Generalized moment expansion for Brownian relaxation processes

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The generalized moment expansion has previously only been used to provide an effective algorithm for the approximation of the time dependence of observables connected with reactive Brownian processes. We extend this algorithm to describe the relaxation of observables in nonreactive processes. The wide applicability of the method is demonstrated for various examples: equilibrium correlation functions like autocorrelation functions and dynamic structure factors, particle number correlation functions monitoring diffusive redistribution, and barrier crossing problems.

I. INTRODUCTION

Processes in the condensed phase are often governed by Brownian motion and can be described by Fokker–Planck equations or their discrete analog, master equations. Examples are the transport of biomolecules in cell compartments and membranes,[1] the motion of atoms and side groups in proteins,[2] and the stochastic motion along the reaction coordinates of chemical and biochemical reactions.[3-5] These processes can be monitored through the measurement of certain observables. Of particular interest is most often the long-time behavior of these observables. Models for stochastic processes admit analytical solutions only for very simple cases and long-time integration of the evolution equations governing stochastic transport, e.g., Fokker–Planck and master equations, is time consuming and susceptible to numerical errors. Therefore, a simple and effective approximation procedure for the description of the time dependence of observables is needed, especially one that reproduces the long-time behavior correctly. For the case of one-dimensional reactive processes involving Brownian motion an approximation based on the generalized moment expansion of observables,[6-8] an extension of the first passage time approximation,[9-15] meets these requirements. In the remainder of this paper we will refer to this algorithm as the "generalized moment approximation" (GMA).

Many processes of interest are nonreactive and asymptotically produce a nonvanishing equilibrium distribution. In these cases the stochastic motion is probed mainly by measurement of equilibrium correlation functions as in light-scattering, Mössbauer, or NMR spectroscopy. For these cases the GMA was, up to now, not applicable since it relies on the evaluation of the inverse of the Fokker–Planck operator or its adjoint; because of the vanishing eigenvalue corresponding to the stationary distribution this inverse does not exist. An exception is Mössbauer spectroscopy,[6,7] where the finite lifetime of the excited nucleus renders the corresponding Fokker–Planck operator nonsingular.

In this article we will remedy that restriction and generalize the GMA to the description of relaxation in nonreactive processes. In Sec. II we will define the stochastic processes and observables that will be considered. Section III gives the GMA for these processes and Sec. IV discusses a simple form of the GMA, the "mean relaxation time" approximation (MRTA). In Sec. V we provide the GMA for processes on a discrete linear lattice. This section should prove useful for numerical applications which most often involve discretization schemes. Finally, in Sec. VI, we illustrate and test the algorithm by considering various observables of diffusive processes. We will consider mainly free diffusion in an interval since for this process exact solutions are available.

II. BROWNIAN PROCESSES AND OBSERVABLES

We will consider one-dimensional nonreactive diffusive processes along a coordinate x in the interval $[a, b]$. A generalization to higher-dimensional processes which, due to a high degree of symmetry, can be described in terms of one-dimensional equations is straightforward. If the underlying Brownian process is in the strong friction limit, the time development of the probability distribution $p(x, t|x_0)$ is described by the Fokker–Planck equation[16,17]

$$\partial_t p(x, t|x_0) = L(x)p(x, t|x_0),$$

$$p(x, t = 0|x_0) = \delta(x - x_0), \tag{2.1}$$

with the Fokker–Planck operator

$$L(x) = \partial_x D(x)\{\partial_x + \beta[\partial_x U(x)]\}, \tag{2.2}$$

where $D(x)$ is the diffusion coefficient, $U(x)$ is the potential governing the deterministic part of the motion, and $\beta = 1/k_B T$. The diffusion coefficient $D(x)$ may be position dependent but must be nonvanishing inside the interval. The operator (2.2) guarantees that the fluctuation-dissipation theorem holds. We may note that, utilizing the thermal distribution $p_0(x) \sim \exp[-\beta U(x)]$, one can cast Eq. (2.2) into the form

$$L(x) = \partial_x D(x)p_0(x)\partial_x[p_0(x)]^{-1}. \tag{2.2'}$$

Equations (2.1) and (2.2) have to be supplemented with reflective boundary conditions

$$\{\partial_x + \beta[\partial_x U(x)]\}p(x, t|x_0)|_{x=a,b} = 0, \qquad (2.3)$$

which guarantee conservation of probability and, thus, the existence of a stationary solution, namely, the Boltzmann distribution $p_0(x)$.

The observables considered are of the type

$$M(t) = \int_a^b dx \int_a^b dx_0 f(x)p(x, t|x_0)g(x_0), \qquad (2.4)$$

where $g(x)$ can be viewed as an initial distribution and $f(x)$ is a test function that monitors the distribution at time t. Equation (2.4) describes a wide variety of observables and we will give various examples in Sec. VI. The observable has the initial value $M(0) = \langle f(x)g_0(x) \rangle$ and relaxes asymptotically to $M(\infty) = \langle f(x) \rangle \langle g_0(x) \rangle$. Here $\langle \ \rangle$ denotes thermal average and we defined

$$g_0(x) = g(x)/p_0(x), \qquad (2.5)$$

where $p_0(x)$ from now on will be the *normalized* Boltzmann distribution. Since the time development of $M(t)$ is solely due to the relaxation process $M(0) \rightarrow M(\infty)$, one needs to consider only

$$\Delta M(t) = M(t) - M(\infty). \qquad (2.6)$$

This function can be cast into a form which is mathematically more convenient. For this purpose we express the Green's function (2.1) by an exponential operator

$$p(x, t|x_0) = \{\exp[L(x)t]\}_b \delta(x - x_0), \qquad (2.7)$$

where $\{ \ \}_b$ denotes that the function space is restricted to functions which obey the appropriate boundary conditions of Eq. (2.3). By means of the projection operator J_0,

$$J_0 h(x) = p_0(x) \int_a^b dx' \, h(x'), \qquad (2.8)$$

one obtains

$$\Delta M(t) = \int_a^b dx \, f(x)\{\exp[L(x)t](1 - J_0)\}_b g(x). \quad (2.9)$$

The property

$$(1 - J_0)\exp[L(x)t](1 - J_0) = \exp[L(x)t](1 - J_0) \qquad (2.10)$$

provides the definition

$$\{\exp[L(x)t]\}_{b\perp} = \{(1 - J_0)\exp[L(x)t](1 - J_0)\}_b, \qquad (2.11)$$

i.e., $\{ \ \}_{b\perp}$ denotes operation in a space further restricted to functions which obey Eq. (2.3) and are orthogonal to $p_0(x)$. One may then write

$$\Delta M(t) = \int_a^b dx \, f(x)\{\exp[L(x)t]\}_{b\perp} g(x). \qquad (2.12)$$

In the following we prefer to express $\Delta M(t)$ by means of the adjoint Fokker–Planck operator $L^+(x)$ (compare Refs. 11 and 17):

$$L^+(x) = [p_0(x)]^{-1} \partial_x D(x)p_0(x)\partial_x. \qquad (2.13)$$

The resulting expression is

$$\Delta M(t) = \int_a^b dx \, g(x)\{\exp[L^+(x)t]\}_{b+\perp} f(x). \qquad (2.14)$$

Here $\{ \ \}_{b+\perp}$ denotes operation in a space of functions which obey the adjoint boundary condition

$$\partial_x h(x)|_{x=a,b} = 0 \qquad (2.15)$$

and are orthogonal to the function $h(x) = 1$. The orthogonality property required here is produced by the action of the projection operator $(1 - J_0^+)$, where

$$J_0^+ h(x) = \int_a^b dx' \, p_0(x')h(x'). \qquad (2.16)$$

III. GENERALIZED MOMENT APPROXIMATION

Starting point of the generalized-moment approximation (GMA) is the Laplace transformation of the observable [Eq. (2.14)]

$$\Delta \tilde{M}(\omega) = \int_a^b dx \, g(x)\{[\omega - L^+(x)]^{-1}\}_{b+\perp} f(x). \quad (3.1)$$

$\Delta \tilde{M}(\omega)$ can be expanded for low and high frequencies

$$\Delta \tilde{M}(\omega) \underset{\omega \rightarrow 0}{\sim} \sum_{n=0}^{\infty} \mu_{-(n+1)}(-\omega)^n, \qquad (3.2a)$$

$$\Delta \tilde{M}(\omega) \underset{\omega \rightarrow \infty}{\sim} (1/\omega) \sum_{n=0}^{\infty} \mu_n(-1/\omega)^n, \qquad (3.2b)$$

where the expansion coefficients μ_n, the "generalized moments," are given by

$$\mu_n = (-1)^n \int_a^b dx \, g(x)\{[L^+(x)]^n\}_{b+\perp} f(x). \qquad (3.3)$$

In view of the expansions (3.2a) and (3.2b) we will refer to μ_n, $n \geq 0$ as the high-frequency moments, and to μ_n, $n < 0$ as the low-frequency moments.

The moment μ_0 is identical to the initial value $\Delta M(0)$ and assumes the simple form

$$\mu_0 = \langle f(x)g_0(x) \rangle - \langle f(x) \rangle \langle g_0(x) \rangle. \qquad (3.4)$$

For positive n, evaluation of Eq. (3.3) is straightforward. The orthogonality property is satisfied since $L^+(x)$ itself projects onto the orthogonal function space. However, the functions must satisfy boundary condition (2.15). This may be done, for example, by extending the interval from $[a, b]$ to $[a - \epsilon, b + \epsilon]$ with $\epsilon > 0$, and setting

$$\{f(x)\}_{b+} = f(x) - f'(a) \int_{a-\epsilon}^x dy \, H(a - y)$$
$$+ f'(b) \int_x^{b+\epsilon} dy \, H(y - b). \qquad (3.5)$$

$H(x)$ is the Heaviside step function with its derivative $H'(x) = \delta(x)$ and one has to employ the usual rules for calculation with δ distributions. The moments are obtained by taking the limit $\epsilon \rightarrow 0$ after evaluation of Eq. (3.3). In particular, for μ_1 one derives the general result

$$\mu_1 = \langle f'(x)D(x)g_0'(x) \rangle. \qquad (3.6)$$

As is clearly seen, in the case of a constant diffusion coefficient the value of the first high-frequency moment for observables with $f'(x)g_0'(x) = $ const is independent of the form of the potential and, therefore, does not imply any information on the force field. This is, for example,

the case for such important observables like the autocorrelation function or the dynamic structure factor (see Sec. VI).

For negative n the moments can be expressed by simple quadratures. For this purpose we define the function ($n > 0$)

$$\mu_{-n}(x) = (-1)^n \{[L^+(x)]^{-n}\}_{b+\perp} f(x). \tag{3.7}$$

Multiplication of this relation by the operator $[L^+(x)]_{b+\perp}$ yields

$$\{L^+(x)\}_{b+\perp} \mu_{-n}(x) = -\mu_{-(n-1)}(x). \tag{3.8}$$

One should note that the solutions of this equation need to satisfy the restrictions imposed by $\{\ \ \}_{b+\perp}$. For $n = 1$ holds, in particular,

$$\{L^+(x)\}_{b+\perp} \mu_{-1}(x) = -[f(x) - \langle f(x) \rangle]. \tag{3.9}$$

One can, therefore, obtain $\mu_{-n}(x)$ by recursive solution of Eqs. (3.9) and (3.8). These equations can be solved, e.g., following Ref. 11, with the result

$$\mu_{-n}(x) = c - \int_a^x dy [D(y)p_0(y)]^{-1}$$
$$\times \int_a^y dz \, p_0(z)\mu_{-(n-1)}(z), \tag{3.10}$$

where c is an integration constant. This solution obeys the correct boundary conditions (2.15). The constant c is chosen to satisfy the orthogonality property, i.e., application of $(1 - J_0^+)$ should leave the function invariant. After change of integration variables and some rearrangement one obtains

$$\mu_{-n}(x) = \int_a^x dy [D(y)p_0(y)]^{-1} \int_y^b dz \, p_0(z)\mu_{-(n-1)}(z)$$
$$\times \int_a^y dz' \, p_0(z') + \int_x^b dy [D(y)p_0(y)]^{-1}$$
$$\times \int_a^y dz \, p_0(z)\mu_{-(n-1)}(z) \int_y^b dz' \, p_0(z'). \tag{3.11}$$

The moment μ_{-n} is then determined by

$$\mu_{-n} = \int_a^b dx \, g(x)\mu_{-n}(x), \tag{3.12}$$

which after change of integration variables and rearrangement gives

$$\mu_{-n} = \int_a^b dx [D(x)p_0(x)]^{-1} \int_a^x dy \, p_0(y)\mu_{-(n-1)}(y)$$
$$\times \int_a^x dz \, p_0(z)[g_0(z) - \langle g_0(z) \rangle]. \tag{3.13}$$

This expresses μ_{-n} in terms of $\mu_{-(n-1)}(x)$. For $n = 1$ holds

$$\mu_{-1} = \int_a^b dx [D(x)p_0(x)]^{-1} \int_a^x dy \, p_0(y)[f(y) - \langle f(y) \rangle]$$
$$\times \int_a^x dz \, p_0(z)[g_0(z) - \langle g_0(z) \rangle]. \tag{3.14}$$

For many observables, especially correlation functions,

$g(x)$ assumes the form $g(x) = cf^*(x)p_0(x)$, with c being a constant. Equation (3.14) can then be written as

$$\mu_{-1} = c \int_a^b dx [D(x)p_0(x)]^{-1}$$
$$\times \left| \int_a^x dy \, p_0(y)[f(y) - \langle f(y) \rangle] \right|^2. \tag{3.15}$$

Equations (3.11)–(3.15) demonstrate that the moments with negative index, which, according to Eq. (3.2a), account for the low-frequency behavior of observables in relaxation processes, can be evaluated by means of simple quadratures. We will show now how the moments μ_n can be employed to approximate the observable $\Delta M(t)$.

We want to approximate $\Delta \tilde{M}(\omega)$ by a Padé approximant $\Delta \tilde{m}(\omega)$. The functional form of $\Delta \tilde{m}(\omega)$ should be such that the corresponding time-dependent function $\Delta \tilde{m}(t)$ is a series of N exponentials describing the relaxation of $\Delta M(t)$ to $\Delta M(\infty) = 0$. This implies that $\Delta \tilde{m}(\omega)$ is an $[N - 1, N]$-Padé approximant which can be written in the form[18]

$$\Delta \tilde{m}(\omega) = \sum_{n=1}^N a_n/(\lambda_n + \omega) \tag{3.16a}$$

or, correspondingly,

$$\Delta m(t) = \sum_{n=1}^N a_n \exp(-\lambda_n t). \tag{3.16b}$$

$\Delta \tilde{m}(\omega)$ should describe the low- and high-frequency behavior of Eq. (3.2) of $\Delta \tilde{M}(\omega)$ to a desired degree. We require that $\Delta \tilde{m}(\omega)$ reproduces N_h high- and N_l low-frequency moments. Since $\Delta \tilde{m}(\omega)$ is determined by an even number of constants a_n and λ_n one needs to choose $N_h + N_l = 2N$. We refer to the resulting description as the (N_h, N_l)-generalized-moment approximation (GMA). This description represents a two-sided Padé approximation.[19,20] The moments determine the parameters a_n and λ_n of Eq. (3.16) through the relations

$$\sum_{n=1}^N a_n \lambda_n^m = \mu_m,$$
$$m = -N_l, -N_l + 1, \ldots, N_h - 1. \tag{3.17}$$

Algebraic solution of Eq. (3.17) is feasible only for $N = 1, 2$. In this paper we will apply the approximation only for $N = 1$ or $N = 2$. The solution of Eq. (3.17) for $N = 2$ is provided in Appendix A. For $N > 2$ the numerical solution of Eq. (3.17) is possible by means of an equivalent eigenvalue problem stated in Refs. 6 and 8.

IV. MEAN RELAXATION TIME APPROXIMATION

The most simple and often satisfactory GMA is the $(1, 1)$ approximation which reproduces the moments μ_0 and μ_{-1}. In this case, the relaxation of $\Delta M(t)$ is approximated by a single exponential

$$\Delta M(t) \simeq \mu_0 \exp(-t/\tau). \tag{4.1}$$

The relaxation time is given by $\tau = \mu_{-1}/\mu_0$. Since

$$\mu_0 = \Delta M(t = 0), \tag{4.2a}$$

$$\mu_{-1} = \Delta M(\omega = 0) = \int_0^\infty dt \, \Delta M(t), \tag{4.2b}$$

the relaxation time τ can be written in the form

$$\tau = \int_0^\infty dt \, \Delta M(t)/\Delta M(0) = \int_0^\infty dt \, t P_r(t). \tag{4.3}$$

In the case of monotonous $\Delta M(t)$ the rate

$$P_r(t) = -\partial_t \, \Delta M(t)/\Delta M(0) \tag{4.4}$$

can be viewed as a "relaxation time distribution" of the diffusion process. We therefore refer to τ as the "mean relaxation time" and to the approximation (4.1) as the "mean relaxation time approximation" (MRTA).

This approximation is completely analogous to the "mean first passage time approximation" in reaction–diffusion processes. In this case τ is the mean time for a first contact with a reactive boundary. Correspondingly the distribution equivalent to Eq. (4.4) is the "first passage time distribution.[10]"

We will demonstrate in Sec. VI that Eq. (4.1) provides a satisfactory approximation for the relaxation of some observables. In most cases τ provides a good estimate for the time constant with which the observables approach their equilibrium values in the long-time limit.

We may note that Lipari and Szabo[21-23] already proposed an algorithm analogous to the MRTA for the description of fluorescence depolarization and NMR relaxation. Weaver[24] and Deutch[13] discussed such a description for a related problem: the particle number in a reactive process with a special reactive boundary condition that admits a nonvanishing stationary distribution.

V. BIRTH–DEATH PROCESSES

In some cases, stochastic transport can be described equally well by Markoff processes in a discrete state space. Such a description also results from most numerical approximation schemes to Eq. (2.1) that involve a discretization of the spatial coordinate x, e.g., in Refs. 8, 25, and 26. In this section we consider, therefore, the relaxation of a system governed by transitions between neighboring states on a linear lattice of dimension N, i.e., a birth–death process. The results of this section should be also useful in numerical applications in case an analytical evaluation of the moments according to Eqs. (3.11)–(3.14) is not possible, e.g., due to a complicated analytical form of $D(x)$ and $U(x)$.

The distribution on the lattice, described by the vector $\mathbf{P}(t)$, satisfies the master equation

$$(d/dt)\mathbf{P}(t) = \mathbf{A}\mathbf{P}(t), \tag{5.1}$$

where $\mathbf{A}$ is a tridiagonal $N \times N$ matrix

$$\mathbf{A} = \begin{pmatrix} -l_2 & m_1 & 0 & \cdots \\ l_2 & -m_1 - l_3 & m_2 & \cdots \\ 0 & l_3 & -m_2 - l_4 & \cdots \\ \vdots & & & \ddots & m_{N-1} \\ & & & l_N & -m_{N-1} \end{pmatrix}. \tag{5.2}$$

The matrix $\mathbf{A}$ satisfies the condition

$$\mathbf{1}^T\mathbf{A} = \mathbf{0}^T,$$

$$\mathbf{A}\mathbf{P}_0 = \mathbf{0}, \tag{5.3}$$

where we used the convection $\mathbf{1}^T = (1, 1, \cdots)$, $\mathbf{0}^T = (0, 0, \cdots)$. $\mathbf{P}_0$ is the normalized equilibrium distribution recursively defined through the *detailed balance* condition

$$P_{0,i}l_{i+1} = P_{0,i+1}m_i. \tag{5.4}$$

The relaxation to thermal equilibrium can be monitored through measurement of observables of the type

$$\Delta M(t) = \mathbf{f}^T[\exp(\mathbf{A}t)(1 - \mathbf{J}_0)]\mathbf{g}, \tag{5.5}$$

where the quantities appearing here are defined in analogy to Sec. II. 1 is the identity matrix and $\mathbf{J}_0$ the projection operator onto the equilibrium distribution represented by the dyadic operator

$$\mathbf{J}_0 = \mathbf{P}_0\mathbf{1}^T. \tag{5.6}$$

Since $\mathbf{A}$ and $\mathbf{J}_0$ commute, the identity

$$\exp(\mathbf{A}t)(1 - \mathbf{J}_0) = (1 - \mathbf{J}_0)\exp(\mathbf{A}t)(1 - \mathbf{J}_0) \tag{5.7}$$

holds and the Laplace-transformed time-evolution operator can be written in the form

$$\int_0^\infty dt \, e^{-\omega t} \exp(\mathbf{A}t)(1 - \mathbf{J}_0)$$

$$= (1 - \mathbf{J}_0)[\omega - \mathbf{A}]^{-1}(1 - \mathbf{J}_0). \tag{5.8}$$

The generalized moment expansion can be applied as in Sec. III. There we have preferred to employ the adjoint operator L^+ since for continuous problems Eqs. (3.8), (3.9), and the adjoint boundary conditions are easier to handle than the corresponding equations with L. In the discrete situation the adjoint operator does not offer any particular convenience and, hence, we do not switch to the adjoint of $\mathbf{A}$. We then seek to determine the moments

$$\mu_n = \mathbf{f}^T(1 - \mathbf{J}_0)\mathbf{A}^n(1 - \mathbf{J}_0)\mathbf{g}. \tag{5.9}$$

The evaluation for $n \geq 0$ is straightforward. In particular for the first high-frequency moment an expression can be found, corresponding to that of Eq. (3.6),

$$\mu_1 = \sum_{n=1}^{N-1} \Delta f_n l_{n+1} \Delta g_{0n} P_{0n}$$

$$= \langle \Delta f_n l_{n+1} \Delta g_{0n} \rangle, \tag{5.10}$$

where $\Delta\mathbf{f}$ is a vector of dimension $N - 1$ given by

$$\Delta\mathbf{f}^T = (f_2 - f_1, f_3 - f_2, \ldots, f_N - f_{N-1}), \tag{5.11}$$

$\Delta\mathbf{g}_0$ is defined correspondingly with $g_{0n} = g_n/P_{0n}$.

In the case $n < 0$ one can construct μ_n recursively once the vector

$$\mathbf{x} = \mathbf{A}^{-1}(1 - \mathbf{J}_0)\mathbf{g} \tag{5.12}$$

can be evaluated for arbitrary $\mathbf{g}$. $\mathbf{x}$ can be obtained as the solution of

$$\mathbf{A}\mathbf{x} = (1 - \mathbf{J}_0)\mathbf{g}. \tag{5.13}$$

Because of Eq. (5.9) a solution x is needed which is orthogonal to P_0.

In order to solve Eq. (5.13) one factorizes

$$A = LU, \qquad (5.14)$$

with L and U chosen in the form

$$L = \begin{pmatrix} 1 & 0 & 0 & \cdots \\ \beta_2 & 1 & 0 & \cdots \\ 0 & \beta_3 & 1 & \\ \vdots & & & \ddots \end{pmatrix}, \qquad (5.15)$$

$$U = \begin{pmatrix} \alpha_1 & m_1 & 0 & \cdots \\ 0 & \alpha_2 & m_2 & \cdots \\ 0 & 0 & \alpha_3 & \\ \vdots & & & \ddots \end{pmatrix}. \qquad (5.16)$$

The elements of L and U can be evaluated according to a simple scheme given, for example, in Ref. 27, and one obtains

$$\alpha_i = -l_{i+1}, \quad i = 1, 2, \ldots, N - 1,$$

$$\alpha_N = 0,$$

$$\beta_i = -1, \quad i = 2, 3, \ldots, N. \qquad (5.17)$$

The solution of Eq. (5.13) can then be determined in two steps. One first solves for y,

$$Ly = (1 - J_0)g \qquad (5.18)$$

and then for x,

$$Ux = y. \qquad (5.19)$$

Since one seeks a solution x orthogonal to P_0 one determines first a special solution x' of Eq. (5.19) determined by

$$x'_N = 0 \qquad (5.20)$$

and then adds a homogeneous solution of Eq. (5.19) to obtain the required x. From Eq. (5.4) follows:

$$UP_0 = 0, \qquad (5.21)$$

i.e., P_0 is the homogeneous solution. Therefore, application of $(1 - J_0)$,

$$x = (1 - J_0)x' \qquad (5.22)$$

yields the correct solution. This may be tested by comparing both sides of Eq. (5.13). x can now be constructed. From Eq. (5.18) follows:

$$y_j = \sum_{k=1}^{j} [(1 - J_0)g]_k \qquad (5.23)$$

and from Eqs. (5.19) and (5.20) for the special solution x',

$$x'_N = 0,$$

$$x'_j = (m_j x'_{j+1} - y_j)/l_{j+1},$$

$$j = N - 1, N - 2, \ldots, 1. \qquad (5.24)$$

Finally, the desired x is

$$x_j = x'_j - P_{0,j} \sum_{k=1}^{N} x'_k. \qquad (5.25)$$

From this result discrete versions of Eqs. (3.11)–(3.15) may be derived. Here we give only the result for the first low-frequency moment, corresponding to Eq. (3.14),

$$\mu_{-1} = \sum_{n=1}^{N-1} (l_{n+1} P_{0n})^{-1} \sum_{i=1}^{n} P_{0i}(f_i - \langle f \rangle)$$

$$\times \sum_{j=1}^{n} P_{0j}(g_{0j} - \langle g_0 \rangle), \qquad (5.26)$$

where $\langle f \rangle = \mathbf{f}^T P_0$ and $\langle g_0 \rangle = \mathbf{g}_0^T P_0$; analog expressions are found for the other moments. However, for $n < -1$ an evaluation of the moments according to Eqs. (5.9) and (5.23)–(5.25) should be more practical numerically.

The moments can be evaluated for processes more general than birth–death processes if one can employ suitable algorithms to solve Eq. (5.13) for a more general class of operators. The solution is feasible for operators A represented by a band matrix and may be possible if A is represented by sparse matrices. In the latter case, which corresponds to two-dimensional or higher-dimensional lattices, one may employ sparse matrix algorithms (see, for example, Ref. 28) or iterative algorithms which keep the structure of the matrix unchanged. The convergence of such iterative schemes can be accelerated by suitable choices of over-relaxation schemes (see, e.g., Ref. 27, Chap. 5.6).

VI. APPLICATIONS

In this section we will be mainly concerned with observables connected with free diffusion in the interval $[0, R]$ with a constant diffusion coefficient D. This simple Brownian process has been chosen since in this case the Greens' function (2.1) and, therefore, the observables (2.4) can be evaluated exactly. The exact expressions provide a test for the approximate descriptions. However, we like to emphasize that the virtue of MRTA and GMA lies in their applicability to Brownian processes with arbitrary $D(x)$ and $U(x)$.

We will limit ourselves to (1, 1) and (2, 2) GMA's, since this will prove sufficient for the observables considered, i.e., the graphical representation of approximate and exact expression nearly coincide. However, in other situations more moments may have to be included for a satisfying approximation.[8,29] In any case, the quality of an N-exponential approximation (3.16) may be tested by comparison with the $(N + 1)$-exponential approximation.

The Greens' function $p(x, t|x_0)$ in the case of free diffusion in the interval $[0, R]$ is

$$p(x, t|x_0) = (1/R) + (2/R) \sum_{n=1}^{\infty} \exp[-(n\pi)^2 Dt/R^2]$$

$$\times \cos(n\pi x/R)\cos(n\pi x_0/R). \qquad (6.1)$$

The exact time dependence of every observable that will be discussed can be derived by inserting Eq. (6.1) into

Eq. (2.4). We will use this to compare the results of the MRTA and the GMA with the exact solution. The moments for the different observables considered are supplied in Appendix B.

A. Autocorrelation function

We first want to approximate the autocorrelation function

$$C(t) = \langle\langle \delta x(t) \delta x(0) \rangle\rangle \qquad (6.2)$$

of a particle undergoing free diffusion in the interval $[0, R]$ by the MRTA. $\delta x(t)$ is given by $\delta x(t) = x(t) - \langle x \rangle$ and $\langle\langle \ \rangle\rangle$ denotes thermal average over initial conditions. Therefore, this observable is given by Eq. (2.4) with $f(x) = x = g_0(x)$. Calculation of the moments μ_0 and μ_{-1} from Eqs. (3.4) and (3.15) is straightforward. The MRTA is then given by $C(t) \simeq C(0)\exp(-t/\tau)$, with $C(0) = [\langle x^2 \rangle - \langle x \rangle^2]$ and relaxation time $\tau = (1/10)R^2/D$. This relaxation time is very close to the negative inverse of the first nonzero eigenvalue $-\lambda_1^{-1} = \pi^{-2}R^2/D$.

Figure 1 demonstrates the close agreement between the approximated and the exact autocorrelation function. Furthermore, it illustrates the superiority of the MRTA over the high-frequency, i.e., short-time, (2, 0) approximation which is employed in conventional Padé approximations of correlation functions. The corresponding relaxation time $\tau = (1/12)R^2/D$ is valid only over extremely short times and fails at long times.

We may note that in the case of a harmonic potential, where the exact correlation function (6.2) is given by a single exponential, this single time constant is necessarily reproduced by MRTA.

B. Dynamic structure factor

The dynamic structure factor for diffusive motion, an observable that can be probed with many different experimental methods, is given by
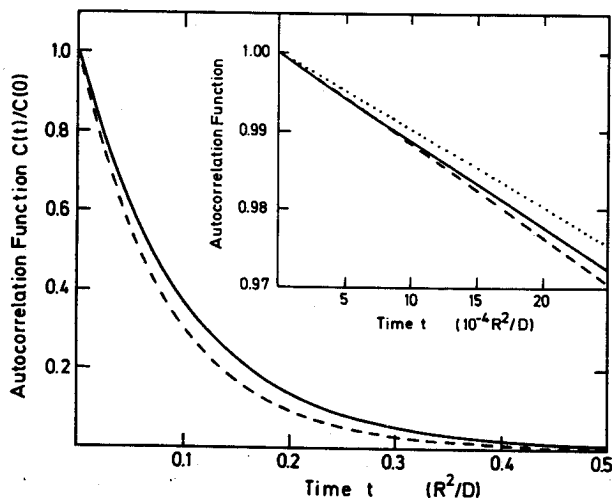

FIG. 1. Autocorrelation function (6.2) for free diffusion in the interval $[0, R]$. (—) exact solution calculated from Eq. (6.1), ($\cdots$) MRTA, (---) (2, 0) GMA, i.e., short-time approximation. At longer times the MRTA cannot be resolved from the exact solution within the accuracy of the drawing and, therefore, is not shown separately in the large figure.
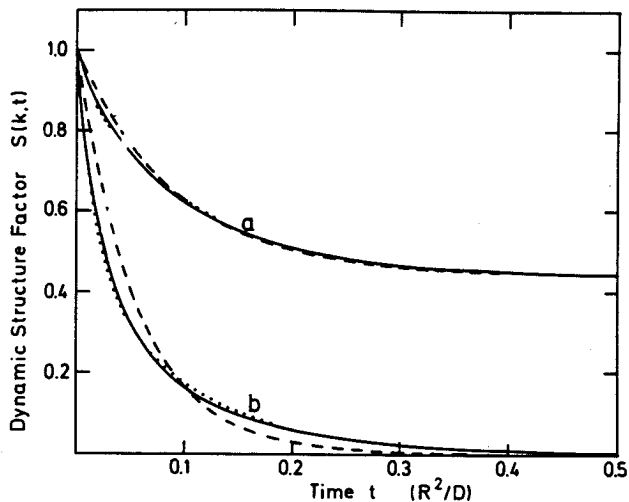

FIG. 2. Dynamic structure factor (6.3) for free diffusion in the interval $[0, R]$. (—) exact solution calculated from Eq. (6.1), (---) MRTA, ($\cdots$) (2, 2) GMA; (a) $kR = 3.0$, (b) $kR = 6.0$.

$$S(k, t) = \langle\langle \exp\{ik[x(t) - x(0)]\} \rangle\rangle, \qquad (6.3)$$

where k is the wave vector of the probing radiation. It can be written in the form $S(k, t) = S(\infty) + \Delta S(k, t)$, where the equilibrium value is the Debye–Waller factor $S(\infty) = |\langle \exp(ikx) \rangle|^2$. In case of free diffusion in the interval $[0, R]$ the Debye–Waller factor is $S(\infty) = [\sin^2(kR/2)]/(kR/2)^2$. We will approximate $\Delta S(k, t)$ with the help of the GMA. Within our formalism $S(k, t)$ is given by Eq. (2.4) with $f(x) = \exp(ikx)$ and $g_0(x) = \exp(-ikx)$. The moments evaluated according to Eqs. (3.7), (3.11)–(3.15) are given in Appendix B 2.

Figure 2 presents the (1, 1) and (2, 2) approximation for $S(k, t)$ for two different k values. As can be seen, the MRTA provides a good estimate of the time scale of the relaxation process and yields a good description in the case of small k. The (2, 2)-GMA description of the dynamic structure factor is found in close agreement with the exact description for both k values.

Mössbauer spectroscopy monitors the dynamic structure factor of a diffusing atom within the lifetime Γ^{-1} of the excited nucleus. Following Singwi and Sjölander[30] the absorption intensity in the case of classical motion, apart from material constants, is given by

$$I(\Omega) \sim \mathrm{Re}\left\{ \int_0^\infty dt \, \exp[-(i\Omega + \Gamma/2)t]S(k, t) \right\}$$

$$= \mathrm{Re}[\tilde{S}(k, i\Omega + \Gamma/2)]. \qquad (6.4)$$

This expression implies that for the absorption spectrum the Laplace-transformed structure factor $\tilde{S}$ has to be evaluated for frequencies $\omega = \Gamma/2 + i\Omega$. The GMA corresponds, therefore, to a two-sided Padé approximation at $\Omega = \infty$ and $\Omega = i\Gamma/2$. This differs from the approximation applied in Ref. 7, where we determined a two-sided Padé approximation at $\Omega = \infty$ and $\Omega = 0$. Still, the total intensity $\int d\omega \, I(\omega)$ is given by μ_0 and described correctly. However, the intensity maximum and its derivatives at $\Omega = 0$ are not reproduced exactly in the present treatment and will be described correctly only for a GMA

involving a larger number of moments. However, if all relaxation times of the process are much shorter than the lifetime of the excited nucleus, i.e., the eigenvalues of the corresponding Fokker–Planck operator are much larger than Γ, the ensuing error is very small and the two methods describe the low-frequency behavior of $I(\Omega)$ equally well. We therefore employed the MRTA method already in Ref. 29 to estimate the contribution of fast diffusive relaxation processes in the substates of a multi-minimum potential.

One should note that the exact functional form of the absorption spectrum (6.4) for Brownian processes is a superposition of an infinite number of Lorentzian lines (see Ref. 7). On the other hand, every exponential function in Eq. (3.16b) gives rise to a single Lorentzian and an additional Lorentzian with natural linewidth Γ is due to the Debye–Waller factor. Therefore, an N-exponential description of the structure factor $S(k, t)$ results in an $(N + 1)$-Lorentzian description of the exact absorption spectrum $I(\Omega)$.

Figure 3 demonstrates the validity of the GMA for different values of $\Gamma R^2/D$, i.e., different ratios of excitation
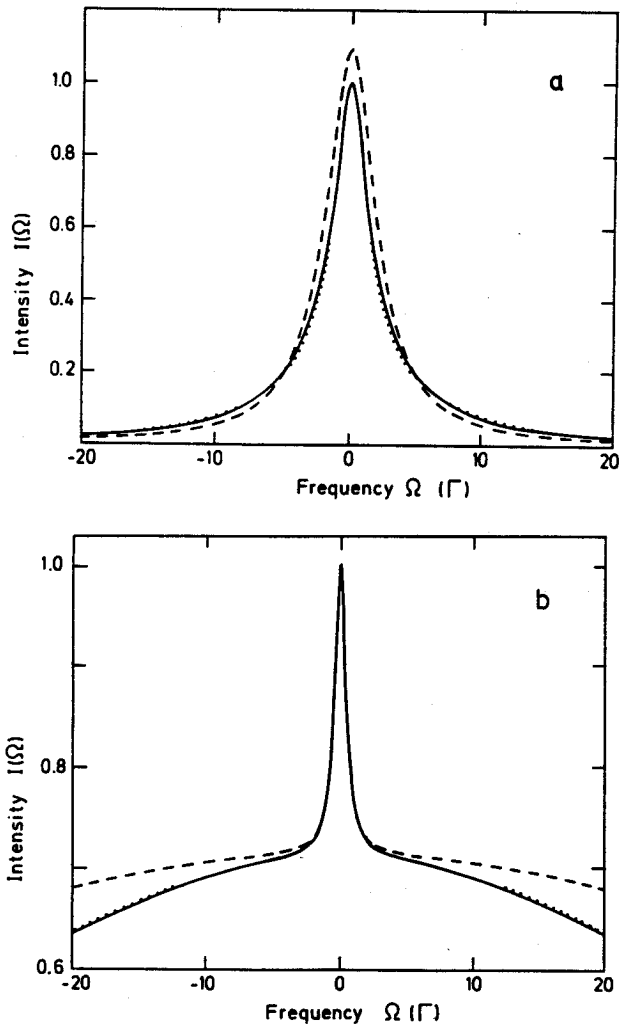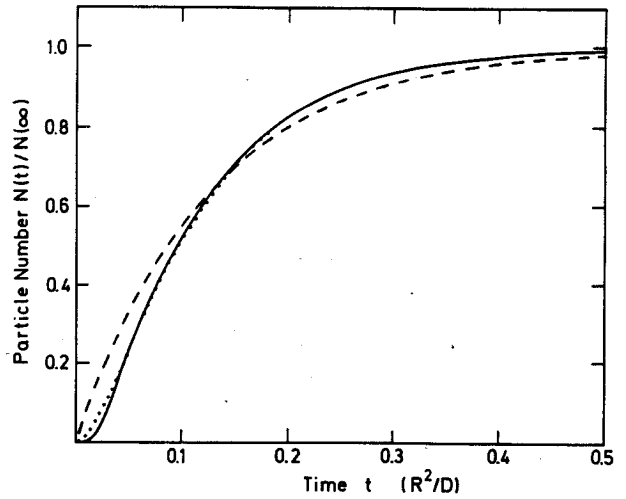

FIG. 4. Particle number (6.5) within the interval $[0, a]$ for free diffusion in the interval $[0, R]$ with a starting δ distribution at x_0; (—) exact solution calculated from Eq. (6.1), (- - -) MRTA, ($\cdots$) (2, 2) GMA; $x_0/R = 1.0$, $a/R = 0.5$.

FIG. 3. Mössbauer absorption spectrum (6.4) for free diffusion in the interval $[0, R]$; (—) exact line shape calculated from Eq. (6.1); (- - -) MRTA, ($\cdots$) (2, 2) GMA; (a) $kR = 6.0$, $\Gamma R^2/D = 10.0$, (b) $kR = 6.0$, $\Gamma R^2/D = 0.2$; the intensity is given in units of the exact intensity at $\Omega = 0$.

lifetime and the time scale of diffusive motion. Figure 3(a) presents the case $\Gamma R^2/D = 10$, i.e., Γ^{-1} is much shorter than the time scale of diffusive motion. In this case the MRTA fails to describe the low-frequency part of the absorption spectrum. However, the (2, 2) GMA provides a satisfactory approximation for the whole spectrum. In case the diffusive processes are much faster than the decay of the nuclear excitation, as considered in Fig. 3(b) with $\Gamma R^2/D = 0.2$, the MRTA gives a reasonable description of the low-frequency behavior of the spectrum and yields a good estimate of the intensity of the background. The (2, 2) GMA closely reproduces the exact line shape.

C. Diffusive redistribution

In this example we want to describe the appearance of molecules within a certain spatial interval in case the molecules have started diffusion at a distant site. We will assume free diffusion within the interval $[0, R]$. The particles start with a delta distribution at x_0 and the number of particles within the interval $[0, a]$ is monitored. The observable is therefore

$$N_1(t) = \int_0^R dx\, H(a - x)p(x, t|x_0), \qquad (6.5)$$

where we assume $x_0 > a$. Moments are calculated as described above. Figure 4 compares the (1, 1) and the (2, 2) approximations with the exact result. A good estimate of the time scale of relaxation is already given by the (1, 1) approximation. The (2, 2) approximation predicts also the lag phase, i.e., the time needed before particles appear in the interval $[0, a]$. The problem considered here is comparable to the one discussed in Sec. VI of Ref. 14. However, there the particles were monitored by reaction at a boundary, whereas in our description the monitoring area may be placed arbitrarily within the diffusion space.
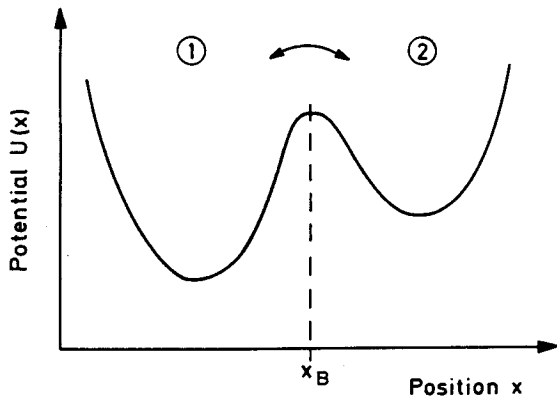
FIG. 5. Schematic bistable potential assumed for the calculation of the mean relaxation time approximation to diffusive barrier crossing.

D. Diffusive barrier crossing

We will discuss now the MRTA for relaxation in a bistable potential as shown in Fig. 5. For initial distributions we consider two cases, which both place the particles inside well 2.

(a) $g(x) = \delta(x - x_0)$, with $x_B < x_0$,
(b) $g(x) = p_0(x)/N_2(\infty)$, for $x > x_B$ and $g(x) = 0$ for $x < x_B$, with $N_2(\infty) = \int_a^b dx\, H(x - x_B)p_0(x)$, where $p_0(x)$ is the normalized Boltzmann distribution in the potential of Fig. 5.

The relaxation process will be monitored by observing the time development of the particle number in potential well 2,

$$N_2(t) = \int_a^b dx\, H(x - x_B)p(x, t|x_0)g(x_0), \qquad (6.6)$$

hence $f(x) = H(x - x_B)$ in Eq. (2.4). The result for the zeroth moment is $\mu_0 = N_1(\infty) = 1 - N_2(\infty)$ for both cases. In case (a) the first low-frequency moment can be written in the form

$$\mu_{-1} = N_1(\infty)N_2(\infty)[\tau_{12}(x_B)$$
$$+ N_2^{-1}(\infty)\tau(x_B|x_0) - \tau_{21}(x_B)], \qquad (6.7)$$

where τ, τ_{12}, and τ_{21} are mean first passage times.[11,14] $\tau(x_B|x_0)$, given by

$$\tau(x_B|x_0) = \int_{x_B}^{x_0} dx[D(x)p_0(x)]^{-1} \int_x^b dy\, p_0(y) \qquad (6.8)$$

is the mean first passage time for a particle starting at x_0 to reach x_B. τ_{12} and τ_{21}, given by $[p_{1,2}(x) = p_0(x)/N_{1,2}(\infty)]$:

$$\tau_{12}(x_B) = \int_a^{x_B} dx[D(x)p_1(x)]^{-1}\left[\int_a^x dy\, p_1(y)\right]^2, \quad (6.9a)$$

$$\tau_{21}(x_B) = \int_{x_B}^b dx[D(x)p_2(x)]^{-1}\left[\int_x^b dy\, p_2(y)\right]^2 \quad (6.9b)$$

are the mean first passage times to reach the barrier x_B from a point left or right of the barrier, respectively, averaged over the thermal distribution of starting points in the respective wells.[14] Case (b) leads to the result

$$\mu_{-1} = N_1(\infty)[N_2(\infty)\tau_{12}(x_B) + N_1(\infty)\tau_{21}(x_B)]. \quad (6.10)$$

These moments yield for the relaxation times in case (a)

$$\tau = N_2(\infty)\tau_{12}(x_B) + \tau(x_B|x_0) - N_2(\infty)\tau_{21}(x_B), \qquad (6.11a)$$

and in case (b)

$$\tau = N_2(\infty)\tau_{12}(x_B) + N_1(\infty)\tau_{21}(x_B). \qquad (6.11b)$$

Equation (6.11b) reproduces the result of Ref. 14. However, there the derivation involved the first passage time approximation and the assumption of a stationary transition state at x_B (compare also Ref. 17, Chap. 9). With the use of the MRTA such an assumption is not needed.

In case of free diffusion, i.e., no barrier between wells, Eq. (6.11a) describes the MRTA for the foregoing example since $N_2(t) = 1 - N_1(t)$. The free diffusion analog to Eq. (6.11b) is the following situation: particles are confined initially to the interval $[a, R]$ with a constant distribution and the particle number which remains in this interval at later times is monitored. Figure 6 shows that the MRTA describes the overall relaxation of the particle number $N_2(t)$ rather well. However, it does not account for the sharp initial decrease of $N_2(t)$ which exhibits an infinite slope at $t = 0$. This behavior is due to the discontinuity of the initial distribution at $x = a$. On the other hand, it is this singular behavior at $t = 0$ that renders the conventional short-time Padé approximations impossible in this case.

E. Upper limit of relaxation times

Larsen[31] has recently discussed an exact upper limit for relaxation times of diffusive processes. He derived his expression by taking the continuum limit of the corresponding result for a tridiagonal matrix master equation. Here we will rederive his formula within our formalism.

As a starting point we note that the solution of Eqs. (2.1)–(2.3) may be given by a spectral expansion

$$p(x, t|x_0) = \sum_{n=0}^{\infty} \exp(\lambda_n t)\psi_n(x)\psi_n^+(x_0), \qquad (6.12)$$

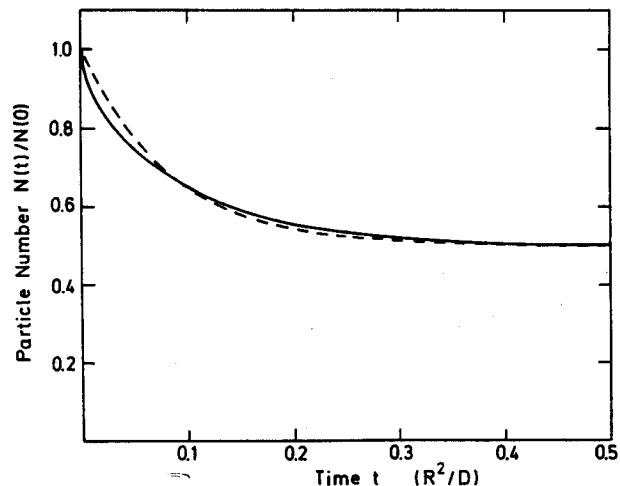where $\lambda_n \leqslant 0$ are the eigenvalues, $\psi_n(x)$ and $\psi_n^+(x)$ are

FIG. 6. Particle number in the interval $[a, R]$ for free diffusion in the interval $[0, R]$ with a constant starting distribution in $[a, R]$; (—) exact solution calculated from Eq. (6.1), (- - -) MRTA; $a/R = 0.5$.

eigenfunctions of $L(x)$ and $L^+(x)$, respectively, with normalization $\int dx\, \psi_n(x)\psi_m^+(x) = \delta_{nm}$. The (single) zero eigenvalue $\lambda_0 = 0$ corresponds to the equilibrium distribution $\psi_0(x) = p_0(x)$. For $n > 0$ the eigenvalues λ_n are the inverse relaxation times $\tau_n = (-\lambda_n)^{-1}$. Larsen notes that the sum of these relaxation times gives an exact upper limit to the actual relaxation time of a system

$$\tau_{\text{relax}} \leqslant \tau_{\lim} = \sum_{n=1}^{\infty} \tau_n. \tag{6.13}$$

Our derivation of an expression for $\tau_{\lim}$ starts with the definition

$$\Delta p(x, t|x) = p(x, t|x) - p_0(x). \tag{6.14}$$

Utilizing the normalization of the eigenfunctions it is easily seen that, performing time and space integration over $\Delta p(x, t|x)$, results in

$$\int_0^\infty dt \int_a^b dx\, \Delta p(x, t|x)$$

$$= \int_0^\infty dt \int_x^b dx \sum_{n=1}^{\infty} \exp(-t/\tau_n)\psi_n(x)\psi_n^+(x)$$

$$= \sum_{n=1}^{\infty} \tau_n. \tag{6.15}$$

Hence $\tau_{\lim}$ is associated with the observable $M[z](t) = \Delta p(z, t|z)$ with moments $\mu_n[z]$. As can be shown from Eq. (6.15), $\tau_{\lim}$ is given by integration over the first low-frequency moment

$$\tau_{\lim} = \int_a^b dz\, \mu_{-1}[z]. \tag{6.16}$$

In the formalism of Sec. II, $M[z](t)$ is given by $f(x) = \delta(x - z) = g(x)$. Evaluation of μ_{-1} according to Eq. (3.14) gives

$$\mu_{-1}[z] = p_0(z)\left\{\int_a^z dx[D(x)p_0(x)]^{-1}\left[\int_a^x dy\, p_0(y)\right]^2\right.$$

$$\left. + \int_z^b dx[D(x)p_0(x)]^{-1}\left[\int_x^b dy\, p_0(y)\right]^2\right\}. \tag{6.17}$$

Integration over z after some manipulation reproduces Larsen's result

$$\tau_{\lim} = \int_a^b dx[D(x)p_0(x)]^{-1} \int_0^x dy\, p_0(y) \int_x^b dz\, p_0(z). \tag{6.18}$$

We may note that Larsen proposes to use $\tau_{\lim}$ as an estimate for the time scale of the relaxation process. However, as is already seen from definition (6.13), $\tau_{\lim}$ overestimates this time scale; e.g., for free diffusion this limit is given by $\tau_{\lim} = (1/6)R^2/D$, whereas, for example, the mean relaxation time for the autocorrelation function (6.2) is $\tau = (1/10)R^2/D$ and the longest relaxation time is $\tau_1 = \pi^{-2}R^2/D$. Moreover, there are simple cases where this overestimate leads to fatal results. In the case of a harmonic potential, expression (6.18) diverges. This is evident, since for the harmonic potential the eigenvalues

have the property $\lambda_n \sim n$ from which $\tau_{\lim} \sim \Sigma_n\, n^{-1}$ follows, i.e., a divergent sum. But relaxation processes in such a potential occur obviously with a finite time constant. We therefore propose to use the MRTA method of Sec. IV for estimates of relaxation times. This also seems more suitable since it takes into account the different properties of different observables.

ACKNOWLEDGMENTS

APPENDIX A: SOLUTION OF EQ. (3.17)

In this Appendix we provide the solution of Eq. (3.17) for the (2, 2) GMA, i.e., the approximation reproducing the moments μ_1, μ_0, μ_{-1}, and μ_{-2} of the exact observables. With the definitions

$$A = \mu_{-1}^2 - \mu_0\mu_{-2}, \tag{A1a}$$

$$B = \mu_0\mu_{-1} - \mu_1\mu_{-2}, \tag{A1b}$$

$$C = \mu_0^2 - \mu_1\mu_{-1}, \tag{A1c}$$

the parameters $a_{1,2}$ and $\lambda_{1,2}$ of approximation (3.16) are given by

$$\lambda_{1,2} = [B \pm (B^2 - 4AC)^{1/2}]/2A, \tag{A2a}$$

$$a_{1,2} = \pm(\lambda_{2,1}\mu_0 - \mu_1)/(\lambda_2 - \lambda_1). \tag{A2b}$$

APPENDIX B: CALCULATED MOMENTS

In this Appendix we provide the moments for the examples of Sec. VI. We will use the abbreviations $A = a/R$, $K = kR/2$, $T = R^2/D$, and $X = x_0/R$.

1. Autocorrelation function (6.2)

$$\mu_1 = R^2/T, \tag{B1a}$$

$$\mu_0 = (1/12)R^2, \tag{B1b}$$

$$\mu_{-1} = (1/120)R^2T. \tag{B1c}$$

2. Dynamic structure factor (6.3)

$$\mu_1 = 4K^2/T, \tag{B2a}$$

$$\mu_0 = 1 - \sin^2(K)/K^2, \tag{B2b}$$

$$\mu_{-1} = \{1 - \sin^2(K)[1/3 + 1/K^2]\}T/K^2, \tag{B2c}$$

$$\mu_{-2} = \{8/K^2 + (4/3)[\cos^2(K)(1 + 3/K^2) + \sin^2(K)$$
$$\times (1/15 - 1/K^2 - 9/K^4)]\}T^2/64K^2. \tag{B2d}$$

3. Diffusive redistribution (6.5)

$$\mu_1 = 0, \tag{B3a}$$

$$\mu_0 = -A, \tag{B3b}$$

$$\mu_{-1} = A[(1 - X)^2 - (1 - A^2)/3]T/2, \tag{B3c}$$

$$\mu_{-2} = A[15(1 - X)^2(1 - 2A^2 + 2X - X^2)$$
$$- (7 - 10A^2 + 3A^4)]T^2/360. \tag{B3d}$$

4. Diffusive barrier crossing (6.6)

$$\mu_0 = 1 - A, \tag{B4a}$$

$$\mu_{-1} = A(1 - A)^2/3, \tag{B4b}$$

$$\tau = A(1 - A)/3. \tag{B4c}$$

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