# Fast Numerical Integrator for Stochastic Differential Equations with Nonstationary Multiplicative Noise†

**Eli Hershkovitz and Rigoberto Hernandez***

*School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332-0400*

*Received: October 9, 2000; In Final Form: January 9, 2001*

Several nonstationary extensions of the generalized Langevin equation describing chemical reaction dynamics have involved a multiplicative noise term. This includes the cases of space dependent friction, time dependent friction, and nontrivial combinations thereof through the so-called irreversible generalized Langevin equation (iGLE). In the present work, a fourth-order numerical integration scheme that leads to dramatically reduced computation times is shown to be applicable in all of these cases.

## I. Introduction

Whenever a chemical process may be described classically, the solution of Hamilton's equations of motion formally provides all the necessary dynamical information. However, for very large systems, such a solution is not generally available. In such systems, reduced-dimensional—projective—approaches allow the problem to be tractable, though the dynamics will no longer be Hamiltonian. In the present work, a fast numerical algorithm is developed for the numerical integration of reduced-dimensional systems whose projected environment may include nonstationary responses in time or space.

Specifically, the dynamics of a generalized variable **x** may be written in a multidimensional closed differential form,

$$\dot{x}_i = f_i[\mathbf{x}(t)]. \tag{1}$$

In the case of a classical system, **x** reduces to a 2*N*-dimensional phase space vector, (**q**, **p**), over an *N*-dimensional configuration space consisting of the coordinates of all the particles in the system. (Within the context of classical systems, the use of a generalized space is useful insofar as the phase space is sometimes extended to include nonsympletic dynamical variables.) This mechanical system may be coupled to some larger system, the bath or outer reservoir, with a large number of degrees of freedom. These so-called bath modes may be treated implicitly through a projection onto the space of the chosen mechanical system. The instantaneous effects of these modes are often treated statistically by drawing them from a probability distribution of the actual forces, with which the equations of motion take the form of a stochastic differential equation (SDE),

$$\dot{x}_i = f_i[\mathbf{x}(t);\, t] + g_{i,j}[\mathbf{x}(t);t]\xi_j(t), \tag{2}$$

where $f_i$ is the deterministic "drift" part of the motion, $g_{i,j}$ is the "diffusion matrix," and $\xi_j$ are Gaussian random forces whose variance depends on macroscopic bath observables, e.g., temperature or density. In many cases, these equations may only be solved numerically, typically using one of two possible approaches: The first is the Fokker−Plank approach,[1] in which a partial differential equation for the probability is derived from the SDE. This approach is not pursued here because the Fokker−Planck equation—that is one in which the Kramers−Moyal expansion includes only the first 2 terms exactly—will not necessarily be available for all cases of the nonstationary colored generalized Langevin equation. Even in the limiting case of multiplicative noise that is the focus of this work and in which such a construction is possible, a numerical procedure would be necessary to solve the corresponding Fokker−Planck equation in the low to moderate friction regimes. We focus, instead, on the direct numerical integration of eq 2 using a finite difference algorithm over an ensemble of trajectories.[2−13]

The first and most common SDE to be used in physics is the Langevin equation[14−16] which may be written in a symplectic form as

$$\dot{q}_i = \frac{1}{m_i}p_i \tag{3a}$$

$$\dot{p}_i = -\frac{\partial V(q)}{\partial q_i} - \frac{\gamma_i}{m_i}p_i + \xi_i(t), \tag{3b}$$

where **q** and **p** are the position and momentum vectors, respectively, and $V(\mathbf{q})$ is the system potential. The masses $\{m_i\}$ will be taken to be equal to 1 throughout either because they are 1 or because the use of mass-weighted coordinates effectively sets them to 1. The projection of the bath onto the system enters through a dissipative term, the friction $\gamma$, and an effective random force, $\xi_i$, that is connected to $\gamma$ via the second fluctuation-dissipation theorem,[17]

$$\langle \xi_i(t_1)\xi_j(t_2)\rangle = 2\frac{\gamma_i}{\beta}\delta(t_1 - t_2)\delta_{ij} \tag{4}$$

where $\beta[\equiv (k_BT)^{-1}]$ is the inverse temperature. Assuming that the higher-order cumulants are zero and that the noise has no correlation in time, the noise terms $\xi_i$ can be taken from a Gaussian random distribution. This distribution is commonly referred to as white noise because its spectral density is a constant. Though seemingly easy to integrate using a numerical finite difference scheme, the nondifferentiable nature of the Gaussian white noise leads to convergence problems. This can be rigorously resolved by choosing a consistent integration scheme such as that in the Stratanovich or Ito calculus.[2] Throughout this work, we shall either use the Stratanovich calculus implicitly and/or work in regimes in which the results between the two do not differ.[1]

† Part of the special issue "William H. Miller Festschrift".

* To whom correspondence should be addressed. E-mail: hernandez@chemistry.gatech.edu.

10.1021/jp0037044 CCC: $20.00 
Published on Web 02/21/2001

The latter case occurs, for example, when the random force is correlated in time with the physical interpretation that the bath has a memory of its past configurations. This correlation is intuitively (physically) necessary for short times, and its cumulative effects have been seen in real systems at longer times.[18−21] When memory effects are included within eq 2, the generalized Langevin equation (GLE) is obtained. In the one-dimensional case, this stochastic integro-differential equation may be written as

$$\dot{p} = -V'(q) - \int^t dt'\, \gamma_0(t - t')p(t') + \xi_0(t), \qquad (5)$$

where the random force $\xi_0(t)$ is correlated in time according to a stationary friction kernel $\gamma_0(t_1 - t_2)$ through the fluctuation dissipation theorem,

$$\langle \xi_0(t_1)\xi_0(t_2)\rangle = \frac{1}{\beta}\gamma_0(t_1 - t_2). \qquad (6)$$

There is a price for the increased complexity of this more realistic description: The GLE includes an integral of the past trajectory's momentum over a nonlocal friction kernel. Its numerical calculation generally entails larger computational demands both in memory (to retain the trajectories) and in time (to integrate over the past trajectories at each time step.) But its integration is well conditioned as the random forces are differentiable.

The LE and the GLE are additive SDEs, i.e., the diffusion term does not depend on the system coordinates. The requirement of stationarity further limits these models to systems where the system dynamics do not influence the behavior of its thermally equilibrated bath. However, there are a variety of processes where the GLE must include nonstationary terms, e.g., polymerizations in dense or inhomogeneous environments[22−24] or in the of explicitly time-dependent diffusion coefficients in rocking ratchets.[25,26] The former example has been described with the use of the irreversible GLE (iGLE).[22,27] The GLE with space-dependent friction[28−30] has also recently come into wide use in describing nonequilibrium dynamical phenomena, e.g., the dynamics of particles in environments with fluctuating barriers,[32] activated rate processes,[32] the thermal relaxation with nontrivial bath system coupling,[28,33] polymer dynamics,[24] and the mobility in spatially inhomogeneous systems.[34,35] Because the iGLE includes the GLE with space-dependent friction in one limit, all of these SDEs will be referred to as iGLEs in this article.

As is the case with the GLE, the direct integration of the iGLE may be slow. This numerical ineffeciency may be circumvented by taking advantage of the multiplicative noise structure in the iGLE and converting it into an SDE of the form of eq 2 albeit over a larger dimensional space. In doing so, however, the uncorrelated random force now reintroduces the ambiguity in the quadrature due to the discontinuous random forces. Although integration schemes for the Stratanovich or Ito calculus resolving this problem are known, they either have a lower order of accuracy[2] or contain a cumbersome structure.[6] In this work, a fast numerical integration scheme for the SDE[13] is shown to be generalizable to those SDEs that correspond to the iGLE, namely with space- and/or time-dependent multiplicative noise, wherein the stationary component of the memory is exponentially decaying. This method is advantageous because it is convergent to fourth order using a small and finite set of terms. It also resolves the ambiguity in the stochastic integration insofar as the numerical integrations give the same results to fourth order regardless of the choice of Stratanovich or Ito calculus. In a variety of examples, described in sections II and III, the numerical calculations are much faster and can be performed to a higher degree of accuracy for colored noise than for white noise. In section III, the fourth-order algorithm for the time dependent iGLE with an exponential friction kernel is introduced. In section IV, the algorithm is developed and examined for the space dependent case, thereby showing that is applicable for both space- and time- dependent multiplicative noise with the iGLE.

## II. Numerical Integration of the SDE

The numerical integration of the GLE in eq 5 may be accomplished through the use of a finite-difference scheme based on the Taylor expansion of the corresponding SDE in eq 2 up to some minimum time step, $\Delta t$.[2,3,4] In the solution of ordinary diffential equations, variants of this approach are the multistep, Runge−Kutta, implicit, and explicit methods.[36] In this section, a one-step collocation method is shown to be particularly useful in solving the SDE.[5,13]

Integrating eq 2 over a time step $h$ relative to some arbitrary origin in time, 0, gives the position step of the $i^{\text{th}}$ coordinate as

$$\delta x_i(h) \equiv x_i(h) - x_i(0) = \int_0^h ds\, f_i[\mathbf{x}(s)] + \int_0^h ds\, g_i[\mathbf{x}(s)]\xi_i(s). \qquad (7)$$

A Taylor expansion of the integrands of this expression with respect to the coordinates provides an estimate of the position step,

$$\delta x_i(h) = \int_0^h ds \left[f_i^0 + f_{i,x_k}^0\, \delta x_k(s) + \frac{1}{2} f_{i,x_k x_m}^0\, \delta x_k(s)\delta x_m(s) + ...\right] + \int_0^h ds\xi_i \left[g_i^0 + g_{i,x_k}^0\, \delta x_k(s) + \frac{1}{2} g_{i,x_k x_m}^0\, \delta x_k(s)\delta x_m(s) + \frac{1}{3!} g_{i,x_k x_m x_l}^0\, \delta x_k(s)\delta x_m(s)\delta x_l(s) + ...\right], \qquad (8)$$

where $f_{i,x_k x_l,...}^0$ and $g_{i,x_k x_l,...}^0$ denote partial derivatives at $t = 0$ of the corresponding functions with respect to the coordinates, $\{x_k, x_l, ...\}$. At order $N$, this expansion may be rearranged[13] as

$$x_i^N(h) = \sum_{j'=1}^{N} \delta x_i^{(j'/2)}(h), \qquad (9)$$

where the variance of each term is a polynomial of order $j'$ in $h$ and $x_i^N$ is accurate to order $N$. The lowest-order term $\delta x_i^{(1/2)}$ is the solution of the expansion in eq 8 cutoff to lowest order in $h$. In a given iterative step, the next order term, $\delta x_i^{(j)}$, is obtained by inserting the lower-order terms,$\{\delta x_i^{(j')}\}$ for $j'$ less than $j$, into the sum on the LHS with the RHS expansion truncated at the next order in $h$. The terms in the resulting expansion, to order $N$, may be written explicitly as

$$\delta x_i^{(1/2)}(h) = g_i^0 \int_0^h ds\xi_i(s) \qquad (10a)$$

$$\delta x_i^{(1)}(h) = f_i^0 h + g_{i,x_k}^0 \int_0^h ds\xi_i(s)\, \delta x_k^{(1/2)}(s) \qquad (10b)$$

$$\delta x_i^{(j)}(h) = \sum_{\mathbf{I}\in\Omega_{j-1\mathbf{x}(\mathbf{I})}} \sum C_{\mathbf{x}(\mathbf{I})} \cdot f_{i,\mathbf{x}(\mathbf{I})}^0 \int_0^h ds \prod_m \delta x_m^{(I_m)}(s) + \sum_{\mathbf{I}\in\Omega_{j-1/2\mathbf{x}(\mathbf{I})}} \sum C_{\mathbf{x}(\mathbf{I})} \cdot g_{i,\mathbf{x}(\mathbf{I})}^0 \int_0^h ds\xi_i(s) \prod_m \delta x_m^{(I_m)}(s), \qquad (10c)$$

where $\Omega_k$ is the space of vectors $\mathbf{I}[\equiv\{I_1, I_2, ...\}]$ with arbitrary dimensionality whose elements are in the set of half integers satisfying the property,

$$\sum_{l=1} I_l = k, \tag{11}$$

$\mathbf{x(I)}$ is a vector with the same dimensionality as $\mathbf{I}$ that has the variables of the SDE as the entries, the inner summation sums over all possible combinations of $\mathbf{x(I)}$, $f_{i,\mathbf{x(I)}}$ is the partial derivative of $f_j$ with respect to the coordinates in the vector $\mathbf{x(I)}$ and $C_{\mathbf{x(I)}}$ is a combinatorial factor from the Taylor expansion. The sum includes all the combinations in $\mathbf{x(I)}$. The new feature that has been introduced to resolve the definition of the stochastic integration is the infinitesimal integral,

$$Z_{1,i} \equiv \int_0^h ds \xi_i(s). \tag{12}$$

If $\xi_i(s)$ is Gaussian distributed, then $Z_{1,i}$ will also be Gaussian distributed with the correlation relation,

$$\langle Z_{1,i}(t_1) Z_{1,i}(t_2)\rangle = (g_i^0)^2\, \delta(t_1 - t_2)h. \tag{13}$$

Its contribution to the expansion is of order of $o(h^{1/2})$ as may be readily obtained.[2] The higher order terms in $\delta x(h)$ may be written in terms of a new set of Gaussian stochastic variables $Z_{j,i}(h)$ defined recursively as

$$Z_{j,i}(h) = \int_0^h ds\, Z_{(j-1),i}(s) \tag{14}$$

For convenience, the solution of eq 9 is separated into a deterministic and a stochastic, random, part,

$$x_i^N(h) = x_{i,det}^N(h) + x_{i,ran}^N(h), \tag{15}$$

according to the simple rule that the stochastic part consists of all terms containing a random force, $Z_{j,i}(h)$. The correlation of these stochastic variables $Z_{j,i}(h)$ is Gaussian, as is shown in Refs 8 and 13. Other noise terms, which are not necessarily Gaussian, do appear in the iterative expansion, but these cancel in the cases to be discussed below.

In the Langevin equation, the resulting expansion contains few terms because of the equation of motion has a symplectic structure, and the diffusion matrix is a constant. The last sum in eq 10c has all but the zeroth order term cancel to zero. All terms where the index of the random term $Z_j(h)$ is odd or where $\alpha_{\mathbf{I}}$ includes more than one even $\alpha_n$ in the first term also cancel to zero. The final result includes the deterministic expansion of the equation of motion with an additional Gaussian variable for each additional order in the expansion. (The exact structure of the terms may be found in Ref 13). The following sections will examine the generalization of the algorithm to include larger classes of physical problems where the structure is not symplectic and the diffusion matrix depends on either time or space coordinates.

## III. Time-Dependent Multiplicative Friction

**A. Formalism.** A special family of problems that can be solved using the high-order scheme is the iGLE,

$$\dot{p} = -V'(q) - \int^t dt' g(t) g(t') \gamma_0(t - t') p(t') + g(t)\xi_0(t), \tag{16}$$

where $\xi_0$ is a random force connected to the friction by the fluctuation dissipation relation,

$$\langle \xi_0(t_1)\xi_0(t_2)\rangle = \frac{1}{\beta}\gamma_0(t_1 - t_2), \tag{17}$$

and $g(t)$ is a time-dependent function describing the evolution of the coupling to the system's environment due to the collective motion of the closed environment or some outside forces in an open environment. The iGLE is specified with a choice of $\gamma_0$; a natural choice of $\gamma_0$ is exponentially decaying in the time difference, i.e.,

$$\gamma_0(t_1 - t_2) = \gamma_0(0) e^{-|t_1 - t_2|/\tau}, \tag{18}$$

where $\gamma_0(0)$ is the instantaneous friction strength, and $\tau$ is the correlation time of the response. This form has the advantage that $\xi_0(t)$ is the solution of an Ornstein process, i.e.,

$$\dot{\xi}_0(t) = -\frac{1}{\tau}\xi_0 + \xi_G(t), \tag{19}$$

where $\xi_G(t)$ is an uncorrelated Gaussian random number with the second moment

$$\langle \xi_G{}^2\rangle = \frac{2\gamma_0(0)}{\beta\tau}. \tag{20}$$

In previous work, the auxiliary equation for $\xi_0(t)$ has been treated on a different footing then the iGLE with the use of a multiple-time step scheme.[22,23] This approach has had the advantage that the algorithm is presumably generalizable to arbitrary forms of $\gamma_0$, and it ensures that the random forces are properly correlated.

However, within the restriction of the exponential memory kernel of eq 18, a well-known auxiliary equation may be used instead that is also better suited to the fast numerical integrator described in the previous section. Introducing the auxiliary variable,

$$z \equiv -\int^t dt'\, g(t')\gamma_0(t - t')p(t') + \xi_0(t), \tag{21}$$

the iGLE of eq 16 may be rewritten in the form,[37]

$$\dot{q} = p \tag{22a}$$

$$\dot{p} = -V'(q) + g(t)z \tag{22b}$$

$$\dot{z} = -\frac{z}{\tau} - \gamma_0(0)g(t)p + \xi_G, \tag{22c}$$

where $\xi_G$ is an uncorrelated Gaussian random number as before. The ensemble averages over trajectories on this extended space requires an average over initial conditions. The positions will be specified below. The momenta are chosen from a Boltzmann distribution. The auxiliary variable $z(0)$ is chosen according to an auxiliary Boltzmann distribution that is a Gaussian distribution with second moment determined by

$$\langle z^2(0)\rangle = \frac{1}{\beta}\gamma_0(0). \tag{23}$$

The equations of motion over the extended space, eq 22, may be Taylor expanded as in the previous section in order to express them in the form necessary for the fast numerical integrator. Because of the time dependence in $g(t)$, the Taylor expansion must now also include time derivatives. This results in several additional terms. Nonetheless, the compact structure of eq 22 substantially reduces the number of nontrivial terms. In particular, all terms that would result in non-Gaussian correlations, including the functional of the random noise, vanish at each order in the expansion. The terms which do contribute and which

did not appear in the earlier expansion of nonstationary SDEs have the general form,

$$\prod_{j=1}^{N}\{f^{0}_{j,\mathbf{x}(\mathbf{I})}\int_{0}^{h} dt\,[t^{k_j}Z^{m_j}]\}, \tag{24}$$

where $j$ is a dummy index labeling the terms, and $\mathbf{x}(\mathbf{I})$ is a corresponding vector defined as in the previous section. Since the expression inside the integral is composed of multiplication of a Gaussian term with a smooth deterministic function, there is no dependence on the type of the stochastic integral; hence, this integral can be solved in standard fashion using integration by parts.[2]

Collecting all the terms of the Taylor expansion up to the fourth order in $h$ gives, as in eq 15, a deterministic part in which no stochastic terms appear and a stochastic part which includes four Gaussian random noise terms of known form. The stochastic contribution to each variable is

$$q_{ran} = (g_0 + h\dot{g}_0)Z_3 - \left(2\dot{g}_0 + \frac{g_0}{\tau}\right)Z_4 \tag{25a}$$

$$p_{ran} = \left(g_0 + \dot{g}_0 h + \frac{1}{2}\ddot{g}_0 h^2\right)Z_2 - \left(\frac{g_0}{\tau} + \dot{g}_0 + \frac{\dot{g}_0}{\tau}h + \ddot{g}_0 h\right)Z_3 \left(V''g_0 + \gamma_0(0)g_0^2 - \frac{g_0}{\tau^2} - \frac{\dot{g}_0}{\tau} - \ddot{g}_0\right)Z_4 \tag{25b}$$

$$z_{ran} = Z_1 - \frac{1}{\tau}Z_2 - \left(\gamma_0(0)g_0^2 - \frac{1}{\tau^2} + 2\gamma_0(0)g_0\dot{g}_0 h\right)Z_3 + \left(2\gamma_0(0)\frac{g_0^2}{\tau} - \frac{1}{\tau^3} + 3\gamma_0(0)g_0\dot{g}_0\right)Z_4. \tag{25c}$$

Performing the Taylor expansion gives an additional non-Gaussian random noise term to the order of $h^4$ of the form,

$$g'(q)g(q)\int_{0}^{h} dtZ_3(t)Z_1(t). \tag{26}$$

In the underdamped regime, the contribution of this term is smaller than the other deterministic variables by a factor of $\gamma/\beta$. Hence the algorithm may safely be considered to be better than third order in accuracy regardless of the friction strength, and it will be referred to loosely as (a weakly) fourth-order method.

**B. Nonstationary Dynamics on the Double-Well.** The efficiency of the fast numerical algorithm has been explored through the study of the energy relaxation of various systems to its equipartition value. The limiting behavior is expected for the time-dependent and space-dependent iGLE because the Boltzmann distribution is a steady-state solution of the corresponding GLE.[38] In particular, for the LE, the relaxation is known to behave as a single exponential.[1] The same result has also been obtained for space-dependent friction in the limits of quadratic coupling and low friction.[28] It is, however, not obvious how the energy will relax in the time dependent problem.

To explore the accuracy and feasibility of the fourth-order algorithm, we first study the energy relaxation in the double-well potential,

$$V(q) = q^4 - 2q^2, \tag{27}$$

for a $g(t)$ represented by a switching function,

$$g(t)^2 = g^2(-\infty) + \frac{1}{2}[g^2(\infty) - g^2(-\infty)]\left[\tanh\frac{t}{2\tau_g}\right], \tag{28}$$

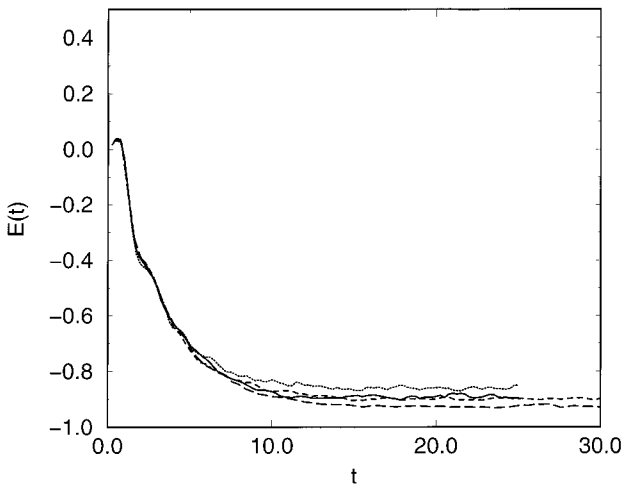


**Figure 1.** Energy relaxation in a double-well potential with exponential stationary friction kernel and nonstationary modulation in $g$ set to a switching function. The ensemble averages involve 5000 trajectories all starting from the barrier. The parameters of the simulations are $\gamma^2_{-\infty} = 0, \gamma^2_{+\infty} = 10$, $\tau_g = 1$, $\beta = 10$, $\gamma = 1$, $\tau = 1$. The Euler integration of the SDE with step sizes of $h = 0.001$, $h = 0.01$, and $h = 0.2$ are displayed as a solid, short-dashed and dotted curve, respectively. These are compared to the long-dashed curve, which is the result of integration of the SDE with the time-dependent fourth-order algorithm. As can be seen, both methods converge for small enough step sizes for long time to the equipartition value.

within the iGLE in eq 25c. This switching function has been used in Ref 22 to describe a smooth change in the environment from steady-state behavior at times far in the past ($t \rightarrow -\infty$) to a different steady-state behavior at times far in the future ($t \rightarrow +\infty$) due to a change in the system and solvent interaction. The transition from $g(-\infty)$ to $g(\infty)$ takes place over a finite transition time, $\tau_g$. The energy relaxation of a particle starting from the barrier of the double-well potential has been integrated using both the usual Euler method[2] and the fourth-order algorithm of this work. As shown in Figure 1, for small time steps, both methods relax to equipartition similarly. Figure 1 also presents the step sizes for which each of the methods experiences a breakdown. It can be seen that the fourth-order method remains accurate for step sizes a few orders of magnitude larger than that of the Euler method. The fourth-order algorithm is accurate up to a step size of $h = 0.2$, whereas the Euler method loses accuracy for step sizes larger than $h = 0.001$.

A second model for the nonstationary friction behavior in a double-well potential is that in which the $g(t)$ is represented by a power law in time, $g \propto t^{\alpha}$. Such a form can be given a physical interpretation. It has earlier been suggested that

$$g \propto \langle x\rangle^{\alpha}, \tag{29}$$

where $x$ represents the length of a given growing polymer, and $\alpha$ is a characteristic growth scaling exponent.[23] This growth may be further related to time through a scaling function,

$$\langle x\rangle^{\alpha} \propto t^{\alpha'}, \tag{30}$$

during an unquenched growth regime. Combining these scaling relations, provides the result,

$$g \propto t^{\alpha'}, \tag{31}$$

for the characteristic growth in $\langle x\rangle$ during an intermediate growth regime. To avoid the nondissipative regimes at $t \rightarrow -\infty$, the

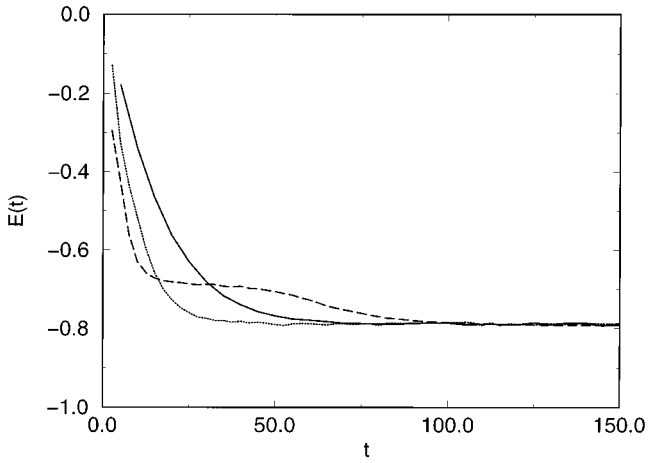


**Figure 2.** Energy relaxation in a double-well potential with exponential stationary friction kernel and nonstationary modulation in $g$ set to a power law in time, $g(t) = (1 + t)^{\alpha}$. The ensemble averages involve 10 000 trajectories all starting from the barrier. The parameters are $\beta = 5$, $\gamma_o(o) = 1.0$, and $\tau = 3$. The integration step size in the fourth-order integrator is $h = 0.025$. The solid, dotted, and dashed curve are the results obtained for the scaling exponent $\alpha$ equal to 0.25, 0.5, and 1.0, respectively.

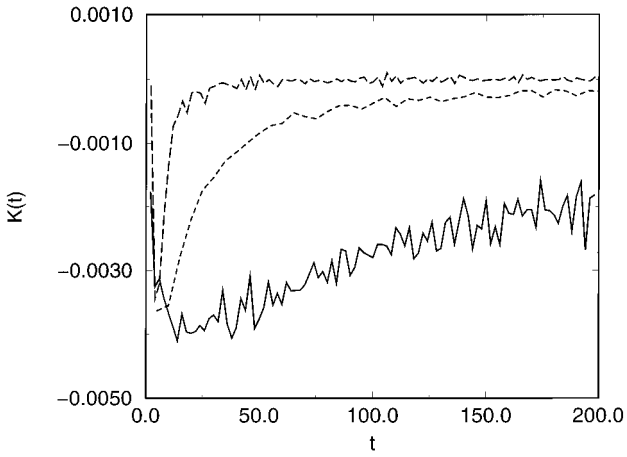


**Figure 3.** Time-dependent reaction rates for the transition in a double well from the right to left well at parameters as in Figure 2, but with the nonstaionary part now equal to $g(t) = .(0001 + at)^{\alpha}$. The numerical integration is performed with 2 500 000 particles starting from the right well at thermal equilibrium with $\beta = 5$, $a = 0.3$, $\gamma_o(o) = 1.0$, and $\tau = 3$. The solid, dotted, and dashed curve are the results obtained for the scaling exponent $\alpha$ equal to 0.25, 0.5, and 1.0, respectively. Convergence has been achieved with step sizes of 0.25 in the first two cases and 0.01 in the thid case.

nonstationary time dependence in the random force is taken to be

$$g(t) = (1 + t)^{\alpha}, \tag{32}$$

for time $t$ greater than zero and one otherwise. The scaling exponents are taken from the set: $\alpha \in \{.25, .5, 1\}$. Figure 2 displays the average energy relaxation of an ensemble of trajectories started at the barrier.

As can be seen, the system always reaches equipartition. For strong friction, the nature of the relaxation is far from exponential. This is an outcome of the fact that kinetic energy relaxation is much faster than the potential energy relaxation, whereas the latter is slow when the diffusion process is slow.

Given that the fourth-order integrator is accurate for the iGLE, it can be used to obtain other observables for nonstationary reactive systems. In particular, the calculation of the rates of time-dependent reactions or diffusion in time-dependent environments are of current general interest. As a concrete example, the escape rates in the double-well potential of eq 27 will be calculated for the nonstationary time dependence in the random force,

$$g(t) = (.0001 + at)^{\alpha}. \tag{33}$$

An accurate analytical expression[39] for the reactive rates exist for the (stationary and local) 1D LE and it has been used successfully[40] on the double-well potential. With the inclusion of the time dependence in the friction, the reactive flux is no longer constant and cannot be found with the known analytical solutions. Furthermore, because the friction strength changes in time, the conventional reactive flux method[40] is not applicable. Thus, the only way to calculate the reactive flux is the direct integration of an ensemble of particles starting from equilibrium in one of the wells and finding the rate with the relation,

$$\kappa(t) = \frac{1}{n_1 - n_2}\frac{d(n_1 - n_2)}{dt}, \tag{34}$$

at the so-called saddle times.[41,42] Of course, this method demands much longer integration time than the reactive flux method but it is feasible because of the efficiency of the fast fourth-order integrator. The rates for this process with various power law friction strengths are presented in Figure 3. As can be seen, the reaction rates follow the well-known turnover picture[39,40] but with an additional dependency on time.

## IV. Space-Dependent Friction

**A. Formalism.** A second class of nonstationary friction kernels that can be solved using the high-order scheme of this work is that of the iGLE with space-dependent friction,

$$\dot{p} = -V'(q) - \int^t dt' g(q(t))g(q(t'))\gamma_0(t - t')p(t') + g(q(t))\xi_0(t). \tag{35}$$

The use of an exponential friction kernel for $\gamma_0$ as in eq 18 allows for the transformation of this system to an extended space in analogy to the construction of eq 22. The equations of motion in this extended space are[32]

$$\dot{q} = p \tag{36a}$$

$$\dot{p} = -V'(q) + g(q)z \tag{36b}$$

$$\dot{z} = -\frac{z}{\tau} - \gamma_0(0)g(q)\dot{q} + \xi_G \tag{36c}$$

where $\xi_G$ and $z$ are correlated as in eqs 20 and 23, respectively. This construction has effectively transfered the iGLE into a simpler set of three SDEs with additive noise. Such a trick can be performed on any iGLE with colored (multiplicative) noise in which the stationary memory kernel can be decomposed into a sum of exponents. As this includes a large number of problems of physical interest, the method is in fact more general than it may have initially appeared.

After some algebra, the stochastic part of the integrated variables is obtained:

$$q_{\mathrm{ran}} = (g_0 + hg_0'p^0)Z_3 - \left(2g_0'p^0 + \frac{g_0}{\tau}\right)Z_4 \qquad (37a)$$

$$p_{\mathrm{ran}} = \left[g_0 + g_0'p_0h + \frac{1}{2}g_0'(-V_0' + g_0z_0)h^2 + \frac{g_0''}{2}p_0^2h^2\right]Z_2 - \left[\frac{g_0}{\tau} + g_0'p_0 + \frac{1}{\tau}g_0'p_0h + g_0'(V_0' - g_0z_0)h + g_0''p_0^2h\right]Z_3 - \left[g_0V_0'' + \gamma_0(0)g_0^2 - \frac{g_0}{\tau^2} - \frac{gp_0}{\tau} + g_0'(V_0' - g_0z_0) - g_0''p_0^2\right]Z_4 \qquad (37b)$$

$$z_{\mathrm{ran}} = Z_1 - \frac{1}{\tau}Z_2 - \left[\gamma_0(0)g_0^2 - \frac{1}{\tau^2} + 2\gamma_0(0)g_0g_0'p_0h\right]Z_3 + \left[2\frac{\gamma_0(0)}{\tau}g_0^2 - \frac{1}{\tau^3} + 3\gamma_0(0)g_0g_0'p_0\right]Z_4. \qquad (37c)$$

While there seems to be an inflation in the number of terms as compared to eq 25, most of the terms have a similar structure and allow for economic algorithmic programming.

**B. Nonstationary Dynamics with Periodic Space Dependence.** As before, the system dynamics may be modeled through the use of a double-well potential. However, instead of using a time-dependent *g*-function, in this case we use a space-dependent one. In particular, we use a periodic form,

$$g(q) = \sin^2\left(\frac{\pi}{2}q\right) + \epsilon, \qquad (38)$$

with the stationary part given by the exponential friction as required by the assumptions above. The frequency of the space-depence has been taken here to match the short-ranged periodicity of the double-well insofar as the system will experience maximal friction in the potential well and minimal friction at the barrier. This assumption is physically realizable when the confinement effects of the barrier influence the dynamics.[35] (In future work, we will explore the resonance behavior as a function of different frequencies in the periodic friction.) The relaxation of particles from an initial nonequilibrium distribution at the barrier has been obtained using both the usual Euler method[2] and the fourth-order algorithm of this work. As may be seen in Figure 4, both approaches are in good agreement, although the fourth-order algorithm is substantially faster.

An alternate model for the system dynamics is that of a tilted washboard potential, i.e., a sum of a periodic function and a linear function in position. This potential has been used in our group to model polymerization dynamics in the context of the space- and time-dependent nonstationarity.[23,24] It has also been studied by Dan et al.[34] to model the mobility in spatially inhomogeneous systems in the context of periodic space-dependent friction to examine and describe the stochastic resonances in the drift velocity. In this case, the friction is explicitly taken to be proportional to the periodic component of the potential with a specified phase delay. Dan et al.[34] have obtained an analytical expression for the mobility,

$$\mu = \frac{\langle dq/dt\rangle}{F}, \qquad (39)$$

in the strong friction limit, where the GLE reduces to the Smoluchowski equation, and found it to depend strongly on the phase delay between the friction and the potential. To make use of the fourth-order algorithm of this work, we first generalize

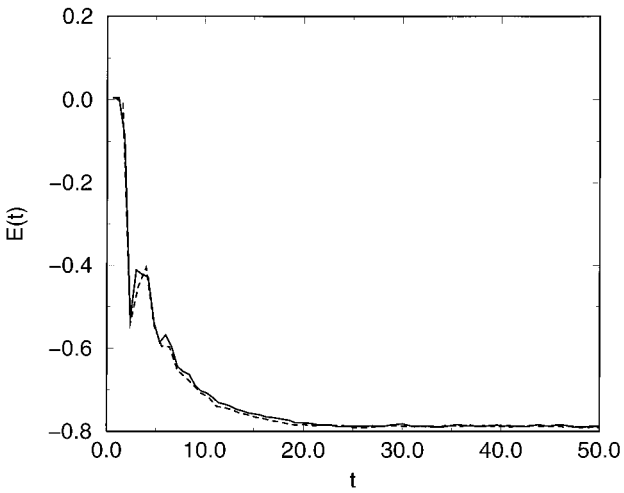


**Figure 4.** Energy relaxation in a double-well potential with exponential stationary friction kernel and a nonstationary modulation in *g* that is explicitly space-dependent. The numerical integration is performed with an initial nonequilibrium distribution of 5000 trajectories localized at the barrier with thermalized momenta according to $\beta = 5$. (The remaining parameters are $\gamma = 3$, $\tau = 1$ and $\epsilon = 0.001$.) The dashed curve is the average relaxation obtained using the Euler method with step size $h = 0.000\,01$; the bold curve is the result of the integration using the fast algorithm with step size $h = 0.05$.

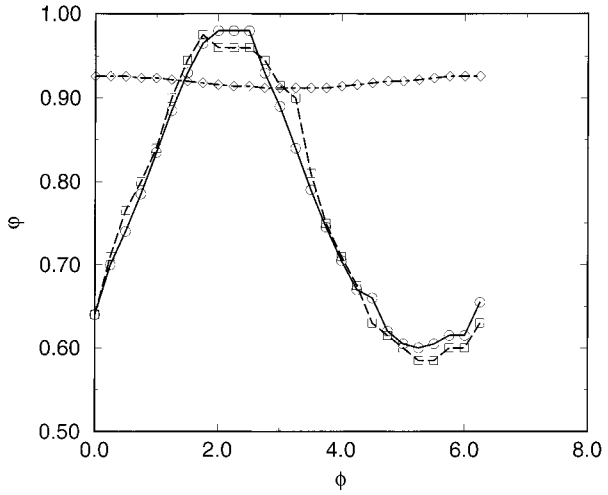


**Figure 5.** The modified current $\varphi = \gamma\langle p\rangle$ as a function of the phase $\phi$ for the example in the text. The average current is obtained for an initial nonequilibrium distribution of 5000 particles localized at the barrier with thermalized momenta according to $\beta = 1$. (The remaining parameters are $\lambda = 0.5$, $\tau = 0.1$ and $f = 1.5$.) The integration is performed for large enough times that the current goes to an average plateau value. The time step is taken to be $h = 0.025$ for $\gamma = 0.2$ and $\gamma = 5$ (represented by diamonds and circles, respectively) and $h = 0.01$ for $\gamma = 15$ (represented by squares).

their local friction for the stationary part to be the exponential friction with $\tau = 0.1$. For the potential,

$$V(q) = -\cos(q) + Fq, \qquad (40)$$

the explicit form of the modulation in the nonstationary space dependence in the random noise is $g(q) = [1 - \lambda\cos(q + \phi)]$. Using the space-dependent integrator of eq 37c, we have calculated the normalized mobility $\bar{\mu} = \gamma\mu$ at several friction strengths as a function of the phase are shown in Figure 5. This normalized mobility does not depend on the friction strength. In the overdamped case, we can see a strong dependence on the phase with a structure similar to the case presented in Ref 34. There are only minor differences between the cases of $\gamma =$

5 and $\gamma = 15$, reflecting the degeneracy of the Langevin equation to the Smoluchowski equation in the overdamped regime. For the case of $\gamma = 0.2$, the friction is weak enough so that the problem can no longer be solved with the analytical method of Ref 34 when neglecting the inertia term. The numerical results in Figure 5 demonstrate that even in the weak friction limit, the mobility depends on the phase delay. This dependence is much weaker than that found in the overdamped case and is substantially different in its behavior. Although the maximum and minimum are inside the $[0,2\pi]$ interval in the overdamped case, the maximum for the underdamped case is at the edges of this interval. In summary, the use of the fourth-order integrator has allowed us to accurately capture the behavior over all friction strengths that was earlier seen in Ref 34 in the high-friction limit.

## V. Summary

Although the iGLE and the space dependent GLE have a seemingly simple structure, an analytical solution is presently not known; hence, a good numerical integrator is a matter of necessity. In this work, a fourth-order numerical integration scheme has been introduced that is appropriate for the solution of a large class of stochastic differential equations, including the space and time dependent iGLE with exponential memory kernel. This class of SDEs have physical importance in the field of nonstationary Brownian motion. Possible applications include polymerization reactions and surface transport as has been discussed in the text. The accuracy of the integrator has been shown for both double-well and periodic potentials. The latter also provided a case study of the resonant behavior between the frequency of the potential and the solvent response through a space-dependent potential.

It is easy to combine the two cases of sections III and IV in order to obtain an integration scheme for problems with the friction and random forces involving both time and space coordinates. The algorithm presented here is fourth order in accuracy, which is by far better than existing schemes which are second order or less, and opens the possibilities of obtaining numerical solutions in a reasonable amount of time. In multidimensional problems where the solutions are usually not stable, the accuracy of the fourth-order method should be essential to obtain accurate and converged results for nontrivial step sizes.

The fourth-order algorithm designed here for iGLE's with a stationary friction kernel for exponentially decaying memory can be applied for larger classes of problems. Using the method of continued fractions,[1] an arbitrary friction kernel can be expanded as a sum of exponentials. When the expansion converges, the modified fourth-order algorithm for an iGLE with exponential decaying stationary kernels can be used to solve each of the corresponding SDEs. It is still a challenge to solve problems with memory kernels, e.g., the Gaussian kernel and the cutoff kernel, for which such an expansion does not converge. But this may not be a significant loss in generality as it has been shown that such kernels lead to unusual dynamics as well as unusual thermodynamic behavior.[43]

Though not explored in this article, the current method may also be useful in exploring the iGLE when the strength of the random forces depends self-consistently on characteristic observables of a finite or infinite ensemble of tagged particles.[23,24] Such a system is equivalent to a high-dimensional Langevin equation composed of replicas of the Langevin equation that are coupled by low-order terms. With the use of the fourth-order method of this article, it may be possible to obtain converged numerical results for this class of self-consistent iGLE's.

**Acknowledgment.** This work has been supported by a National Science Foundation CAREER Award under Grant No. NSF 97-03372. R.H. is an Alfred P. Sloan Fellow, a Cottrell Scholar of the Research Corporation, and a Blanchard Assistant Professor of Chemistry at Georgia Tech.

## References and Notes

(1) Risken, H. *The Fokker−Planck Equation*; Springer-Verlag: New York, 1989.

(2) Kloeden, P.; Platen, E. *Numerical Solution of Stochastic Differential Equations*; Springer-Verlag: Berlin, 1995.

(3) Allen, M. P.; Tildesley, D. J. *Computer Simulations of Liquids*; Oxford: New York, 1987.

(4) Mannella, R. In *Noise in Non Linear Dynamical Systems*; Moss, F.; McClintock, P., Eds.; Cambridge University Press: Cambridge; New York, 1989; Vol. 3, p 189.

(5) Mannella, R.; Pallechi, V. *Phys. Rev. A* **1989**, *40*, 3381.

(6) Helfand, E. *B. S. T. J.* **1979**, *58*, 2289.

(7) Greenside, H. S.; Helfand, E. *B. S. T. J.* **1981**, *60*, 1927.

(8) Honeycutt, R. *Phys. Rev. A* **1992**, *45*, 600.

(9) Honeycutt, R. *Phys. Rev. A* **1992**, *45*, 604.

(10) Fox, R.; Gatland, I.; Roy, R.; Vemuri, G. *Phys. Rev. A* **1988**, *38*, 5938.

(11) Linkwitz, S.; Grabert, H.; Turlot, E.; Estéve, D.; Devoret, M. H. *Phys. Rev. A* **1992**, *45*, R3369.

(12) Milshtein, G.; Tretyakov, M. *J. Stat. Phys.* **1994**, *77*, 691.

(13) Hershkovitz, E. *J. Chem. Phys.* **1998**, *108*, 9253.

(14) Brown, R. *Philos. Mag.* **1828**, *4*, 161, **1829**, *6*, 161.

(15) Einstein, A. *Ann. Phys.* **1905**, *17*, 549, **1906**, *19*, 371.

(16) Langevin, P. *C. R. Acad. Sci. Paris* **1908**, *146*, 530.

(17) Kubo, R. *Rep. Prog. Theor. Phys.* **1966**, *29*, 255.

(18) Zwanzig, R.; Bixon, M. *Phys. Rev. A* **1970**, *2*, 2005.

(19) Metiu, H.; Oxtoby, D.; Freed, K. F. *Phys. Rev. A* **1977**, *15*, 361.

(20) Straub, J. E.; Borkovec, M.; Berne, B. J. *J. Chem. Phys.* **1985**, *83*, 3172.

(21) Straub, J. E.; Borkovec, M.; Berne, B. J. *J. Chem. Phys.* **1986**, *84*, 1788.

(22) Hernandez, R.; Somer, F. L. *J. Phys. Chem. B* **1999**, *103*, 1064.

(23) Hernandez, R.; Somer, F. L. *J. Phys. Chem. B* **1999**, *103*, 1070.

(24) Somer, F. L.; Hernandez, R. *J. Phys. Chem. B* **2000**, *104*, 3456.

(25) Bartussek, R.; Hänggi, P.; Linder, B.; Schimansky-Geier, L. *Physica D* **1997**, *109*, 17.

(26) Bartussek, R.; Hänggi, P.; Kissner, J. *Eur. Lett* **1994**, *28*, 459.

(27) Hernandez, R. *J. Chem. Phys.* **1999**, *110*, 7701.

(28) Lindenberg, K.; Seshadri, V. *Physica A* **1981**, *109*, 483.

(29) Carmeli, B.; Nitzan, A. *Chem. Phys. Lett.* **1983**, *102*, 517.

(30) Lindenberg, K.; Cortés, E. *Physica A* **1984**, *126*, 489.

(31) Reimann, P.; Hänggi, P. In *Stochastic Dynamics*; Schimansky-Geier, L., Pöchel, T., Eds.; Springer: Berlin, 1997; p 127.

(32) Haynes, G. R.; Voth, G. A.; Pollak, E. *J. Chem. Phys.* **1994**, *101*, 7811.

(33) Cortés, E.; West, B. J.; Lindenberg, K. *J. Chem. Phys.* **1985**, *82*, 2708.

(34) Dan, D.; Mahato, M.; Jayannavar, A. *Phys. Rev. E* **1999**, *60*, 6421.

(35) Faucheux, L. P.; Libchaber, A. J. *Phys. Rev. E* **2000**, *49*, 5158.

(36) Press, W. H.; Flannery, B. P.; Teukolsy, S. A.; Vetterling, W. T. *Numerical Recipes*; Cambridge University Press: Cambridge, UK, 1988.

(37) Frishman, A. M.; Pollak, E. *J. Chem. Phys.* **1993**, *15*, 9532.

(38) Kubo, R. In *Fluctuation, Relaxation and Resonance in Magnetic Systems*; Haar, T., Ed.; Oliver and Boyd: Edinburgh, 1961.

(39) Mel'nikov, V.; Meshkov, S. *J. Chem. Phys.* **1986**, *85*, 1018.

(40) Pollak, E.; Grabert, H.; Hänggi, P. *J. Chem. Phys.* **1989**, *91*, 4073.

(41) Chandler, D. *J. Chem. Phys.* **1978**, *68*, 2959.

(42) Berne, B. J. In *Multiple Time Scales*; Brackbill, J. U., Cohen, B. I., Eds.; Academic: New York, 1985.

(43) Reese, S.; Tucker, S.; Schenter, G. *J. Chem. Phys.* **1995**, *102*, 104.