Fractional diffusion in a periodic potential: Overdamped and inertia corrected solutions for the spectrum of the velocity correlation function

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Anomalous diffusion of a particle in a cosine periodic potential is treated using fractional diffusion equations in both phase and configuration space. Exact solutions of two distinct forms of the fractional Klein-Kramers (Fokker-Planck) equation for the distribution function in phase space are obtained via matrix continued fractions yielding the average velocity, the velocity autocorrelation function, its spectrum, etc. In the overdamped limit, the results yielded by both equations agree with those from a fractional probability density diffusion equation in configuration space. A simple analytic solution for the spectrum of the velocity correlation function is also given using the effective eigenvalue approximation. The results represent generalizations of the conventional solutions for the normal diffusion of a Brownian particle in a cosine potential to fractional dynamics (giving rise to anomalous diffusion).

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I. INTRODUCTION

Both the free Brownian motion and that in a field of force are of fundamental importance in problems involving relaxation and resonance phenomena in stochastic systems [1,2]. The best known example is the translational diffusion of noninteracting Brownian particles treated by Einstein [3] with a host of applications in physics, chemistry, biology, etc. Einstein's theory relies on a *discrete time random walk*. Here the random walker or particle makes a jump of a *fixed mean square length* in a *fixed time*. The Einstein theory of normal diffusion has been generalized to fractional diffusion (see Refs. [4–6] for a review) in order to describe anomalous relaxation and diffusion processes in disordered complex systems (such as amorphous polymers, glass forming liquids, etc.) using a *continuous time random walk* (CTRW), a concept introduced by Montroll and Weiss [7,8]. In the most general case of the CTRW, the random walker may jump an *arbitrary* length in *arbitrary* time. In the noninertial limit and in one dimension, the dynamics of the walker are described by a fractional diffusion equation for the distribution function $f(x,t)$ in configuration space incorporating both a waiting time probability density function governing the random time intervals between single microscopic jumps of the particles and a jump length probability distribution [9]. A simple case of the CTRW arises by assuming that the jump length and jump time random variables are *decoupled* leading in the limit of a large sequence of jump times to the following fractional Fokker-Planck equation in configuration space (for a review see Refs. [5,7])

$$\frac{\partial f}{\partial t} = {}_0D_t^{1-\sigma} K_\sigma \frac{\partial}{\partial x}\left[\frac{\partial f}{\partial x} + \frac{f}{kT}\frac{\partial V}{\partial x}\right]. \tag{1}$$

Here x specifies the position of the walker at time t, $-\infty < x < \infty$, kT is the thermal energy, K_σ is a generalized diffusion coefficient, and $V(x)$ denotes the external potential. The operator ${}_{t_0}D_t^{1-\sigma} \equiv \frac{\partial}{\partial t}\,{}_{t_0}D_t^{-\sigma}$ in Eq. (1) is defined via the convolution (the Riemann-Liouville fractional integral definition) [6],

$${}_{t_0}D_t^{-\sigma} f(x,t) = \frac{1}{\Gamma(\sigma)}\int_{t_0}^{t}\frac{f(x\ ,t')dt'}{(t-t')^{1-\sigma}}, \tag{2}$$

where $\Gamma(z)$ is the gamma function. Values of σ in the range $0 < \sigma < 1$ correspond to subdiffusion phenomena ($\sigma = 1$ corresponds to normal diffusion).

Since inertial effects are ignored in the fractional Fokker-Planck Eq. (1), the latter cannot describe the high-frequency (short-time) dynamics in anomalous diffusion at all. In the normal Brownian motion, inertial effects are included via the Fokker-Planck equation (which for a separable and additive Hamiltonian is known as the Klein-Kramers equation) for the distribution function of particles $W(x,p,t)$ in phase space $(x, p = m\dot{x})$ [1,10] (m is the mass of the particle). In order to incorporate these effects, Metzler [12] and Metzler and Klafter [13] have proposed a fractional Klein-Kramers equation for the distribution function $W = W(x,\dot{x},t)$, viz.,

$$\frac{\partial W}{\partial t} = {}_0D_t^{1-\alpha}\tau^{1-\alpha}\left[-\dot{x}\frac{\partial W}{\partial x} + \frac{1}{m}\frac{dV}{dx}\frac{\partial W}{\partial \dot{x}} + \beta\left(\frac{\partial}{\partial \dot{x}}(\dot{x}W) + \frac{kT}{m}\frac{\partial^2 W}{\partial \dot{x}^2}\right)\right], \tag{3}$$

where τ is the mean time between successive trapping events (waiting time between jumps) and β is a friction coefficient arising from the heat bath. Equation (3) describes a multiple trapping picture, whereby the tagged particle executes translational Brownian motion. However, the particle gets successively immobilized in traps whose mean distance apart is $(kT/m)\tau$. The time intervals spent in the traps are governed by the waiting time probability density function $w(t) \sim A_\alpha t^{-1-\alpha}$ $(0 < \alpha < 1)$. Now the entire Klein-Kramers operator in the square brackets of Eq. (3) acts nonlocally in time (i.e., drift friction and diffusion terms are under the time convolution and are thus affected by the memory). However, a model based on a fractional Fokker-Planck-like Eq. (3) may provide a physically unacceptable picture of the behavior of observables such as the dynamic susceptibility in the high frequency limit $\omega \to \infty$ [14]. The root of this difficulty apparently being that in writing Eq. (3), the convective derivative or Liouville term, in the underlying Klein-Kramers equation, is operated upon by the fractional derivative. However, this problem does not arise in the fractional Fokker-Planck equation proposed by Barkai and Silbey [15]:

$$\frac{\partial W}{\partial t} = -\dot{x}\frac{\partial W}{\partial x} + \frac{1}{m}\frac{dV}{dx}\frac{\partial W}{\partial \dot{x}} + {}_0D_t^{1-\alpha}\tau^{1-\alpha}\beta\left[\frac{\partial}{\partial \dot{x}}(\dot{x}W) + \frac{kT}{m}\frac{\partial^2 W}{\partial \dot{x}^2}\right]. \tag{4}$$

Here the fractional derivative term acts solely on the dissipative part of the normal Klein-Kramers operator so that the Liouville term retains its classical form. In order to justify a diffusion equation like Eq. (4), Barkai and Silbey [15] consider a "Brownian" test particle moving freely in one dimension and colliding elastically at random times with particles of the heat bath which are assumed to move much more rapidly than the test particle. The times between collision events are assumed to be independent, identically distributed, random variables, implying that the number of collisions in a time interval $(0,t)$ is a renewal process. This hypothesis is reasonable, according to Barkai and Silbey, if the bath particles thermalize rapidly and if the motion of the test particle is relatively slow. Various applications of the above fractional diffusion equations to anomalous diffusion in a potential as well as alternative versions of fractional Klein-Kramers equations have been given (e.g., in Refs. [14–21]).

Fractional diffusion equations, such as Eqs. (1), (3), and (4), can be solved just as the normal diffusion equation [1,10] (e.g., by the method of separation of the variables). The separation procedure yields an equation of Sturm-Liouville type and has been extended to analogous fractional diffusion models involving a potential by Metzler *et al.* [17], Coffey *et al.* [14,19], and others. Furthermore, the numerically efficient solution method based on ordinary and matrix continued fractions, which has been developed for normal diffusion [1,10], can be directly applied to the problem of fractional diffusion [10,14].

Here we shall consider fractional diffusion in a cosine periodic potential, viz.,

$$V(x) = -V_0\cos(2\pi x/a). \tag{5}$$

The normal diffusion in this potential can be applied to the noise driven motion in areas as diverse as the motion of the defects or interstitials in crystalline materials, diffusion of ions in (so-called) superionic conductors, atomic surface diffusion, etc. [1,22,23]. For normal diffusion in a periodic potential, a large number of specialized solutions exist usually for particular observables (see, e.g., [1,10,23,24]). For example, the average velocity $\langle\dot{x}\rangle(t)$ and the spectrum of the velocity autocorrelation function (ACF) $\langle\dot{x}(0)\dot{x}(t)\rangle_0$, were treated in Refs. [1,10,23,24]. Furthermore, certain characteristics of the fractional diffusion in periodic potentials, such as the anomalous diffusion coefficient, have been studied in Refs. [25–27]. However, our main objective here is to ascertain how inertial effects in anomalous diffusion modify the dynamical characteristics $[\langle\dot{x}\rangle(t)$, etc.] in a periodic potential, a problem which has hitherto received little attention. With this goal in mind, we shall present both matrix continued fraction solutions of the fractional diffusion equations (1), (3), and (4) as well as simple approximate formulas. We shall first evaluate the spectrum of $\langle\dot{x}(0)\dot{x}(t)\rangle_0$ using the noninertial fractional diffusion Eq. (1), which provides us with a benchmark solution. Moreover, the inertial effects will be treated using both the Barkai-Silbey and Metzler-Klafter fractional Fokker-Planck equations (3) and (4). The differential-recurrence relations generated from these equations will be solved for bounded periodic initial conditions using ordinary and matrix continued fractions yielding both the time-independent and the time-dependent periodic solutions. These solutions will then be used to determine the relevant dynamical quantities.

II. OVERDAMPED ANOMALOUS DIFFUSION IN A PERIODIC POTENTIAL

It is convenient to introduce in Eq. (1) the normalized coordinate $2\pi x/a \to x$ and potential $V(x)/(kT) \to V(x) = -b\cos x$ $[b = V_0/(kT)$ is the barrier or inverse temperature parameter]. We are interested in the linear response to a small ac force $b\Delta e^{i\omega t}$. Thus we suppose that the potential $V(x) = -b\cos x$ is augmented by a small ac term $-xb\Delta e^{i\omega t}$ which has been applied in the infinite past $t_0 = -\infty$ so that all transients have died away. Then, Eq. (1) becomes

$$\tau^\sigma\frac{\partial f}{\partial t} = {}_{-\infty}D_t^{1-\sigma}\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial x} + f\frac{\partial V}{\partial x}\right), \tag{6}$$

where $\tau^\sigma = a^2/(4\pi^2K_\sigma)$. For the periodic (in x) solution of Eq. (6) [i.e., $f(x,t) = f(x+2\pi,t)$], the distribution function $f(x,t)$ can be expanded in a Fourier series in x as

$$f(x,t) = \frac{1}{2\pi}\sum_{n=-\infty}^{\infty} c_n(t)e^{inx}, \tag{7}$$

where $c_n(t) = \langle e^{-inx}\rangle(t)$ and the angular brackets $\langle\rangle(t)$ denote the ensemble averaging, viz.,

$$\langle(\cdot)\rangle(t) = \int_{-\pi}^{\pi}(\cdot)f(x,t)dx. \tag{8}$$

Furthermore, in the linear approximation in Δ, we may now seek a solution of Eq. (6) as $f(x,t) = f_0(x) + f_1(x,\omega)\Delta e^{i\omega t}$, where $f_0(x) = Z^{-1}\exp(b\cos x)$ is a stationary (equilibrium) solution in the *absence* of the ac force so that

$$c_n(t) = c_n^0 + c_n(\omega)\Delta e^{i\omega t}, \tag{9}$$

where Z is the partition function,

$$c_n^0 = \int_{-\pi}^{\pi} e^{-inx} f_0(x)dx \text{ and } c_n(\omega) = \int_{-\pi}^{\pi} e^{-inx} f_1(x,\omega)dx.$$

On substituting Eqs. (7) and (9) into Eq. (6), we have by orthogonality the three-term recurrence relations for the Fourier coefficients c_n^0 and $c_n(\omega)$, viz.,

$$\frac{b}{2}\left(c_{n-1}^0 - c_{n+1}^0\right) - nc_n^0 = 0, \tag{10}$$

$$[n^2 + (i\omega\tau)^\sigma]c_n(\omega) - \frac{bn}{2}[c_{n-1}(\omega) - c_{n+1}(\omega)] = -ibnc_n^0. \tag{11}$$

The frequency independent Eq. (10) has a closed form solution [10], Chapter 5,

$$c_n^0 = I_n(b)/I_0(b), \tag{12}$$

where $I_n(z)$ is the modified Bessel function of the first kind of order n [28]. By invoking the general method for solving nonhomogeneous differential-recurrence equations [1,10] and since $c_0(\omega) = 0$, we have the solution of Eq. (11) for the Fourier coefficient $c_1(\omega)$ in terms of continued fractions,

$$c_1(\omega) = 2i\sum_{n=1}^{\infty}(-1)^n c_n^0 \prod_{p=1}^{n}\Delta_p, \tag{13}$$

where Δ_n are infinite continued fractions defined by the recurrence equation,

$$\Delta_n = \frac{1}{2}\left[\frac{(i\omega\tau)^\sigma}{nb} + \frac{n}{b} + \frac{1}{2}\Delta_{n+1}\right]^{-1}.$$

Furthermore, by symmetry, we have $c_{-1}(\omega) = c_1^*(-\omega)$, where the asterisk denotes the complex conjugate. If all the other Fourier coefficients are required, $c_n(\omega)$ $(n = 2,3,..)$, for example, for the calculation of $f(x,t)$ from Eq. (7), they can also be calculated in terms of the continued fractions Δ_n as described in detail in Refs. [1,10].

In the noninertial limit, the mean drift velocity $\langle\dot{x}\rangle(t)$ for the linear response to a probing ac force $b\Delta e^{i\omega t}$ can be calculated as

$$\begin{aligned}\langle\dot{x}\rangle(t) &= -\tau^{1-\sigma}{}_{-\infty}D_t^{1-\sigma}\langle\partial_x V\rangle(t)\\ &= b\,\tau^{1-\sigma}{}_{-\infty}D_t^{1-\sigma}[\Delta e^{i\omega t} - \langle\sin x\rangle(t)]\\ &= b\Delta(i\omega\tau)^{1-\sigma}\left[1 - \frac{c_{-1}(\omega) - c_1(\omega)}{2i}\right]e^{i\omega t}. \end{aligned}\tag{14}$$

The definition of $\langle\dot{x}\rangle(t)$ embodied in Eq. (14) is simply a fractional generalization of the definition of the mean drift velocity of a Brownian particle in the normal *noninertial* diffusion in a potential, viz., $\langle\dot{x}\rangle(t) = -\langle\partial_x V\rangle(t)$ [1]. We remark that in the overdamped (noninertial) limit, the velocity $\dot{x}$ is not an independent variable; it is defined formally via the coordinate-dependent drift coefficient [1]. Such a definition implies that $\dot{x} = 0$ in the absence of a potential. Now, $\langle\dot{x}\rangle(t)$ from Eq. (14) can be written as

$$\langle\dot{x}\rangle(t) = \tilde{C}_v(\omega)b\Delta e^{i\omega t}, \tag{15}$$

where

$$\tilde{C}_v(\omega) = (i\omega\tau)^{1-\sigma}\left[1 - \frac{c_{-1}(\omega) - c_1(\omega)}{2i}\right]. \tag{16}$$

According to Kubo's linear response theory [1,29], $\tilde{C}_v(\omega)$ in Eq. (15) has the meaning of a generalized dynamic susceptibility, which is related to the one-sided Fourier transform of the equilibrium velocity ACF $\langle\dot{x}(0)\dot{x}(t)\rangle_0$ via $\tilde{C}_v(\omega) = \int_0^\infty \langle\dot{x}(0)\dot{x}(t)\rangle_0 e^{i\omega t}dt$ (the angular brackets $\langle\rangle_0$ denote equilibrium ensemble averaging). We remark that in the noninertial limit, the velocity ACF $\langle\dot{x}(0)\dot{x}(t)\rangle_0$ has a meaning only in the presence of a potential and is defined just as that of any other coordinate-dependent dynamic variable $A(x)$, viz. [1],

$$\langle A(0)A(t)\rangle_0 = \int_{x_1}^{x_2}\int_{x_1}^{x_2} A(x_0)A(x)f(x,t\,|x_0,0)f_0(x_0)dxdx_0, \tag{17}$$

where $A(t) = A[x(t)]$, $x_0 = x(0)$, $x_1 \leqslant x_0,x \leqslant x_2$, $f(x,t|x_0,0)$ is the Green function of Eq. (1) satisfying the initial condition $f(x,0|x_0,0) = \delta(x - x_0)$, and $\delta(x - x_0)$ is the Dirac delta function.

Just as normal diffusion, we can also obtain a simple approximate equation for the velocity ACF and its spectrum using the effective eigenvalue method [29]. Thus we suppose that the recurrence Eq. (11) for $n = \pm 1$ can be replaced by the approximate equation,

$$[\lambda_{ef}^{\pm} + (i\omega\tau)^\sigma]c_{\pm 1}(\omega) = \mp ibc_{\pm 1}^0,$$

or

$$c_{\pm 1}(\omega) = \mp\frac{ibI_1(b)/I_0(b)}{\lambda_{ef} + (i\omega\tau)^\sigma}, \tag{18}$$

where $\lambda_{ef} = \lambda_{ef}^+ = \lambda_{ef}^-$ is the effective eigenvalue for the *normal* diffusion given by (see Appendix A)

$$\lambda_{ef} = \frac{bI_0(b)I_1(b)}{I_0^2(b) - 1}. \tag{19}$$

Here we have noticed that $c_1^0 = c_{-1}^0 = I_1(b)/I_0(b)$. For $b \ll 1$ and $b \gg 1$, $\lambda_{ef} \approx 1 + 3b^2/16$ and $\lambda_{ef} \sim b$, respectively. Hence, using Eqs. (16), (18), and (19), we have

$$\tilde{C}_v(\omega) = (i\omega\tau)^{1-\sigma}\left(1 - \frac{bI_1(b)/I_0(b)}{\lambda_{ef} + (i\omega\tau)^\sigma}\right). \tag{20}$$

The approximation, Eq. (18), implies that in linear transient responses, the relaxation functions $c_{\pm 1}(t) = \sum_p c_p^{\pm}E_\sigma[-\lambda_p(t/\tau)^\sigma]$ comprising a superposition of an *infinite* number of Mittag-Leffler functions $E_\sigma[-\lambda_p(t/\tau)^\sigma]$ [10] may be approximated by a *single* Mittag-Leffler function $c_{\pm 1}(t) \approx c_{\pm 1}(0)E_\sigma[-\lambda_{ef}(t/\tau)^\sigma]$ only [λ_p are the eigenvalues of the normal diffusion operator ($\sigma = 1$) and $E_\sigma(z)$ is the Mittag-Leffler function [4].

The real and imaginary parts of $\tilde{C}_v(\omega)$ calculated from the continued fraction solution, Eqs. (13) and (16), and from the approximate Eq. (20) are shown in Fig. 1. Apparently, the agreement between the numerical calculations and Eq. (20) is good (the maximum relative deviation between the corresponding curves does not exceed a few percent). Similar (or

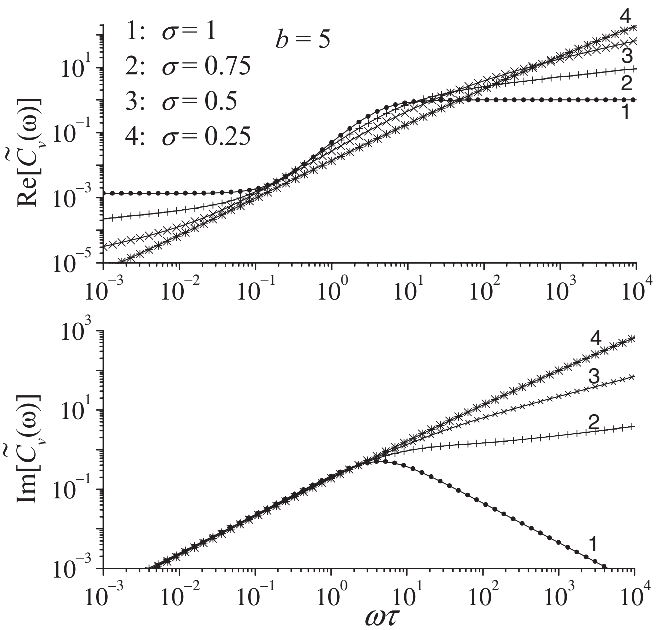

FIG. 1. $\mathrm{Re}[\tilde{C}_v(\omega)]$ and $\mathrm{Im}[\tilde{C}_v(\omega)]$ vs $\omega\tau$ for various of σ and $b = 5$: comparison of the continued fraction solution Eq. (16) and approximate Eq. (20) (symbols).

even better) agreement exists for *all* b and σ. Thus, one may conclude that Eq. (20) accurately describes $\mathrm{Re}[\tilde{C}_v(\omega)]$ and $\mathrm{Im}[\tilde{C}_v(\omega)]$ for all frequencies of interest in wide ranges of the barrier height (b) and anomalous exponent (σ) parameters. We remark that the effective eigenvalue approximation also works well for normal diffusion ($\sigma = 1$).

III. INERTIAL EFFECTS IN ANOMALOUS DIFFUSION

The above solution only holds at low frequencies because it completely ignores inertial effects. We now consider these effects in the translational Brownian motion of a particle in a periodic potential Eq. (5) using the Metzler-Klafter and Barkai-Silbey kinetic models. In the normalized variables,

$$x \to \frac{2\pi x}{a}, \quad t \to \frac{t}{\eta}, \quad b = \frac{V_0}{kT}, \quad \beta' = \frac{\eta\zeta}{m}, \quad \eta = \frac{a}{2\pi}\sqrt{\frac{m}{2kT}},$$

the fractional Fokker-Planck equations (3) and (4) for the distribution function $W(x,\dot{x},t)$ may be written as

$$\frac{\partial W}{\partial t} = (\tau/\eta)^{1-\alpha}\,{}_{-\infty}D_t^{1-\alpha}\left[-\dot{x}\frac{\partial W}{\partial x} + \frac{1}{2}\frac{dV}{dx}\frac{\partial W}{\partial \dot{x}} + \beta'\frac{\partial}{\partial \dot{x}}\left(\dot{x}W + \frac{1}{2}\frac{\partial W}{\partial \dot{x}}\right)\right], \tag{21}$$

and

$$\frac{\partial W}{\partial t} = -\dot{x}\frac{\partial W}{\partial x} + \frac{1}{2}\frac{dV}{dx}\frac{\partial W}{\partial \dot{x}} + (\tau/\eta)^{1-\alpha}\,{}_{-\infty}D_t^{1-\alpha} \times \beta'\frac{\partial}{\partial \dot{x}}\left(\dot{x}W + \frac{1}{2}\frac{\partial W}{\partial \dot{x}}\right), \tag{22}$$

where $\tau = 2\beta'\eta$. The distribution function $W(x,\dot{x},t)$ for both equations can then be expanded in a generalized Fourier series as

$$W(x,\dot{x},t) = \frac{1}{2\pi^{3/2}}e^{-\dot{x}^2}\sum_{n=0}^{\infty}\sum_{q=-\infty}^{\infty}\frac{1}{2^n n!}c_{n,q}(t)H_n(\dot{x})e^{iqx}, \tag{23}$$

where $H_n(z)$ are the Hermite polynomials [28] and

$$c_{n,p}(t) = \langle e^{-ipx}H_n(\dot{x})\rangle(t) = \int_{-\pi}^{\pi}\int_{-\infty}^{\infty} e^{-ipx}H_n(\dot{x}) \times W(x,\dot{x},t)dx\,d\dot{x}, \tag{24}$$

due to the orthogonality properties of the H_n and e^{-ipx} while the angular brackets $\langle\rangle(t)$ denote ensemble averaging, viz.,

$$\langle(\cdot)\rangle(t) = \int_{-\pi}^{\pi}\int_{-\infty}^{\infty}(\cdot)W(x,\dot{x},t)dx\,d\dot{x}. \tag{25}$$

In particular, because $H_1(\dot{x}) = 2\dot{x}$ [28],

$$c_{1,0}(t)/2 = \langle\dot{x}\rangle(t). \tag{26}$$

yields the average velocity.

Just as the noninertial case, in order to evaluate the linear response to a small alternating force $b\Delta e^{i\omega t}$, we may seek a solution of the fractional Fokker-Planck Eqs. (21) and (22) as

$$W(x,\dot{x},t) = W_0(x,\dot{x}) + W_1(x,\dot{x},\omega)\Delta e^{i\omega t}, \tag{27}$$

where

$$W_0(x,\dot{x}) = Z^{-1}\exp(-\dot{x}^2 + b\cos x) \tag{28}$$

is the (equilibrium) Boltzmann distribution in the *absence* of the ac force (Z is the partition function) so that the Fourier coefficients $c_{n,p}(t)$ from Eq. (24) become

$$c_{n,p}(t) = c^0_{n,p} + c_{n,p}(\omega)\Delta e^{i\omega t}, \tag{29}$$

with

$$c^0_{n,p} = \int_{-\pi}^{\pi}\int_{-\infty}^{\infty} e^{-ipx}H_n(\dot{x})W_0(x,\dot{x})dx\,d\dot{x} = \delta_{n0}\frac{I_p(b)}{I_0(b)} \tag{30}$$

(δ_{nm} is Kronecker's delta) and

$$c_{n,p}(\omega) = \int_{-\pi}^{\pi}\int_{-\infty}^{\infty} e^{-ipx}H_n(\dot{x})W_1(x,\dot{x},\omega)dx\,d\dot{x}. \tag{31}$$

On noting that the potential $V(x) = -b\cos x$ is augmented by a small ac term $-xb\Delta e^{i\omega t}$ and substituting Eqs. (23) and (27)–(31) into Eqs. (21) and (22), we have after some algebra the recurrence equations for $c_{n,q}(\omega)$, viz.,

$$\left[\frac{(i\omega\tau)^\alpha}{2\beta'} + n\beta'\right]c_{n,q}(\omega) + \frac{iq}{2}[c_{n+1,q}(\omega) + 2nc_{n-1,q}(\omega)] + \frac{inb}{2}[c_{n-1,q+1}(\omega) - c_{n-1,q-1}(\omega)] = bn(i\omega\tau)^{1-\alpha}c^0_{n-1,q}, \tag{32}$$

and

$$\left[\frac{i\omega\tau}{2\beta'} + n\beta'(i\omega\tau)^{1-\alpha}\right]c_{n,q}(\omega) + \frac{iq}{2}[c_{n+1,q}(\omega)+2nc_{n-1,q}(\omega)] + \frac{inb}{2}[c_{n-1,q+1}(\omega) - c_{n-1,q-1}(\omega)] = bnc^0_{n-1,q}, \tag{33}$$

for the Metzler-Klafter and Barkai-Silbey models, respectively. Here we have used the relations [28],

$$\frac{d}{dx}H_n(x) = 2nH_{n-1}(x) \quad \text{and}$$
$$H_{n+1}(x) = 2xH_n(x) - 2nH_{n-1}(x).$$

Equations (32) and (33) can be solved for $c_{n,q}(\omega)$ using matrix continued fractions as described in Appendix B. Having calculated $c_{1,0}(\omega)$, we can evaluate the mean drift velocity $\langle \dot{x} \rangle(t) = \beta' c_{1,0}(\omega)\Delta e^{i\omega t}$ and velocity ACF spectrum $\tilde{C}_v(\omega) = \int_0^\infty \langle \dot{x}(0)\dot{x}(t)\rangle_0 e^{i\omega t} dt$ via

$$\tilde{C}_v(\omega) = (\beta'/b)c_{1,0}(\omega). \tag{34}$$

We remark that the ACF $\langle \dot{x}(0)\dot{x}(t)\rangle_0$ is now defined as

$$\langle \dot{x}(0)\dot{x}(t)\rangle_0 = \int_{-\pi}^{\pi}\int_{-\pi}^{\pi}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \dot{x}_0 \dot{x} W(x,\dot{x},t\,|x_0,\dot{x}_0,0) \times W_0(x_0,\dot{x}_0)dx\,dx_0\,d\dot{x}\,d\dot{x}_0, \tag{35}$$

where $x_0 = x(0)$, $\dot{x}_0 = \dot{x}(0)$, $W(x,\dot{x},t|x_0,\dot{x}_0,0)$ is the Green function of Eq. (21) or (22) satisfying the initial condition,

$$W(x,\dot{x},0\,|x_0,\dot{x}_0,0) = \delta(x - x_0)\delta(\dot{x} - \dot{x}_0).$$

To compare the above results with the overdamped (noninertial) case ($\beta' \gg 1$) given above by Eq. (20), we note that in order to describe subdiffusion in configuration space using the Barkai-Silbey model, one must write the fractional exponent as $\sigma = 2 - \alpha$ [14]. Thus in calculations, we will take $\sigma = 2 - \alpha$ and $\sigma = \alpha$ for the Barkai-Silbey and Metzler-Klafter models, respectively [14], yielding $\mathrm{Re}[\tilde{C}_v(\omega)]$ and $\mathrm{Im}[\tilde{C}_v(\omega)]$ vs ω for various values of the barrier height b, friction coefficient β', and fractional exponent σ as shown in Figs. 2–5. Apparently for $\beta' \geqslant 1$, the low-frequency part of the ACF spectrum may be approximated by the noninertial Eq. (20) (see Figs. 4 and 5). For very small friction $\beta' \ll 1$ (large inertial effects), a sharp resonance peak appears at high frequencies (see Figs. 2–4). This high-frequency resonance band is due to the fast inertial oscillations of the particles in the potential wells and appears in the vicinity of the fundamental frequency of the almost free periodic motion of the particle in the

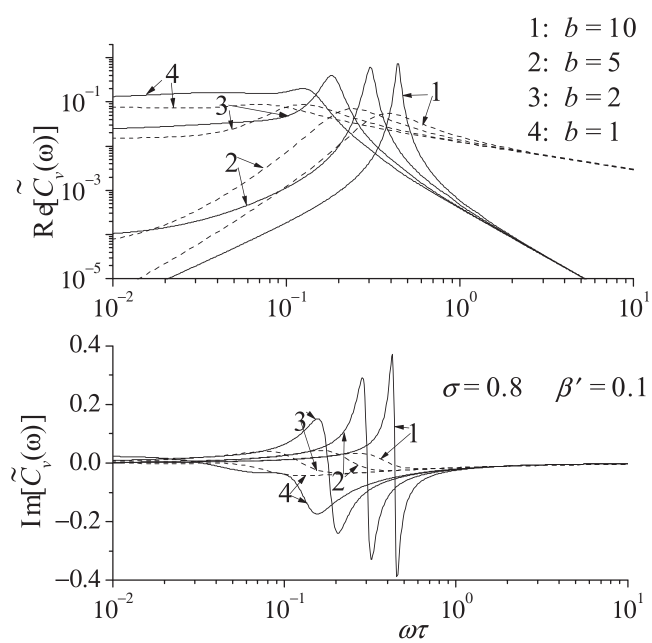

FIG. 2. $\mathrm{Re}[\tilde{C}_v(\omega)]$ and $\mathrm{Im}[\tilde{C}_v(\omega)]$ vs $\omega\eta$ for $\beta' = 0.1$, $\sigma = 0.8$, and various barrier heights b for the Barkai-Silbey (solid lines) and Metzler-Klafter (dashed lines) models.

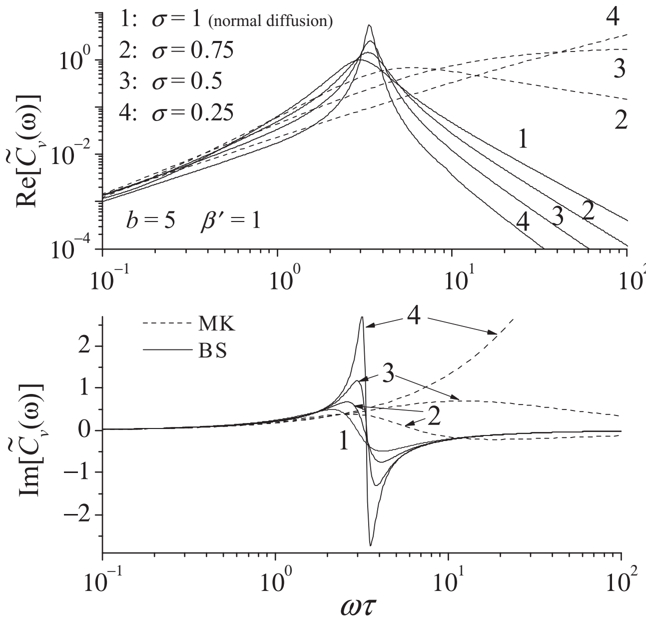

FIG. 3. $\mathrm{Re}[\tilde{C}_v(\omega)]$ and $\mathrm{Im}[\tilde{C}_v(\omega)]$ vs $\omega\tau$ for $\beta' = 1$, $b = 5$, and various σ for the Barkai-Silbey (solid lines) and Metzler-Klafter (dashed lines) models.

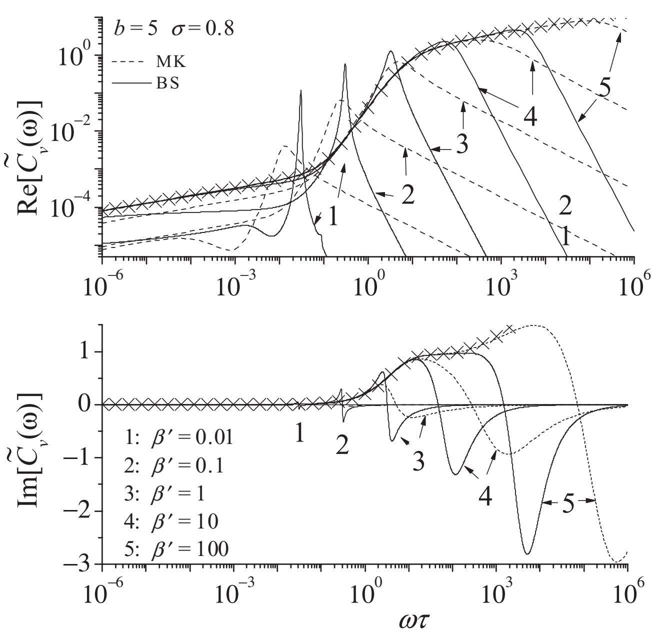

FIG. 4. $\mathrm{Re}[\tilde{C}_v(\omega)]$ and $\mathrm{Im}[\tilde{C}_v(\omega)]$ vs $\omega\eta$ for $b = 5$, $\sigma = 0.8$, and various damping β' for the Barkai-Silbey (solid lines) and Metzler-Klafter (dashed lines) models. (Symbols) The effective eigenvalue Eq. (42) which is a good approximation for the low-frequency behavior for $\beta' \geqslant 1$.

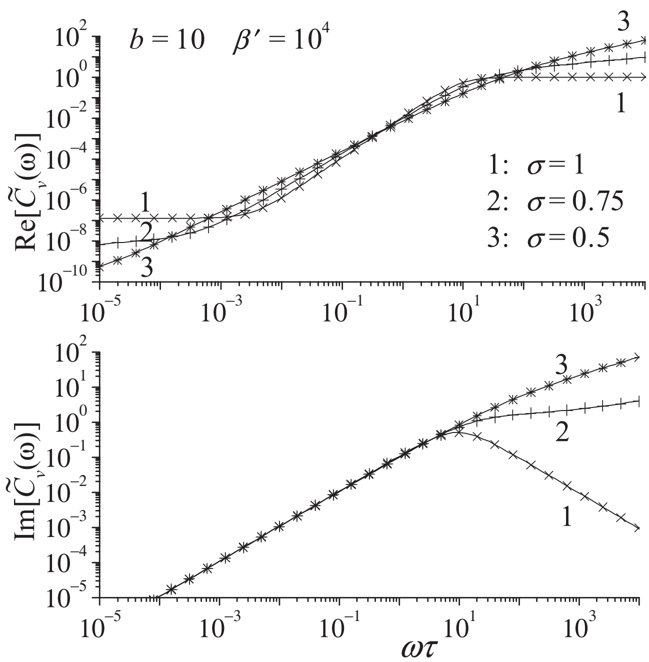

FIG. 5. Comparison of the matrix continued fraction solution Eq. (B2) and the approximate Eq. (42) (symbols) in the high damping limit and low frequencies for the Barkai-Silbey and Metzler-Klafter FKKEs (for high damping, both models yield results coinciding to graphical accuracy).

(anharmonic) potential $V(x) = -b\cos x$. For $b \gg 1$, $\beta' \ll 1$, and $\alpha = 1$, the characteristic frequency of the high-frequency oscillations ω_L can be estimated from the analytic solution [1] for the velocity correlation function $\langle \dot{x}(0)\dot{x}(t)\rangle_0$ for vanishing damping, $\beta' \to 0$, as $\omega_L \sim \sqrt{b/2}\eta^{-1}$ [1]. Furthermore, as in normal Brownian dynamics, inertial effects cause a rapid falloff of $\mathrm{Re}[\tilde{C}_v(\omega)]$ at high frequencies. However, for the Barkai-Silbey model, this falloff is far more rapid than that for the Metzler-Klafter model. Moreover, at small σ, say $\sigma = 0.25$, for the Metzler-Klafter model, $\mathrm{Re}[\tilde{C}_v(\omega)]$ *increases* with increasing ω. This leads to the (unphysical) *divergence* of the spectral moment $\int_0^\infty \mathrm{Re}[\tilde{C}_v(\omega)]\,d\omega$ of the velocity ACF just as noninertial diffusion (both normal and anomalous). For the Barkai-Silbey model, this moment is finite ($= \pi/2$ in our normalized variables) and coincides with that for the normal diffusion. The root of this problem appears to be that in the Metzler-Klafter model, the convective derivative or Liouville term in the Klein-Kramers Eq. (3), is operated upon by the fractional derivative as previously noted. As far as the behavior of the high-frequency band as a function of the damping parameter β' is concerned, the half-width of its resonance band increases progressively with increasing β', as one would intuitively expect.

IV. MEAN-SQUARE DISPLACEMENT

The mean-square displacement defined as

$$\langle x^2(t)\rangle_0 = \int_{-\pi}^{\pi}\int_{-\pi}^{\pi}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} x^2 W(x,\dot{x},t\,|x_0,\dot{x}_0,0) \times W_0(x_0,\dot{x}_0)\,dx\,dx_0\,d\dot{x}\,d\dot{x}_0, \tag{36}$$

can also be calculated via the Einstein-Kubo relation [10,13],

$$\langle x^2(t)\rangle_0 = 2\int_0^t\int_0^{t'} \langle \dot{x}(0)\dot{x}(u-t')\rangle_0\,du\,dt' = 2\int_0^t (t-u)\langle \dot{x}(0)\dot{x}(u)\rangle_0 du, \tag{37}$$

which is in the frequency domain,

$$\widetilde{\langle x^2\rangle}(\omega) = 2(i\omega)^{-2}\tilde{C}_v(\omega). \tag{38}$$

Equation (21) first derived for the normal diffusion processes is also valid for anomalous diffusion. This is demonstrated in Ref. [13] for the Barkai and Silbey model. Here we have noted that $\langle x(t)\rangle_0 = 0$.

In the inertial case, the calculations of $\langle x^2(t)\rangle_0$ can be accomplished numerically by determining the inverse Fourier-Laplace transform of Eq. (38). In the noninertial limit, $\langle x^2(t)\rangle_0$ can be calculated analytically. Noting that the one-sided Fourier transform of the Mittag–Leffler function $E_\sigma[-a(t/\tau)^\sigma]$ is

$$\frac{1}{i\omega + a\tau^{-\sigma}(i\omega)^{1-\sigma}},$$

we then have from Eqs. (20) and (38),

$$\langle x^2(t)\rangle_0 = 2[I_0(b)]^{-2}(t/\tau)^\sigma + 2\frac{1-[I_0(b)]^{-2}}{\lambda_{ef}}\{1 - E_\sigma[-\lambda_{ef}(t/\tau)^\sigma]\}. \tag{39}$$

From the properties of $E_\sigma(z)$, which has long-time inverse power-law behavior $E_\sigma(-t^\sigma) \sim t^{-\sigma}/\Gamma(1-\sigma)$ at long times, we have for $t/\tau \gg 1$,

$$\langle x^2(t)\rangle_0 \approx 2[I_0(b)]^{-2}(t/\tau)^\sigma, \tag{40}$$

allowing us to define, following [26], the diffusion coefficient K_σ for anomalous diffusion in a cosine periodic potential as

$$K_\sigma = \Gamma(\sigma+1)\lim_{t\to\infty}\frac{\langle(\Delta x)^2\rangle}{2(t/\tau)^\sigma} = \frac{\Gamma(\sigma+1)}{[I_0(b)]^2}, \tag{41}$$

where $\Gamma(z)$ is the gamma function [28]. For $\sigma = 1$, Eq. (41) yields

$$K_1 = [I_0(b)]^{-2}, \tag{42}$$

which is the known result for the diffusion coefficient $K_1 = \tilde{C}_v(0) = \int_0^\infty \langle \dot{x}(0)\dot{x}(t)\rangle_0 dt$ for normal diffusion, viz., ([1], p. 289). We remark that in the opposite very low damping limit, $\beta' \ll 1$, K_1 can be estimated via ([1], p. 312)

$$K_1 \approx \frac{e^{-b}}{I_0(b)}\left[\frac{0.855\sqrt{\beta'}}{\sqrt[4]{b}} + e^{2b}\sqrt{\frac{\pi b}{2}}\int_0^1 \frac{e^{-2b/x}dx}{x^{3/2}\mathbf{E}(x)}\right], \tag{43}$$

where $\mathbf{E}(x)$ is the complete elliptic integral of the second kind.

V. CONCLUSIONS

The models just outlined concern both low- and high-frequency relaxation processes for anomalous diffusion in a periodic potential and, *inter alia*, constitute a didactic example of exact continued fraction solutions of fractional diffusion equations for both noninertial and inertial anomalous translational diffusion in periodic potentials. The results for inertial anomalous diffusion are obtained from two *distinct* fractional forms of the Klein-Kramers equations (3) and (4), for the evolution of the single-particle distribution function in phase space. In Eq. (4), the fractional derivative acts only on the diffusion or nonconservative term so that the form of the Liouville operator, or convective derivative representing Hamilton's equations for the single particle is preserved. Thus Eq. (4) has the conventional form of a Boltzmann equation for the single-particle distribution function. The preservation of the Liouville term in Eq. (4) means that the high-frequency behavior is entirely controlled by the inertia of the system and so is largely governed by the Newtonian dynamics in a well yielding a physically acceptable result for the dynamic susceptibility. On the other hand for high damping, inertial effects may be ignored (at low frequencies) so that the *anomalous* relaxation in a periodic potential is just as the normal relaxation, accurately determined by the effective-eigenvalue approximation Eq. (20). In this approximation the characteristic time of the *normal* diffusion process, namely, the inverse of the effective eigenvalue appears as an overall time parameter. Our results may therefore be regarded as a generalization of the solutions for the normal Brownian motion in a periodic potential to fractional dynamics (giving rise to anomalous diffusion) so that one can explain in quantitative fashion the anomalous relaxation of systems, where the anomalous exponent σ differs from unity (i.e., the relaxation process is characterized by a broad distribution of relaxation times). Our methods may also be applied to related problems such as anomalous diffusion in tilted periodic and ratchet potentials. Finally, we have confined ourselves to the periodic (phase locked) solutions only. However, the methods can be also generalized to calculate nonperiodic (or running) solutions so as to treat fractional diffusion of the particle as it wanders from well to well of the potential [1].

APPENDIX A: EFFECTIVE EIGENVALUE FOR NORMAL DIFFUSION

To evaluate the effective eigenvalue for normal diffusion in a cosine periodic potential, we suppose that the potential $V(x) = -b\cos x$ is augmented at the instant $t = 0$ by a small term $-xb\Delta$. Following the exposition of Ref. [30] (see also [10], Chap. 5), we may write the coefficients $c_n(t)$ in Eq. (7) as

$$c_n(t) = c_n^{\Delta}(t) + c_n^{\infty}; \tag{A1}$$

the superscript "Δ" denotes the portion of the statistical average which is linear in Δ, and the superscript "∞" denotes the statistical average in the stationary state,

$$c_n^{\infty} = \int_0^{2\pi} e^{-inx} f_{\infty}(x)dx;$$

evaluated using the stationary distribution function $f(x,t \to \infty) = f_{\infty}(x)$ [1,10],

$$f_{\infty}(x) = C^{-1}e^{-V(x)}\left[1 - (1 - e^{-2\pi b\Delta}) \times \int_0^x e^{V(x')}dx' \Big/ \int_0^{2\pi} e^{V(x')}dx'\right], \tag{A2}$$

with $C = \int_0^{2\pi} f_{\infty}(x)dx$ and $V(x) = -b(\Delta + \cos x)$. As $t \to \infty$, we have $\lim_{t\to\infty} c_n^{\Delta}(t) = 0$. Substituting Eq. (A1) into Eq. (6) (with $\sigma = 1$), we obtain an algebraic recurrence equation for c_n^{∞}:

$$(n + ib\Delta)c_n^{\infty} + b\big(c_{n+1}^{\infty} - c_{n-1}^{\infty}\big)/2 = 0, \tag{A3}$$

and a differential-recurrence relation for $c_n^{\Delta}(t)$:

$$\frac{d}{dt}c_n^{\Delta}(t) + n^2 c_n^{\Delta}(t) = \frac{bn}{2}\big[c_{n-1}^{\Delta}(t) - c_{n+1}^{\Delta}(t)\big] - inb\Delta c_n^{\Delta}(t). \tag{A4}$$

Using the effective eigenvalue, we now replace the exact Eq. (A4) for $n = 1$ by the approximate equation,

$$\frac{d}{dt}c_1^{\Delta}(t) + \lambda_{ef} c_1^{\Delta}(t) = 0, \tag{A5}$$

where λ_{ef} is the effective eigenvalue. The approximation Eq. (A5) implies that in the linear transient responses, the relaxation function $c_1^{\Delta}(t)$ comprising a superposition of an infinite number of exponentials $c_1^{\Delta}(t) = \sum_p c_p e^{-\lambda_p t}$ may be approximated by a single exponential $c_1^{\Delta}(t) \approx c_1^{\Delta}(0)e^{-\lambda_{ef} t}$ only [10]. Equations (A5) and (A4) for $n = 1$ yield at $t = 0$,

$$\lambda_{ef} = -\frac{\dot{c}_1^{\Delta}(0)}{c_1^{\Delta}(0)} = 1 + \frac{b}{2}\frac{c_2^{\Delta}(0)}{c_1^{\Delta}(0)}. \tag{A6}$$

Because $c_n^{\Delta}(0) = c_n^0 - c_n^{\infty}$, Eq. (A6) further simplifies to

$$\lambda_{ef} = 1 + \frac{b}{2}\left(\frac{c_2^0 - c_2^{\infty}}{c_1^0 - c_1^{\infty}}\right). \tag{A7}$$

The averages c_1^{∞} and c_2^{∞} in Eq. (A7) are taken over the stationary distribution $P_{\infty}(x)$ [Eq. (A2)]. However, since we are interested only in the linear response to Δ, we can express c_n^{∞} as

$$c_n^{\infty} \approx c_n^0 + \Delta(\partial_{\Delta} c_n^{\infty}|_{\Delta=0}). \tag{A8}$$

The quantities $\partial_{\Delta} c_2^{\infty}|_{\Delta=0} = \partial_{\Delta} c_2^0$ and $\partial_{\Delta} c_1^{\infty}|_{\Delta=0} = \partial_{\Delta} c_1^0$ may be evaluated as follows. Substituting Eq. (A8) into Eq. (A3), we have in the linear approximation in Δ,

$$c_{n+1}^0 - c_{n-1}^0 + 2nc_n^0/b = 0, \tag{A9}$$

$$\partial_{\Delta} c_{n+1}^0 - \partial_{\Delta} c_{n-1}^0 + 2n\partial_{\Delta} c_n^0/b = -2ic_n^0. \tag{A10}$$

The solution of Eq. (A9) is given by Eq. (12) while the solution of Eq. (A10) is given by

$$\partial_{\Delta} c_1^0 = -\frac{2i}{I_0^2(b)}\sum_{n=1}^{\infty}(-1)^{n+1}I_n^2(b). \tag{A11}$$

Now $\partial_\Delta c_2^0$ can be obtained from the recurrence Eq. (A10) for $n = 1$, namely,

$$\partial_\Delta c_2^0 = -i2c_1^0 - 2\partial_\Delta c_1^0/b. \tag{A12}$$

Substituting Eqs. (A10), (A11), and (A12) into Eq. (A7) yields

$$\lambda_{ef} = -\frac{ibc_1^0}{\partial_\Delta c_1^0} = \frac{bI_0(b)I_1(b)}{2\sum_{n=0}^{\infty}(-1)^n I_{n+1}^2(b)}.$$

Because ([10], Chap. 5)

$$2\sum_{n=0}^{\infty}(-1)^n I_{n+1}^2(z) = I_0^2(z) - 1\,,$$

we then obtain Eq. (19).

APPENDIX B: MATRIX CONTINUED FRACTION SOLUTION OF EQ. (33)

Equations (32) and (33) can be written in matrix form in the single variable n as

$$\mathbf{Q}_n^-\mathbf{C}_{n-1} + \mathbf{Q}_n\mathbf{C}_n + \mathbf{Q}_n^+\mathbf{C}_{n+1} = -\delta_{n2}\mathbf{R}_2, \tag{B1}$$

where

$$\mathbf{C}_n = \begin{pmatrix} \vdots \\ c_{n-1,-1}(\omega) \\ c_{n-1,0}(\omega) \\ c_{n-1,1}(\omega) \\ \vdots \end{pmatrix},$$

$$\mathbf{Q}_n^+ = \frac{i}{2}\begin{pmatrix} \ddots & \ddots & \ddots & & \\ \ddots & -1 & 0 & \ddots & \\ \ddots & 0 & 0 & 0 & \ddots \\ & \ddots & 0 & 1 & \ddots \\ & & \ddots & \ddots & \ddots \end{pmatrix},$$

$$\mathbf{Q}_n^- = i(n-1)\begin{pmatrix} \ddots & \ddots & \ddots & \ddots & \\ \ddots & -1 & b/2 & 0 & \ddots \\ \ddots & -b/2 & 0 & b/2 & \ddots \\ \ddots & 0 & -b/2 & 1 & \ddots \\ & \ddots & \ddots & \ddots & \ddots \end{pmatrix},$$

and

$$\mathbf{R}_2 = -b\begin{pmatrix} \vdots \\ c_{0,-1}^0 \\ c_{0,0}^0 \\ c_{0,1}^0 \\ \vdots \end{pmatrix}, \quad \mathbf{Q}_n = \left[\frac{i\omega\tau}{2\beta\prime} + (n-1)\beta\prime(i\omega\tau)^{1-\alpha}\right]\mathbf{I},$$

for the Barkai-Silbey model and

$$\mathbf{R}_2 = -b(i\omega\tau)^{1-\alpha}\begin{pmatrix} \vdots \\ c_{0,-1}^0 \\ c_{0,0}^0 \\ c_{0,1}^0 \\ \vdots \end{pmatrix},$$

$$\mathbf{Q}_n = \left[\frac{1}{2\beta'}(i\omega\tau)^\alpha + (n-1)\beta'\right]\mathbf{I},$$

for the Metzler-Klafter model. Here $c_{0,q}^0 = I_q(b)/I_0(b)$ and $\mathbf{I}$ is the identity matrix.

We can then solve Eq. (33) by using matrix continued fractions,

$$\mathbf{C}_2 = \begin{pmatrix} \vdots \\ c_{1,-1}(\omega) \\ c_{1,0}(\omega) \\ c_{1,1}(\omega) \\ \vdots \end{pmatrix} = \left(\boldsymbol{\Delta}_2\mathbf{Q}_2^-\boldsymbol{\Delta}_1\mathbf{Q}_1^+ + \mathbf{I}\right)\boldsymbol{\Delta}_2\mathbf{R}_2, \tag{B2}$$

where $\boldsymbol{\Delta}_n$ is the infinite matrix continued fraction defined by the recurrence equation,

$$\boldsymbol{\Delta}_n = [-\mathbf{Q}_n - \mathbf{Q}_n^+\boldsymbol{\Delta}_{n+1}\mathbf{Q}_{n+1}^-]^{-1}.$$

If all the other Fourier coefficients are required $c_{n,q}(\omega)$ ($n = 2,3,..$), e.g., for the calculation of $W(x,\dot{x},t)$ from Eq. (23), they can also be calculated in terms of the matrix continued fractions $\boldsymbol{\Delta}_n$ as described in detail in Refs. [1,10].

For very low damping and at low temperatures ($\beta' < 0.01,\ b \geqslant 10^2,\ b/\beta' \geqslant 10^3$), however, the method is difficult to apply because the matrices involved become ill conditioned so that numerical inversions are no longer possible.

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