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Fractional translational diffusion of a Brownian particle in a double well potential

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The fractional translational diffusion of a particle in a double-well potential (excluding inertial effects) is considered. The position correlation function and its spectrum are evaluated using a fractional probability density diffusion equation (based on the diffusion limit of a fractal time random walk). Exact and approximate solutions for the dynamic susceptibility describing the position response to a small external field are obtained. The exact solution is given by matrix continued fractions while the approximate solution relies on the exponential separation of the time scales of the fast "intrawell" and low overbarrier relaxation processes associated with the bistable potential. It is shown that knowledge of the characteristic relaxation times for *normal* diffusion allows one to predict accurately the *anomalous* relaxation behavior of the system for all relevant time scales.

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I. INTRODUCTION

Relaxation and diffusion processes in complex disordered systems such as amorphous polymers, glass forming liquids, etc., exhibit temporal nonlocal behavior arising from energetic disorder causing obstacles or traps both slowing down the motion of the particle and introducing memory effects. The memory effects can be described by a fractional diffusion equation incorporating a waiting time probability density function [1,2] governing the random time intervals between single microscopic jumps of the particles. The fractional diffusion equation stems from the integral equation for a continuous time random walk (CTRW) [3,4]. The situation is thus unlike that in a conventional random walk which is characterized by a microscopic time scale small compared to the observation time. The microscopic time in the conventional random walk is the time the random walker takes to make a single microscopic jump. In this context one should recall that the Einstein theory of the *normal* Brownian motion relies on the diffusion limit of a *discrete* time random walk. Here the random walker makes a jump of a *fixed mean square length* in a *fixed time* thus the only random variable is the direction of the walker, leading automatically via the central limit theorem (in the limit of a large sequence of jumps) to the Wiener process describing the Brownian motion. The CTRW, on the other hand, was introduced by Montroll and Weiss [4] as a way of rendering time continuous in a random walk without necessarily appealing to the diffusion limit. In the most general case of the CTRW, the random walker may jump an arbitrary length in arbitrary time. However, the jump length and jump time random variables are not statistically independent [1,5,6]. In other words a given jump length is penalized by a time cost, and vice versa. A simple case of the CTRW arises when one assumes that the jump length and jump time random variables are decoupled. Thus the jump length variances are always finite; however, the jump times may be arbitrarily long so that they obey a Lévy distribution with its characteristic long tail [5,6]. Thus the jump length distribution ultimately becomes Gaussian with finite jump length variance, while the mean waiting time between jumps diverges due to the underlying Lévy waiting time distribution. Such walks, which possess a discrete hierarchy of time scales, not all of which have the same probability of occurrence, are known as *fractal time random walks* [5]. In the limit of a large sequence of jump times, they yield a fractional Fokker-Planck equation in configuration space [5,7].

Now the relevant fractional diffusion (Fokker-Planck) equation for the distribution function $W(x,t)$ of the one-dimensional noninertial translational motion of a particle in a potential $V(x,t)$ may be written as [1,2]

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

Here x specifies the position of the particle at time t, $-\infty < x < \infty$, kT is the thermal energy, and $K_\sigma = \zeta_\sigma / kT$ is a generalized diffusion coefficient, and ζ_σ is a generalized viscous drag coefficient arising from the heat bath. The operator ${}_0D_t^{1-\sigma} \equiv \frac{\partial}{\partial t}\,{}_0D_t^{-\sigma}$ in Eq. (1) is given by the convolution (the Riemann-Liouville fractional integral definition) [1]

$${}_0D_t^{-\sigma}W(x,t) = \frac{1}{\Gamma(\sigma)}\int_0^t \frac{W(x,t')dt'}{(t-t')^{1-\sigma}}, \tag{2}$$

where $\Gamma(z)$ is the γ function [8]. The physical meaning of the parameter σ is the order of the fractional derivative in the ractional differential equation describing the continuum limit of a random walk with a chaotic set of waiting times (often known as a fractal time random walk). Values of σ in the range $0<\sigma<1$ correspond to subdiffusion phenomena ($\sigma=1$ corresponds to normal diffusion). However, a more physically useful definition of σ is as the fractal dimension of the set of waiting times. The fractal dimension is the scaling of the waiting time segments in the random walk with magnification of the walk. Thus, σ measures the statistical self-similarity (or how the whole resembles its individual constituent parts [5]) of the waiting time segments. In order to construct such an entity in practice a whole discrete hierarchy of time scales such as will arise from energetic disorder is needed. For example a fractal time Poisson process [5] with a waiting time distribution assumes the typical form of a Lévy stable distribution in the limit of large τ. This is explicitly discussed in Ref. [5] where a formula for σ is given and is also discussed in Ref. [9]. The fractal time process is essentially generated by the energetic disorder treated as far as the ensuing temporal behavior is concerned by considering jumps over the wells of a chaotic potential barrier landscape.

The fractional diffusion equation (1) can in principle be solved by the same methods as the normal Fokker-Planck equation. However, to the best of our knowledge no explicit solutions for the fractional translational diffusion in a potential have ever been presented. The only exception appears to be a solution for the harmonic potential given by Metzler *et al.* [10] in terms of an eigenfunction expansion with Mittag-Leffler temporal behavior. This approach has recently been extended to the analogous fractional rotational diffusion models in a periodic potential by Coffey *et al.* [11–13]. There, the authors have developed effective methods of solution of fractional diffusion equations based on ordinary and matrix continued fractions (as is well known the continued fractions are an extremely powerful tool in the solution of normal diffusion equations [7,14]). Here we further generalize the methods of Coffey *et al.* [11–13] for fractional translational diffusion problems. As a particular example, we shall present both exact and approximate solutions for the anomalous diffusion of a particle in a double-well potential, viz.

$$V(x)=\frac{1}{2}ax^2+\frac{1}{4}bx^4, \tag{3}$$

where a and b are constants. The model of normal diffusion in the 2–4 potential Eq. (3) is almost invariably used to describe the noise driven motion in bistable physical and chemical systems. Examples are such diverse subjects as simple isometrization processes [15–19], chemical reaction rate theory [20–28], bistable nonlinear oscillators [29–31], second order phase transitions [32], nuclear fission and fusion [33,34], stochastic resonance [35,36], etc.

The *normal* diffusion in the 2–4 potential in the very high damping limit, where the inertia of the particle may be neglected, has been extensively studied either by using the Kramers escape rate theory or by solution of the appropriate Fokker-Planck (Smoluchowski) equation (see, e.g., Refs. [7,22,25,36–38], and references cited therein). In the VHD limit, the conventional analysis of the problem proceeds from the Smoluchowski equation by either rendering that equation as a Sturm-Liouville problem (e.g., Refs. [25,39]) or by the solution of an infinite hierarchy of linear differential-recurrence relations for statistical moments (e.g., Refs. [40,41]). The same methods may be used if the inertial effects are included (see e.g., Refs. [42,43]). The fractional diffusion equation (1) can in principle be treated in a like manner. The subdiffusion in the double-well potential Eq. (3) has been considered in Refs. [44,45] in terms of an eigenfunction expansion with Mittag-Leffler temporal behavior. In Refs. [44,45], the authors mainly studied the effect of boundary conditions on the transition probability density. In contrast, the purpose of the present paper is to ascertain how the anomalous diffusion in a bistable potential, $b>0$ and $a<0$, modifies the behavior of the position correlation function $C_\sigma(t)=\langle x(0)x(t)\rangle_0/\langle x^2(0)\rangle_0$ and its spectra (which characterize the anomalous relaxation). We shall give exact and approximate solutions for these quantities. Furthermore, we shall demonstrate that the characteristic times of the normal diffusion process, namely, the inverse of the smallest nonvanishing eigenvalue of the Fokker-Planck operator, the integral and effective relaxation times, obtained in Ref. [7], also allow us to describe the anomalous relaxation behavior.

II. BASIC EQUATIONS

By using dimensionless variables and parameters as defined in [7,38], viz.

$$V(y)=\frac{V(x)}{kT}=Ay^2+By^4,\quad y=\frac{x}{\langle x^2\rangle_0^{1/2}},\quad A=\frac{a\langle x^2\rangle_0}{2kT},$$

$$B=\frac{b\langle x^2\rangle_0^2}{4kT},$$

the fractional Fokker-Planck equation becomes

$$\frac{\partial W(y,t)}{\partial t}=\tau^{-\sigma}\,{}_0D_t^{1-\sigma}\frac{\partial}{\partial y}\left[\frac{\partial}{\partial y}W(y,t)+W(y,t)\frac{\partial}{\partial y}V(y,t)\right], \tag{4}$$

where $\tau=\langle x^2\rangle_0/K_1$ has the meaning of the characteristic intertrapping time (waiting time between jumps), K_1 is the diffusion coefficient for normal diffusion, and the angular brackets $\langle(\cdot)\rangle_0=Z^{-1}\int_{-\infty}^{\infty}(\cdot)e^{-V(y)}dy$ mean equilibrium ensemble averages. Here Z is the partition function given by for $A<0$ (which is the case of greatest interest) [7]

$$Z=\int_{-\infty}^{\infty}e^{-V(y)}dy=\sqrt{\pi}(2B)^{-1/4}e^{Q/2}D_{-1/2}(-\sqrt{2Q}), \tag{5}$$

where $D_v(z)$ are Whitaker's parabolic cylinder functions of order v [8] and $Q=A^2/4B$ is the barrier height for the potential $V(y)=Ay^2+By^4$ (see Fig. 1). The normalization condition $\langle y^2\rangle_0=1$ implies that the constants A and B are now not independent [7]

$$B=B(Q)=\frac{1}{8}\frac{D_{-3/2}^2[\mathrm{sgn}(A)\sqrt{2Q}]}{D_{-1/2}^2[\mathrm{sgn}(A)\sqrt{2Q}]}. \tag{6}$$

For $A<0$ and large barriers ($Q\gg1$), $B\sim Q$ while for small Q

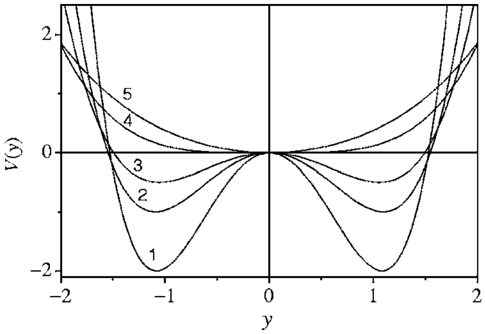

FIG. 1. Potential $V(y)=Ay^2+By^4$ for various values of $A/(2B^{1/2})=-\sqrt{2}$ (curve 1), −1 (2), $-1/\sqrt{2}$ (3), 0 (4), and 1 (5).

$$B=\frac{\Gamma^2(3/4)}{\Gamma^2(1/4)}+\frac{\Gamma(3/4)[\Gamma^2(1/4)+\Gamma(-1/4)\Gamma(3/4)]}{\Gamma^3(1/4)}\sqrt{Q}+\cdots$$
$$\approx 0.1142+0.1835\sqrt{Q}+\cdots$$

One may seek a formal solution of Eq. (4) for $t\geqslant 0$ as [42,43]

$$W(y,t)=\frac{\kappa}{\sqrt{\pi}}e^{-[\kappa^2y^2+V(y)]/2}\sum_{q=1}^{\infty}\frac{c_q(t)H_q(\kappa y)}{\sqrt{2^q q!}}, \tag{7}$$

where κ is a scaling factor chosen so as to ensure optimum convergence of the continued fractions involved as suggested by Voigtlaender and Risken [42] (all results for the observables are independent of κ). By substituting Eq. (7) into Eq. (1) and noting that [8]

$$dH_n(z)/dz=2nH_{n-1}(z) \text{ and } H_{n+1}(z)=2zH_n(z)-2nH_{n-1}(z), \tag{8}$$

we have a seven-term fractional differential recurrence relation for $c_q(t)$, viz.

$$\frac{d}{dt}c_q(t)=\tau^{-\sigma}{}_0D_t^{1-\sigma}[g_q^+c_{q+6}(t)+f_q^+c_{q+4}(t)+e_q^+c_{q+2}(t)+d_qc_q(t)$$
$$+e_q^-c_{q-2}(t)+f_q^-c_{q-4}(t)+g_q^-c_{q-6}(t)], \tag{9}$$

where

$$d_n=-\frac{\sqrt{B}}{2\alpha^6}[4\sqrt{Q}\alpha^6+(\alpha^4+4Q-6)(2n+1)\alpha^4-12\sqrt{Q}\alpha^2(2n^2$$
$$+2n+1)+5(2n+1)(2n^2+2n+3)],$$

$$e_n^+=e_{n+2}^-=\frac{\sqrt{B}}{2\alpha^6}\{\sqrt{(n+1)(n+2)}[(\alpha^4-4Q+6)\alpha^4$$
$$+8\sqrt{Q}\alpha^2(2n+3)-15(n^2+3n+3)]\},$$

$$f_n^+=f_{n+2}^-=-\frac{\sqrt{B}}{2\alpha^6}\sqrt{(n+1)(n+2)(n+3)(n+4)}$$
$$\times[-4\sqrt{Q}\alpha^2+3(2n+5)],$$

$$g_n^+=g_{n+2}^-=-\frac{\sqrt{B}}{2\alpha^6}\sqrt{(n+1)(n+2)(n+3)(n+4)(n+5)(n+6)},$$

and $\alpha=\kappa/B^{1/4}$.

Equation (9) can be solved exactly using matrix continued fractions as in the Appendix. Having determined $c_{2q-1}(t)$, one can calculate the position correlation function

$$C_\sigma(t)=\frac{\alpha ZB^{1/4}}{\sqrt{\pi}}\sum_{q=1}^{\infty}c_{2q-1}(0)c_{2q-1}(t), \tag{10}$$

its spectrum $\tilde{C}_\sigma(\omega)=\int_0^\infty C_\sigma(t)e^{-i\omega t}dt$, and the dynamic susceptibility $\chi(\omega)=\chi'(\omega)-i\chi''(\omega)$ defined as [7]

$$\chi(\omega)=-\int_0^\infty e^{-i\omega t}\frac{d}{dt}C_\sigma(t)dt=1-i\omega\tilde{C}_\sigma(\omega) \tag{11}$$

(see Appendix). We remark that the dynamic susceptibility $\chi(\omega)$ characterizes the ac response of the system to a small perturbation. A knowledge of $\chi(\omega)$ allows one, in particular, to evaluate the signal-to-noise ratio (SNR) of the stochastic resonance at small signal amplitudes, see, e.g., Ref. [36].

In order to understand the anomalous relaxation behavior of $\tilde{C}_\sigma(\omega)$, we first recall that the position correlation function $C_\sigma(t)$ can be formally presented as [10,11]

$$C_\sigma(t)=\sum_p c_pE_\sigma[-\tau\lambda_p(t/\tau)^\sigma], \tag{12}$$

where $E_\sigma(z)$ is the Mittag-Leffler function defined as [1]

$$E_\sigma(z)=\sum_{n=0}^{\infty}\frac{z^n}{\Gamma(1+n\sigma)},$$

λ_p $(\lambda_1<\lambda_2<\lambda_3<\cdots)$ are the eigenvalues of the Fokker-Planck operator for *normal diffusion*, and $\Sigma_pc_p=1$. Equation (12) exemplifies how the eigenvalues of the normal distribution process are altered, in this case reduced, by the nonlocal character of the anomalous diffusion process and how the Mittag-Leffler behavior replaces the exponential relaxation patterns of normal Brownian motion in a potential [for normal diffusion, Eq. (12) takes the familiar form $C_1(t)=\Sigma_pc_p\exp(-\lambda_pt)$]. The eigenvalues of the local process λ_p are related to their Brownian counterparts by the prefactor $\tau^{1-\sigma}$. This scaling effect is significant in the context of escape of particles over potential barriers. There, the smallest nonvanishing eigenvalue λ_1 of the Fokker-Planck equation, written for the Brownian motion in a potential, yields in the high barrier limit, the Kramers escape rate $\Gamma\sim\lambda_1\sim e^{-\Delta V/(kT)}$ (ΔV is the barrier height) [46]. Therefore, in the context of anomalous diffusion, the Kramers escape rate Γ can be best understood as playing the role of a decay parameter in the Mittag-Leffler functions governing the highly *nonexponential* relaxation behavior of the system.

Noting that the Laplace transform of the Mittag-Leffler function is [1]

$$\int_0^\infty e^{-st} E_\sigma[-\lambda_p \tau (t/\tau)^\sigma] dt = \frac{1}{s + \lambda_p (\tau s)^{1-\sigma}},$$

Eqs. (11) and (12) and yield

$$\chi(\omega) = \sum_p \frac{c_p}{1 + (i\omega\tau)^\sigma / (\tau\lambda_p)}. \tag{13}$$

In the low- $\omega \to 0$) and high- ($\omega \to \infty$) frequency limits, the behavior of the susceptibility may now be readily evaluated. We have from Eq. (11) for $\omega \to 0$ and for $\omega \to \infty$, respectively

$$\chi(\omega) \approx 1 - \frac{\tau_{int}}{\tau}(i\omega\tau)^\sigma + \cdots, \tag{14}$$

$$\chi(\omega) \sim \frac{\tau}{(i\omega\tau)^\sigma \tau_{ef}} + \cdots, \tag{15}$$

where the parameters τ_{int} and τ_{ef} are given by

$$\tau_{int} = \sum_p c_p/\lambda_p \text{ and } \tau_{ef} = 1/\sum_p c_p \lambda_p. \tag{16}$$

For *normal diffusion*, these parameters correspond to the correlation (or integral relaxation) time $\tau_{int} = \int_0^\infty C_1(t)dt$ [the area under the correlation function $C_1(t) = \Sigma_p c_p e^{-\lambda_p t}$] and the effective relaxation time $\tau_{ef} = -1/\dot{C}_1(0)$ [which gives precise information on the initial decay of $C_1(t)$]. We remark that no such characteristic times exist in anomalous diffusion ($\sigma < 1$). This is obvious from the long time inverse power law behavior of the Mittag-Leffler function. In anomalous diffusion, the times λ_1^{-1}, τ_{int}, and τ_{ef} are always parameters of the normal diffusion. They exist because in normal diffusion an underlying microscopic time scale exists, namely the duration of an elementary jump, characteristic of the discrete time random walk as used by Einstein.

III. TWO MODE APPROXIMATION FOR $C_\sigma(t)$

As we shall see, two bands appear in the spectrum of $\chi''(\omega)$. The low-frequency band is due to the slowest (overbarrier) relaxation mode; the characteristic frequency ω_c and the half width of this band are determined by the smallest nonvanishing eigenvalue λ_1. Thus, the anomalous low frequency behavior is dominated by the barrier crossing mode as in the normal diffusion. The high-frequency band is due to "intrawell" modes corresponding to the eigenvalues λ_k ($k \neq 1$). These near degenerate intrawell modes are indistinguishable in the frequency spectrum of $\chi''(\omega)$ appearing merely as a single high-frequency band. As shown by Kalmykov *et al.* [11], the susceptibility $\chi(\omega)$ can be effectively described via a two mode approximation, viz.

$$\chi(\omega) = \frac{\Delta_1}{1 + (i\omega/\omega_c)^\sigma} + \frac{1 - \Delta_1}{1 + (i\omega/\omega_W)^\sigma}, \tag{17}$$

where the characteristic frequencies ω_c and ω_W are given by

$$\omega_c = \tau^{-1}(\tau\lambda_1)^{1/\sigma}, \quad \omega_W = \tau^{-1}(\tau/\tau_W)^{1/\sigma}. \tag{18}$$

The parameters Δ_1 and τ_W are defined in terms of the characteristic times of the normal diffusion (the integral relaxation time τ_{int}, the effective relaxation time τ_{ef}, and the inverse of the smallest nonvanishing eigenvalue $1/\lambda_1$) [7,11]

$$\Delta_1 = \frac{\tau_{int}/\tau_{ef} - 1}{\lambda_1 \tau_{int} - 2 + 1/(\lambda_1 \tau_{ef})}, \quad \tau_W = \frac{\lambda_1 \tau_{int} - 1}{\lambda_1 - 1/\tau_{ef}}. \tag{19}$$

In the time domain, such a bimodal approximation is equivalent to assuming that the correlation function $C_\sigma(t)$ yielded by the exact Eq. (12) (which in general comprises an *infinite number* of Mittag-Leffler functions) may be approximated by *two* Mittag-Leffler functions only, viz.

$$C_\sigma(t) \approx \Delta_1 E_\sigma[-(t/\tau)^\sigma \tau\lambda_1] + (1 - \Delta_1) E_\sigma[-(t/\tau)^\sigma \tau/\tau_W]. \tag{20}$$

The characteristic times $1/\lambda_1$, τ_{int}, and τ_{ef} for the *normal* Brownian motion in a double-well potential Eq. (3) have been obtained in Refs. [38,41] (see also [7], Chapter 6). Here we simply use known equations for λ_1, τ_{int}, and τ_{ef} for *normal* diffusion in order to predict the anomalous relaxation behavior. The τ_{int} and τ_{ef} for *normal* diffusion may be expressed in exact closed form, viz. ([7], Chapter 6)

$$\tau_{ef} = \tau, \tag{21}$$

$$\tau_{int} = \tau \frac{\sqrt{\pi} e^{Q/2} D_{-1/2}(-\sqrt{2Q})}{2^{3/4} D_{-3/2}^2(-\sqrt{2Q})} \int_0^\infty e^{(s-\sqrt{Q})^2} [1 - \mathrm{erf}(s - \sqrt{Q})]^2 \frac{ds}{\sqrt{s}}, \tag{22}$$

where $\mathrm{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-z^2} dz$ is the error function [8]. The smallest nonvanishing eigenvalue λ_1 can be estimated in terms of matrix continued fractions from Eq. (34) of the Appendix. Moreover, for all values of Q, λ_1 can be evaluated with very high accuracy from the approximate equation [7]

$$\lambda_1 = \frac{D_{-3/2}(-\sqrt{2Q})}{\tau D_{-1/2}(-\sqrt{2Q})} \left[\frac{e^Q}{1 + \mathrm{erf}(\sqrt{Q})} \int_0^\infty \int_0^\infty e^{-(s-\sqrt{Q})^2 - (t-\sqrt{Q})^2} \times \frac{\mathrm{erf}(\sqrt{2st})}{\sqrt{st}} ds dt \right]^{-1}. \tag{23}$$

In the low temperature limit, $Q \gg 1$, λ_1^{-1} and τ_{int} have the simple asymptotic behavior [7,25]

$$1/\lambda_1 \sim \frac{\tau\pi e^Q}{4\sqrt{2Q}} \left(1 + \frac{5}{8Q} + \cdots\right), \tag{24}$$

$$\tau_{int} \sim \frac{\tau\pi e^Q}{4\sqrt{2Q}} \left(1 + \frac{1}{2Q} + \cdots\right).$$

Equations (17)–(24) allow one readily to estimate the qualitative behavior of the susceptibility $\chi(\omega)$ and its characteristic frequencies ω_c and ω_W. In particular, Eqs. (18)–(21) and (24) yield simple asymptotic equations for the amplitude Δ_1 and characteristic frequencies ω_c and ω_W in the low temperature limit ($Q \gg 1$), viz.

$$\Delta_1 \sim 1 - 1/(8Q), \quad \omega_c \sim (4\sqrt{2Q}/\pi)^{1/\sigma} e^{-Q/\sigma}/\tau, \quad \text{and } \omega_W \sim (8Q)^{1/\sigma}/\tau. \tag{25}$$

Equations (17), (18), (20), and (25) allows one to readily

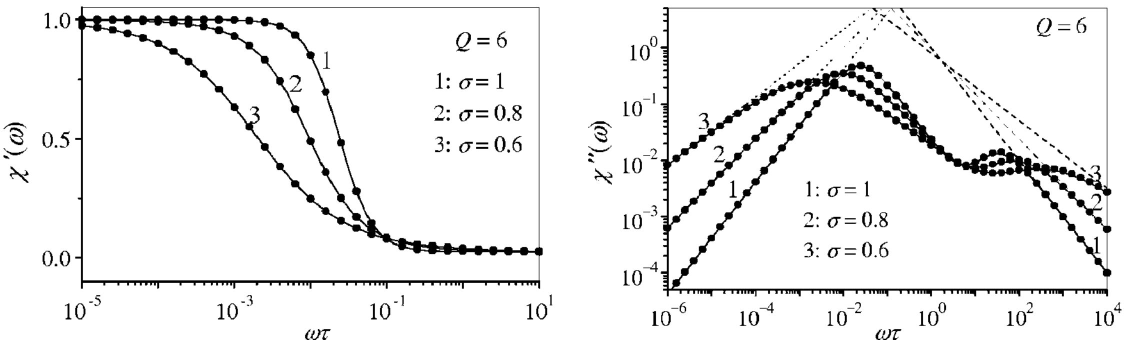

FIG. 2. The real χ' and imaginary χ'' parts of the dynamic susceptibility vs. $\omega\tau$ for the barrier height $Q=6$ and various values of the fractional exponent $\sigma=1$ (normal diffusion), 0.8, and 0.6. Solid lines are the matrix continued fraction solution. Filled circles: the bimodal approximation, Eq. (17). Dashed and dotted lines: the low and high frequency asymptotes, Eqs. (14) and (15).

evaluate $\chi(\omega)$ and $C_\sigma(t)$ at high barriers, $Q \gg 1$.

IV. RESULTS AND DISCUSSION

Calculations of the susceptibility $\chi(\omega)$ from the exact matrix continued fraction solution, Eqs. (27) and (28), and the approximate Eqs. (17) and (18) and are shown in Figs. 2 and 3. Here, the low- and high-frequency asymptotes, Eqs. (14) and (15), are also shown for comparison. The two bands arising in the spectrum of $\chi''(\omega)$ reach a maximum at characteristic frequencies ω_c and ω_W given by Eq. (18). Apparently, the agreement between the exact continued fraction calculations and the approximate Eq. (17) is very good (the maximum relative deviation between the corresponding curves appearing at $\omega \sim \tau^{-1}$, does not exceed a few percent). Similar (or even better) agreement exists for *all* values of Q and σ. Such a high degree of accuracy of the bimodal approximation arises because the infinite number of high-frequency intrawell modes (these individual near degenerate modes are indistinguishable appearing merely as a single high-frequency band in the spectrum) may be approximated effectively by a single mode. Thus, one may conclude that Eq. (17) accurately describes the behavior of $\chi(\omega)$ for all frequencies of interest and for all values of the barrier height (Q) and anomalous exponent (σ) parameters. We remark that the bimodal approximation works extremely well both for anomalous ($\sigma \neq 1$) and normal ($\sigma=1$) cases (various applications for the normal diffusion in a potential are given in Ref. [7]).

Thus the *anomalous* relaxation in a double-well potential is like the normal relaxation again effectively determined by the bimodal approximation, Eqs. (17) and (20); the characteristic times of the *normal* diffusion process, namely, the inverse of the smallest nonvanishing eigenvalue, the integral and effective relaxation times appearing as time parameters. The bimodal approximation constitutes an example of the solution of the noninertial fractional translational diffusion equation in a double-well potential. The simple asymptotic Eqs. (18)–(24) allows one to easily evaluate the characteristic frequencies of the spectrum in terms of the physical model parameters Q and σ. The results obtained may be regarded as a generalization of the solution for the normal Brownian motion in a double well potential to fractional dynamics (giving rise to anomalous diffusion). Furthermore, one may conjecture that this generalized model can explain the anomalous relaxation of complex systems where the anomalous exponent σ differs from unity, i.e., the relaxation process is characterized by a broad distribution of relaxation times.

We must remark however that the fractional diffusion theory can be used only at low frequencies ($\omega\tau \leqslant 1$) just as its normal diffusion counterpart as inertial effects are completely ignored in that theory. For normal diffusion, these effects can be included via the inertial Fokker-Planck (Klein-Kramers) equation [7,14]. One may also include inertial effects in fractional relaxation processes. This is accomplished by utilizing a fractional version of the Klein-Kramers equation for diffusion in phase space [47,48].

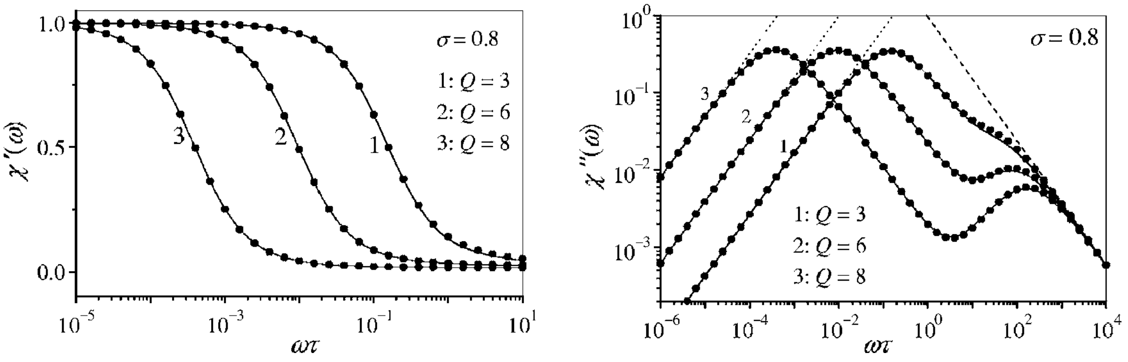

FIG. 3. χ' and χ'' vs. $\omega\tau$ for $\sigma=0.8$ and various values of $Q=3$, 6, and 8. Key as in Fig. 2.

Finally in view of previous work [49,50] in the theory of anomalous translational diffusion we briefly allude to additional mechanisms yielding anomalous diffusion in a potential. Examples are time rescaled Brownian motion or generalized Langevin equations with nonwhite Gaussian noise [49,50] so that the memory function is no longer a δ function. Moreover the concept of a generalized Langevin equation with friction term given by the Riemann-Liouville definition of the fractional derivative has been used by Lutz [51] to analyze translational anomalous diffusion.

ACKNOWLEDGMENTS

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APPENDIX: MATRIX CONTINUED FRACTION SOLUTION

Equation (9) can be rearranged as the set of matrix *three-term* recurrence equations

$$\tau\frac{d}{dt}\mathbf{C}_n(t) = \tau^{1-\sigma}{}_0D_t^{1-\sigma}[\mathbf{Q}_n^-\mathbf{C}_{n-1}(t) + \mathbf{Q}_n\mathbf{C}_n(t) + \mathbf{Q}_n^+\mathbf{C}_{n+1}(t)], \quad (n \geqslant 1), \qquad (26)$$

where the column vectors $\mathbf{C}_n(t)$ and the matrices $\mathbf{Q}_n$, $\mathbf{Q}_n^+$, $\mathbf{Q}_n^-$ are

$$\mathbf{C}_n(t) = \begin{pmatrix} c_{6n-5}(t) \\ c_{6n-3}(t) \\ c_{6n-1}(t) \end{pmatrix},$$

$$\mathbf{Q}_n = \begin{pmatrix} d_{6n-5}^+ & e_{6n-5}^+ & f_{6n-5}^+ \\ e_{6n-5}^+ & d_{6n-3}^+ & e_{6n-3}^+ \\ f_{6n-5}^+ & e_{6n-3}^+ & d_{6n-1}^+ \end{pmatrix},$$

$$\mathbf{Q}_n^+ = \begin{pmatrix} g_{6n-5}^+ & 0 & 0 \\ f_{6n-3}^+ & g_{6n-3}^+ & 0 \\ e_{6n-1}^+ & f_{6n-1}^+ & g_{6n-1}^+ \end{pmatrix},$$

$$\mathbf{Q}_n^- = (\mathbf{Q}_{n-1}^+)^T$$

(the sign "T" designates transposition). Now by one-sided Fourier transformation, Eq. (26) can be rearranged as the set of matrix *three-term* recurrence equations

$$(i\tau\omega)^\sigma\tilde{\mathbf{C}}_n(\omega) - \tau(i\tau\omega)^{\sigma-1}\mathbf{C}_n(0) = \mathbf{Q}_n\tilde{\mathbf{C}}_n(\omega) + \mathbf{Q}_n^+\tilde{\mathbf{C}}_{n+1}(\omega) + \mathbf{Q}_n^-\tilde{\mathbf{C}}_{n-1}(\omega), \qquad (27)$$

where $\tilde{\mathbf{C}}_n(\omega)=\int_0^\infty\mathbf{C}_n(t)e^{-i\omega t}dt$. By invoking the general method [7,14] for solving the tridiagonal matrix recurrence Eq. (26) and noting that $\tilde{\mathbf{C}}_0(\omega)=\mathbf{0}$, we have the exact solution for $\tilde{\mathbf{C}}_1(\omega)$ in terms of matrix continued fractions, viz.

$$\tilde{\mathbf{C}}_1(\omega) = \tau(i\tau\omega)^{\sigma-1}\mathbf{\Delta}_1(i\omega)\left\{\mathbf{C}_1(0) + \sum_{n=2}^{\infty}\left[\prod_{k=2}^{n}\mathbf{Q}_{k-1}^+\mathbf{\Delta}_k(i\omega)\right]\mathbf{C}_n(0)\right\}, \qquad (28)$$

where $\mathbf{\Delta}_n(\omega)$ are the matrix continued fractions defined by the recurrence equation

$$\mathbf{\Delta}_n(\omega) = [(i\tau\omega)^\sigma\mathbf{I} - \mathbf{Q}_n - \mathbf{Q}_n^+\mathbf{\Delta}_{n+1}(\omega)\mathbf{Q}_{n+1}^-]^{-1}. \qquad (29)$$

All other $\tilde{\mathbf{C}}_n(\omega)$ can be calculated from the recurrence Eq. (27). The spectrum of the equilibrium correlation position function $C_\sigma(t)$ is then given by

$$\tilde{C}_\sigma(\omega) = \frac{\alpha ZB^{1/4}}{\sqrt{\pi}}\sum_{n=1}^{\infty}\mathbf{C}_n^T(0)\tilde{\mathbf{C}}_n(\omega) = \frac{\alpha ZB^{1/4}}{\sqrt{\pi}}\sum_{q=1}^{\infty}c_{2q-1}(0)\tilde{c}_{2q-1}(\omega), \qquad (30)$$

where the sign T (transpose) designates transformation of a column vector $\mathbf{C}_n(0)$ to a row vector. Equation (30) follows from the definition of the correlation function $C_\sigma(t)$ [42], viz.

$$C_\sigma(t) = \langle y(0)y(t)\rangle_0 = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}yy_0W(y,t|y_0,0)W_0(y_0)dydy_0, \qquad (31)$$

where $y_0=y(0)$, $W_0(y_0)=e^{-Ay_0^2-By_0^4}/Z$ is equilibrium (Boltzmann) distribution function, and $W(y,t|y_0,0)$ is the transition probability, which satisfies Eq. [1] with the initial condition $W(y,0|y_0,0)=\delta(y-y_0)$ and is defined as

$$W(y,t|y_0,0) = \frac{\kappa}{\sqrt{\pi}}e^{-\kappa^2(y^2+y_0^2)/2-[V(y)-V(y_0)]/2} \times\sum_{q,p=1}^{\infty}\frac{[\mathbf{G}(t)]_{q,p}H_q(\kappa y)H_p(\kappa y_0)}{\sqrt{2^{q+p}q!p!}}.$$

Here

$$[\mathbf{G}(t)]_{q,p} = \frac{\kappa}{\sqrt{\pi 2^{q+p}q!p!}}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}H_q(\kappa y)H_p(\kappa y_0) \times e^{-\kappa^2(y^2+y_0^2)/2+[V(y)-V(y_0)]/2}W(y,t|y_0,0)dydy_0$$

are the matrix elements of the system matrix $\mathbf{G}(t)$. The coefficients $c_q(t)$ are given in terms of elements of the system matrix $\mathbf{G}$ as

$$c_q(t) = \sum_{p=1}^{\infty}[\mathbf{G}(t)]_{q,p}c_p(0) \qquad (32)$$

with the initial conditions

$$c_p(0) = \frac{1}{Z\sqrt{2^p p!B}}\int_{-\infty}^{\infty}xH_p(\alpha x)e^{-(\alpha^2x^2-2\sqrt{Q}x^2+x^4)/2}dx. \qquad (33)$$

Noting Eq. (30), the correlation time $\tau_{int}=\widetilde{C}_1(0)$ and the effective relaxation time $\tau_{ef}=-1/\dot{C}_1(0)$ for normal diffusion, $\sigma=1$, can be calculated in terms of matrix continued fractions as

$$\tau_{int}=\frac{\alpha ZB^{1/4}}{\sqrt{\pi}}\sum_{n=1}^{\infty}\mathbf{C}_n^T(0)\widetilde{\mathbf{C}}_n(0),$$

$$\tau_{ef}=-\left[\frac{\alpha ZB^{1/4}}{\sqrt{\pi}}\sum_{n=1}^{\infty}\mathbf{C}_n^T(0)\dot{\mathbf{C}}_n(0)\right]^{-1};$$

the smallest nonvanishing eigenvalue λ_1 can be evaluated from the secular equation [7,14]

$$\det[\lambda_1\tau\mathbf{I}+\mathbf{Q}_1+\mathbf{Q}_1^{+}\mathbf{\Delta}_2(-\lambda_1)\mathbf{Q}_2^{-}]=0. \qquad (34)$$

[1] R. Metzler and J. Klafter, Phys. Rep. **339**, 1 (2000).
[2] R. Metzler and J. Klafter, Adv. Chem. Phys. **116**, 223 (2001).
[3] E. W. Montroll and M. F. Shlesinger, *On the Wonderful World of Random Walks*, edited by J. L. Lebowitz and E. W. Montroll, in *Non Equilibrium Phenomena II from Stochastics to Hydrodynamics* (Elsevier Science Publishers, BV, Amsterdam, 1984).
[4] E. W. Montroll and G. H. Weiss, J. Math. Phys. **6**, 167 (1965).
[5] W. Paul and J. Baschnagel, *Stochastic Processes from Physics to Finance* (Springer Verlag, Berlin, 1999).
[6] B. J. West, M. Bologna, and P. Grigolini, *Physics of Fractal Operators* (Springer, New York, 2003).
[7] W. T. Coffey, Yu. P. Kalmykov, and J. T. Waldron, *The Langevin Equation*, 2nd edition (World Scientific, Singapore, 2004).
[8] *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. Stegun (Dover, New York, 1964).
[9] V. V. Novikov and V. P. Privalko, Phys. Rev. E **64**, 031504 (2001); V. V. Novikov, K. W. Wojciechowski, and V. P. Privalko, J. Phys.: Condens. Matter **12**, 4869 (2000).
[10] R. Metzler, E. Barkai, and J. Klafter, Phys. Rev. Lett. **82**, 3563 (1999).
[11] Yu.P. Kalmykov, W. T. Coffey, and S. V. Titov, Phys. Rev. E **69**, 021105 (2004).
[12] W. T. Coffey, Yu. P. Kalmykov, S. V. Titov, and J. K. Vij, Phys. Rev. E **72**, 011103 (2005).
[13] W. T. Coffey, Yu. P. Kalmykov, and S. V. Titov, Adv. Chem. Phys. **133**, 285 (2006).
[14] H. Risken, *The Fokker-Planck Equation*, 2nd edition (Springer, Berlin, 1989).
[15] D. Chandler, J. Chem. Phys. **68**, 2959 (1978).
[16] B. J. Berne, J. L. Skinner, and P. G. Wolynes, J. Chem. Phys. **73**, 4314 (1980).
[17] D. L. Hasha, T. Eguchi, and J. Jonas, J. Am. Chem. Soc. **73**, 1571 (1981); *ibid.* **104**, 2290 (1982).
[18] D. K. Garrity and J. L. Skinner, Chem. Phys. Lett. **95**, 46 (1983).
[19] B. Carmeli and A. Nitzan, J. Chem. Phys. **80**, 3596 (1984).
[20] H. A. Kramers, Physica (Amsterdam) **7**, 284 (1940).
[21] H.C. Brinkman, Physica (Amsterdam) **22**, 29 (1956); *ibid.* **22**, 149 (1956).
[22] C. Blomberg, Physica A **86**, 49 (1977); *ibid.* **86**, 67 (1977).
[23] P. B. Visscher, Phys. Rev. B **14**, 347 (1976).
[24] J. L. Skinner and P. G. Wolynes, Chem. Phys. **69**, 2143 (1978); J. Chem. Phys. **72**, 4913 (1980).
[25] R. S. Larson and M. D. Kostin, J. Chem. Phys. **69**, 4821 (1978); , *ibid.* **72**, 1392 (1980).
[26] S. C. Northrup and J. T. Hynes, Chem. Phys. **69**, 5246 (1978); J. Chem. Phys. **69**, 5261 (1978); *ibid.* **73**, 2700 (1980); R. F. Grote and J. T. Hynes, *ibid.* **73**, 2715 (1980).
[27] M. Mangel, J. Chem. Phys. **72**, 6606 (1980).
[28] K. Schulten, Z. Schulten, and A. Szabo, J. Chem. Phys. **74**, 4426 (1981).
[29] M. Bixon and R. Zwanzig, J. Stat. Phys. **3**, 245 (1971).
[30] M. I. Dykman, S. M. Soskin, and M. A. Krivoglaz, Physica A **133**, 53 (1985).
[31] P. Hänggi, Phys. Lett. **78A**, 304 (1980).
[32] J. A. Krumhansl and J. R. Schriefier, Phys. Rev. B **11**, 3535 (1975).
[33] J. D. Bao and Y. Z. Zhuo, Phys. Rev. C **67**, 064606 (2003).
[34] V. M. Kolomietz, S. V. Radionov, and S. Shlomo, Phys. Rev. C **64**, 054302 (2001).
[35] M. I. Dykman, G. P. Golubev, D. G. Luchinsky, P. V. E. McClintock, N. D. Stein, and N. G. Stocks, Phys. Rev. E **49**, 1935 (1994).
[36] L. Gammaitoni, P. Hänggi, P. Jung, and F. Marchesoni, Rev. Mod. Phys. **70**, 223 (1998).
[37] W. T. Coffey, M. W. Evans, and P. Grigolini, *Molecular Diffusion and Spectra* (Wiley, New York, 1984).
[38] A. Perico, R. Pratolongo, K. F. Freed, R. W. Pastor, and A. Szabo, J. Chem. Phys. **98**, 564 (1993).
[39] A. Schenzle and H. Brand, Phys. Rev. A **20**, 1628 (1979).
[40] I. I. Fedchenia, J. Phys. A **25**, 6733 (1992).
[41] Yu. P. Kalmykov, W. T. Coffey, and J. T. Waldron, J. Chem. Phys. **105**, 2112 (1996).
[42] K. Voigtlaender and H. Risken, J. Stat. Phys. **40**, 397 (1985); Chem. Phys. Lett. **105**, 506 (1984).
[43] Yu. P. Kalmykov, W. T. Coffey, and S. V. Titov, J. Chem. Phys. **124**, 024107 (2006).
[44] F. So and K. L. Liu, Physica A **331**, 378 (2004).
[45] C. W. Chow and K. L. Liu, Physica A **341**, 8 (2004).
[46] P. Hänggi, P. Talkner, and M. Borcovec, Rev. Mod. Phys. **62**, 251 (1990).
[47] E. Barkai and R. S. Silbey, J. Phys. Chem. B **104**, 3866 (2000).
[48] R. Metzler and J. Klafter, J. Phys. Chem. B **104**, 3851 (2000).
[49] K. G. Wang and C. W. Lung, Phys. Lett. A **151**, 119 (1990).
[50] K. G. Wang, Phys. Rev. A **45**, 833 (1992).
[51] E. Lutz, Phys. Rev. E **64**, 051106 (2001).