. (15) by Laplace antitransformation we can now write the normalized correlation function $a_0(t)$ and memories

$K_\nu(t)$ for a classical system as

$$a_0(t) = \sum_{j=1}^{\infty} I_j^{(0)} \exp\left(z_j^{(0)}|t|\right), \tag{17a}$$

$$K_\nu(t) = \sum_{j=1}^{\infty} I_j^{(\nu)} \exp\left(z_j^{(\nu)}|t|\right), \tag{17b}$$

where we can now drop the superscript λ having taken the limit to infinity. Here, as well as in Eqs. (15), $I_j^{(\nu)}$ and $z_j^{(\nu)}$ appear as amplitudes and eigenfrequencies, respectively, of a normal mode representation of $a_0(t)$ and $K_\nu(t)$, and they may either be real or form pairs of complex conjugate values in agreement with the reality of all correlation functions of observables of classical systems.

Equations (17) are the main output of this analysis, as they establish as a general result the EF solutions of the GLE (10a). In particular, for the correlation function $a_0(t)$, the solution of the GLE provided by Eq. (17a) in the form of an expansion with respect to a set of exponential functions is a reorganization of, and an alternative to, the usual power expansion

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

where $\langle \omega^n \rangle = (-i)^n (A, A^{(n)})/(A, A)$ is the nth normalized spectral moment of $a_0(t)$. For a classical system $\langle \omega^n \rangle = 0$ for odd n. Moreover, as appears obvious from the definition of the set $\{\Delta_\nu\} = \{\Delta_1, \Delta_2, \ldots, \Delta_\nu\}$, all three sets $\{\Delta_\nu\}$, $\{I_j^{(0)}\}$, $\{z_j^{(0)}\}$ may be expressed in terms of $\{\langle \omega^n \rangle\}$. In particular from the expression of the moments and Eq. (15) we see that $\{I_j^{(0)}\}$ and $\{z_j^{(0)}\}$ satisfy in general a set of relations of the form

$$\sum_{j=1}^{\infty} I_j^{(0)} \left(z_j^{(0)}\right)^k = i^k \langle \omega^k \rangle \tag{19}$$

for $k \geqslant 0$. Similar considerations can also be given for all the memory functions $K_\nu(t)$ of Eq. (17b).

The solutions (17a) and (18) for the time behavior of the correlation function $a_0(t)$ are both exact. However, when approximated as partial summations of a finite number of terms, they are in some sense complementary to each other, since the form (18) is useful in describing the behavior at short times, while (17) can be useful at longer times. In fact, truncation of (18) is equivalent to retain a few lowest-power terms, while the approximation (17a), obtained by keeping the first few exponential functions, amounts to truncating the continued fraction (13a) so that only the lowest powers of z appear in the polynomial ratio of Eqs. (14a). Obviously both approximations violate the physical request that all frequency moments of $(A, A(t))$ must be determined and finite, thus restricting the validity of Eq. (19) to a limited number of values of k.

The normalized power spectrum of $(A, A(t))$, given by $I(\omega) = (1/\pi)\mathrm{Re}\, a_0(z = i\omega)$, is composed of two parts obtained by grouping all $z_j^{(0)}$ according to whether they are real or complex:

$$I(\omega) = \frac{1}{\pi}\left[\sum_p \frac{-I_p z_p}{z_p^2 + \omega^2} + \sum_q \frac{-I_q' z_q' + I_q''(\omega - z_q'')}{(z_q')^2 + (\omega - z_q'')^2}\right], \tag{20}$$

where p labels the real $z_j^{(0)}$ while each q refers to a pair of complex conjugate zeros written as $z_q' \pm i z_q''$, with respective amplitudes $I_q' \pm i I_q''$. Equation (20) gives the power spectrum as a sum of an infinite number of Lorentzian shapes (LF). Low-order approximations of (19) have been already used to analyze experimental spectra [9]. Also, an LF behavior of neutron spectra has been reported by de Schepper and Cohen [10], though derived in the different framework of generalized kinetic theory for hard-sphere fluids.

From the previous discussion we derive the following conclusions:

(1) The time-dependent autocorrelation function $a_0(t)$ of a dynamical variable of a many-body classical system at thermodynamic equilibrium can always be written in terms of an infinite sum of exponential functions; the same is true for all memory functions $K_\nu(t)$. Similarly, the power spectrum of $a_0(t)$ and $K_\nu(t)$ can be written as an infinite sum of Lorentzian shapes.

(2) Normal modes for $a_0(t)$ and $K_\nu(t)$ can then be defined with eigenfrequencies and intensities determined solely by the values of the frequency moments of $a_0(t)$.

(3) The above properties are direct consequences of the dynamical description given by the Liouville equation (1).

(4) In practical cases the exponential representation of either $a_0(t)$ or $K_\nu(t)$ must be approximated. The obvious way of approximating, similarly to what is done in power series expansions, is then to retain few modes in the summations (17). In doing so, one automatically goes into a long-time representation where the properties at $t = 0$ cannot be exactly reproduced; the theoretical spectra at sufficiently high frequency will not be able to represent real experimental spectra. The EF expression of $a_0(t)$ in general converges at long times faster than the power expansion (18) because it includes in an effective way all powers of t.

(5) The "few"-mode approximation, which can be directly applied either to $a_0(t)$ or to $I(\omega)$ with the restriction $1 \leqslant j \leqslant \nu_0$, from the practical point of view is exactly the same as truncating the continued fraction representation of the spectra (13a) at an appropriate level ν_0; however, it is directly linked to the concept of retaining an appropriate number of normal modes in the description of the correlation which is not evident at all in the continued fraction alone. This truncation can be carried out by exploiting the Markovian approximation to the memory function $K_{\nu_0}(t)$; i.e., $K_{\nu_0}(t) = 2\Delta_{\nu_0}\delta(t)$. All the other $K_\nu(t)$ with $\nu < \nu_0$ are then represented by sums of exponential functions, meaning that the Markovian approximation is consistent with the present theory since it maintains the EF and LF structures.

(6) The "few"-mode approximation, as well as the truncation of the continued fraction (13a) at the level ν_0, has the same effect as the contraction of the general Hilbert space S down to ν_0 dimensions, which is the same as considering for the reconstruction of $a_0(t)$ and $I(\omega)$ only the manifold

$\{f_1, f_2, \ldots, f_{\nu_0}\}$. The previous observation links the few-mode approximation to the well-defined physical fact of considering in the time evolution of $a_0(t)$ only correlations of $A(t)$ with $A^{(\nu)}$ up to $\nu = \nu_0$.

We believe that the general solution of the dynamic problem in a many-body classical system of particles given by the EF representation of the autocorrelation $a_0(t)$ permits us to define in a very general form appropriate eigenfrequencies of modes which drive the time evolution of any autocorrelation in the many-body system. This EF representation should be the starting point for the search of approximated forms in the analysis of experimental spectra. This approach leads in a natural way to the determination of the eigenmodes of $a_0(t)$ by fitting to the available data a suitably chosen approximation. The values of the eigenfrequencies $z_j^{(0)}$ and of the respective amplitudes $I_j^{(0)}$ depend on the order and the type of performed approximation.

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