JOURNAL OF COMPUTATIONAL PHYSICS 35, 169–182 (1980)

Numerical Integration of the Langevin Equation: Monte Carlo Simulation

DONALD L. ERMAK AND HELEN BUCKHOLZ

Environmental Sciences Division, Lawrence Livermore Laboratory, University of California, Livermore, California 94550

Received February 14, 1978; revised June 6, 1979

Monte Carlo simulation techniques are derived for solving the ordinary Langevin equation of motion for a Brownian particle in the presence of an external force. These methods allow considerable freedom in selecting the size of the time step, which is restricted only by the rate of change in the external force. This approach is extended to the generalized Langevin equation which uses a memory function in the friction force term. General simulation techniques are derived which are independent of the form of the memory function. A special method requiring less storage space is presented for the case of the exponential memory function.

1. INTRODUCTION

The Langevin model of Brownian motion has been used extensively to describe the dynamic behavior of particles in a heat bath under conditions of thermodynamic equilibrium. The model describes the interaction between a Brownian particle and the surrounding bath in a statistical manner, rather than attempting to treat each individual Brownian particle-bath particle interaction. The force on the Brownian particle due to the bath is assumed to be composed of two parts: a frictional force which is proportional to the Brownian particle velocity and a randomly fluctuating force which can be described only in terms of its statistical properties. The Langevin equation is obtained by using this force in Newton's equation of motion.

Solving the Langevin equation is different than solving an ordinary equation of motion for which the solution is a unique trajectory in phase space. The stochastic nature of the Langevin equation allows an infinite number of possible trajectories for any given initial condition. The probability of any one trajectory is governed by the statistical properties of the randomly fluctuating force. Consequently, when solving the Langevin equation, one generally seeks to obtain the average value of a particle property (such as the mean squared displacement) with the average taken over all possible trajectories.

The average particle properties can be calculated directly from the distribution function governing the probability of occurrence of the velocity and displacement as a function of time. If the distribution function can be obtained in an analytic form,

0021-9991/80/050169–14$02.00/0

then the average properties can be readily calculated. This approach has been used extensively for the case of a free Brownian particle, a harmonically bound particle, and for a particle in a constant force field [1, 2].

However, when the Brownian particle experiences more complicated interactions and analytic solutions are not obtainable, then numerical methods of solution are usually needed. An attractive approach is to use a Monte Carlo simulation [3, 4]. In this method the Brownian particle trajectory in phase space is simulated by a sequence of randomly chosen incremental changes in the phase space coordinates. The average value of a desired property can then be estimated by the calculated average taken over the length of the simulation.

Several Monte Carlo techniques have been used to numerically integrate the Langevin equation. Turq, *et al.* [5] and Weiner and Forman [6] use first-order numerical integration of the Langevin equation to simulate the Brownian particle trajectories. These methods are restricted to time steps between successive displacements which are small in comparison to the decay time β^{-1} of the velocity autocorrelation function. The method used by Ermak [7] is derived from the diffusive limit of the Langevin equation and is therefore applicable only when the time step is much longer than the decay time β^{-1}. Doll and Dion [8] have proposed an approach which is based on the independent single-variate velocity and displacement distribution functions. This method neglects the statistical interdependence of the velocity and displacement which can be obtained from the bivariate velocity and displacement distribution function.

The purpose of this work is to present a more general method for integrating the Langevin equation. The method is based on the analytic solution of the stochastic Langevin equation for a single particle in a constant force field. The solution is expressed as the bivariate velocity and displacement distribution function from which velocity and displacement equations are derived. These equations allow the use of intermediate time steps as well as time steps which are either much shorter or much longer than β^{-1}. This approach is then extended to the generalized Langevin equation which uses a memory function in the friction force term. A special simulation method is presented for the case of the exponential memory function.

2. Ordinary Langevin Equation

2.1. *Model System*

The system to be simulated consists of a Brownian particle in a heat bath of volume V. The particle is in thermodynamic equilibrium with the bath at temperature T and is subject to an external force $\mathbf{F}(\mathbf{r}, t)$. The ordinary Langevin equation of motion for the Brownian particle is then

$$m\mathbf{v} = \mathbf{F} - m\beta\mathbf{v} + \mathbf{X}; \qquad t > -\infty. \tag{1}$$

where t is time; m, β, and $\mathbf{v}(t)$ are the mass, friction constant, and velocity of the

particle; and $\mathbf{X}(t)$ is a random force. As previously mentioned, the friction force and random force are used to approximate the interaction of the Brownian particle with the heat bath. The random force is assumed to be independent of the particle velocity and to fluctuate rapidly compared to changes in the velocity. The properties of the random force are described by a Gaussian distribution function with the mean and mean square

$$\begin{aligned} \langle \mathbf{X}(t) \rangle &= 0, \\ \langle \mathbf{X}(t) \cdot \mathbf{X}(t') \rangle &= 6m\beta kT\delta(t - t'). \end{aligned} \tag{2}$$

Together Eqs. (1) and (2) completely describe the dynamic behavior of the Brownian particle in the Langevin model.

2.2. *Simulation Method*

Expressions for the velocity and position can be obtained by successive integrations of Eq. (1) and by restricting the size of the time step t such that the force $\mathbf{F}$ remains essentially constant during t. In general, this condition on the size of the time step is much less restrictive than the condition $t \ll \beta^{-1}$. Integration of Eq. (1) from time t_0 to time $t_0 + t$ yields the equation

$$\mathbf{v} - \mathbf{v}_0 e^{-\beta t} - \frac{\mathbf{F}_0}{m\beta} \cdot (1 - e^{-\beta t}) = \frac{1}{m} \int_0^t e^{-\beta(t-t')} X(t_0 + t')\, dt', \tag{3a}$$

where a subscript 0 on the variables $\mathbf{r}_0$, $\mathbf{v}_0$, and $\mathbf{F}_0$ indicates that it is to be evaluated at the time t_0 and the lack of a subscript 0 on these variables indicates that it is to be evaluated at the time $t_0 + t$. A second integration plus an integration by parts on the $\mathbf{X}(t)$ term produces the result

$$\begin{aligned} \mathbf{r} - \mathbf{r}_0 - \frac{\mathbf{v}_0}{\beta} \cdot (1 - e^{-\beta t}) - \frac{\mathbf{F}_0}{m\beta} \cdot \left[t - \frac{1}{\beta} (1 - e^{-\beta t}) \right] \\ = \frac{1}{m\beta} \int_0^t [1 - e^{-\beta(t-t')}]\, \mathbf{X}(t_0 + t')\, dt'. \end{aligned} \tag{3b}$$

Eqs. (3a) and (3b) cannot be used directly to calculate the velocity and position change due to the random nature of $\mathbf{X}(t)$. One must first calculate the statistical properties of the two integrals involving $\mathbf{X}(t)$. The approach taken here is to use the bivariate probability distribution $w(\mathbf{r}, \mathbf{v}, t)$, which governs the probability that a particle, initially located at $\mathbf{r}_0$ with velocity $\mathbf{v}_0$ and experiencing the force $\mathbf{F}_0$, will be located at $\mathbf{r}$ with velocity $\mathbf{v}$ after time t. Using the methods developed by Chandrasekhar [1], the bivariate probability distribution $w(\mathbf{r}, \mathbf{v}, t)$ can be derived and is found to be

$$w(\mathbf{r}, \mathbf{v}, t) = [4\pi^2(EG - H^2)]^{-3/2} \exp\left\{ \frac{-(GR^2 - 2H\mathbf{R} \cdot \mathbf{V} + EV^2)}{2(EG - H^2)} \right\}, \tag{4}$$

where

$$\mathbf{R} = \mathbf{r} - \mathbf{r}_0 - \frac{\mathbf{v}_0}{\beta}(1 - e^{-\beta t}) - \frac{\mathbf{F}_0}{m\beta}\left[t - \frac{1}{\beta}(1 - e^{-\beta t})\right],$$

$$\mathbf{V} = \mathbf{v} - \mathbf{v}_0 e^{-\beta t} - (\mathbf{F}_0/m\beta)(1 - e^{-\beta t}),$$

$$G = (kT/m)(1 - e^{-2\beta t}),$$

$$H = (kT/m\beta)(1 - e^{-\beta t})^2,$$

$$E = (kT/m\beta^2)(2\beta t - 3 + 4e^{-\beta t} - e^{-2\beta t}).$$

The statistical properties of the bivariate probability distribution can be readily calculated. The displacement and velocity functions, **R** and **V**, have a mean value of zero, a mean squared value of $\langle R^2 \rangle = 3E$ and $\langle V^2 \rangle = 3G$, and an average scalar product of $\langle \mathbf{R} \cdot \mathbf{V} \rangle = 3H$. This latter result indicates that the velocity and displacement are statistically correlated (i.e., $\langle (\mathbf{r} - \mathbf{r}_0) \cdot \mathbf{v} \rangle \neq \langle \mathbf{r} - \mathbf{r}_0 \rangle \cdot \langle \mathbf{v} \rangle$) with the dependence given by $\langle (\mathbf{r} - \mathbf{r}_0) \cdot \mathbf{v} \rangle = \langle \mathbf{r} - \mathbf{r}_0 \rangle \cdot \langle \mathbf{v} \rangle + 3H$.

Simulation of the particle trajectory through phase space is based entirely upon the bivariate probability distribution. Starting from an initial phase space location ($\mathbf{r}_0$, $\mathbf{v}_0$), the force on the particle $\mathbf{F}_0$ is calculated. A new set of velocity and position coordinates ($\mathbf{r}$, $\mathbf{v}$) is then chosen in accordance with the bivariate probability distribution. Methods for making this selection are discussed in the next section. Using the new location, the process is repeated for the duration of the simulation.

2.3. *Velocity and Displacement Equations*

The Gaussian function of Eq. (4) is uniquely defined by its first and second moments. Using these moments, a set of equations is readily obtained for the velocity and displacement change during the time step t. The equations are

$$\mathbf{v} = \mathbf{v}_0 e^{-\beta t} + \frac{F_0}{m\beta}(1 - e^{-\beta t}) + \mathbf{B}_1, \tag{5a}$$

$$\mathbf{r} = \mathbf{r}_0 + \frac{\mathbf{v}_0}{\beta}(1 - e^{-\beta t}) + \frac{\mathbf{F}_0}{m\beta}\left[t - \frac{1}{\beta}(1 - e^{-\beta t})\right] + \mathbf{B}_2, \tag{5b}$$

where $B_1 = B_1(t)$ and $B_2 = B_2(t)$ are random functions of time chosen from the bivariate Gaussian distribution with the properties

$$\langle \mathbf{B}_1 \rangle = \langle \mathbf{B}_2 \rangle = 0, \tag{5c}$$

$$\langle \mathbf{B}_1 \cdot \mathbf{B}_2 \rangle = 3H, \tag{5d}$$

$$\langle B_1^2 \rangle = 3G, \tag{5e}$$

$$\langle B_2^2 \rangle = 3E, \tag{5f}$$

and H, G, and E are given by Eq. (4).

Eqs. (5a) and (5b) have a linear dependence upon $\mathbf{r}_0$, $\mathbf{v}_0$, and $\mathbf{F}_0$ with nonlinear coefficients in time t. The nonlinear coefficients will not increase the computing time for problems with fixed time steps as they will have to be calculated only once at the beginning of the simulation. The random functions $\mathbf{B}_1$ and $\mathbf{B}_2$ are interdependent as expressed by Eq. (5d).

There are numerous methods by which the new phase space coordinates can be chosen from $w(\mathbf{r}, \mathbf{v}, t)$. Another method is to first select the new velocity from the independent velocity distribution function

$$w_1(\mathbf{v}, t) = \int w(\mathbf{r}, \mathbf{v}, t)\, d^3r. \tag{6a}$$

Again using the first and second moments, the velocity equation is

$$\mathbf{v} = \mathbf{v}_0 e^{-\beta t} + (\mathbf{F}_0/m\beta)(1 - e^{-\beta t}) + \mathbf{B}_1\,, \tag{7a}$$

where $\mathbf{B}_1$ is a random velocity change chosen from the Gaussian distribution with a mean value equal to zero and a mean squared value of

$$\langle B_1^2 \rangle = (3kT/m)(1 - e^{-2\beta t}).$$

With the new velocity selected, the new position is chosen from the conditional displacement distribution function

$$w_2(\mathbf{r}, t; v) = \frac{w(\mathbf{r}, \mathbf{v}, t)}{w_1(\mathbf{v}, t)}\,. \tag{6b}$$

The displacement equation is then

$$\mathbf{r} = \mathbf{r}_0 + \frac{1}{\beta}\left(\mathbf{v} + \mathbf{v}_0 - \frac{2\mathbf{F}_0}{m\beta}\right) \cdot \frac{(1 - e^{-\beta t})}{(1 + e^{-\beta t})} + \frac{\mathbf{F}_0}{m\beta}\, t + \mathbf{B}_2\,, \tag{7b}$$

where $\mathbf{B}_2$ is a random displacement chosen from a Gaussian distribution with a mean value of zero and a mean squared value of

$$\langle B_2^2 \rangle = \frac{6kT}{m\beta^2}\left[\beta t - 2\,\frac{(1 - e^{-\beta t})}{1 + e^{-\beta t}}\right].$$

The displacement is seen to have a linear dependence on the new velocity $\mathbf{v}$, as well as the old phase space coordinates $\mathbf{v}_0$ and $\mathbf{r}_0$ and the force $\mathbf{F}_0$. In contrast to Eqs. (5), the random functions $\mathbf{B}_1$ and $\mathbf{B}_2$ are independent, i.e., $\langle \mathbf{B}_1 \cdot \mathbf{B}_2 \rangle = 0$.

Obviously, another set of equations can be obtained by first selecting the new position and then the new velocity. In this case the equations of motion are

$$\mathbf{r} = \mathbf{r}_0 + \frac{\mathbf{v}_0}{\beta}(1 - e^{-\beta t}) + \frac{\mathbf{F}_0}{m\beta}\left[t - \frac{1}{\beta}(1 - e^{-\beta t})\right] + \mathbf{B}_1, \tag{8a}$$

$$\mathbf{v} = \mathbf{v}_0 \cdot (2\beta t e^{-\beta t} - 1 + e^{-2\beta t})/C + \beta[\mathbf{r} - \mathbf{r}_0](1 - e^{-\beta t})^2/C + \frac{\mathbf{F}_0}{m\beta}[\beta t(1 - e^{-2\beta t}) - 2(1 - e^{-\beta t})^2]/C + \mathbf{B}_2, \tag{8b}$$

where again $\mathbf{B}_1$ and $\mathbf{B}_2$ are independent random functions of time chosen from separate Gaussian distributions with the properties

$$\langle \mathbf{B}_1 \rangle = \langle \mathbf{B}_2 \rangle = \langle \mathbf{B}_1 \cdot \mathbf{B}_2 \rangle = 0,$$

$$\langle B_1^2 \rangle = \frac{3kT}{m\beta^2} C,$$

$$\langle B_2^2 \rangle = \frac{6kT}{m}[\beta t(1 - e^{-2\beta t}) - 2(1 - e^{-\beta t})^2]/C,$$

$$C = 2\beta t - 3 + 4e^{-\beta t} - e^{-2\beta t}.$$

Comparing Eqs. (5), (7), and (8), there appear to be three different sets of equations for the motion of the particles. However, these sets of equations are equivalent in the sense that they select the new phase space coordinates in accordance with the bivariate probability distribution $w(\mathbf{r}, \mathbf{v}, t)$. Therefore, the probability of a particular velocity and position change is governed by $w(\mathbf{r}, \mathbf{v}, t)$ and Eqs. (5), (7), and (8) are just different methods of sampling this distribution. The equivalence of these equations can be easily shown by deriving Eq. (5) from Eqs. (7) and (8). Using Eq. (7a) to replace $\mathbf{v}(t)$ in Eq. (7b) yields Eq. (5b) and using Eq. (8a) to replace $\mathbf{r}(t)$ in Eq. (8b) yields Eq. (5a).

As a demonstration of these methods, a number of simulations were conducted on a free particle ($\mathbf{F} = 0$). The statistical properties of a free particle can be calculated analytically for any length of time using Eq. (4) and compared with the simulation results. Using the dimensionless variables $\tau = \beta t$, $\mathbf{u} = (m/3kT)^{1/2}\mathbf{v}$, and $\mathbf{x} = \beta(m/3kT)^{1/2}\mathbf{r}$, the analytic results for the calculated properties are

$$\langle \mathbf{u}(\tau) \cdot \mathbf{u}(0) \rangle = e^{-\tau}, \tag{9a}$$

$$\langle [x(\tau) - x(0)]^2 \rangle = 2(\tau - 1 + e^{-\tau}), \tag{9b}$$

$$\langle \mathbf{u}(\tau) \cdot [\mathbf{x}(\tau) - \mathbf{x}(0)] \rangle = 1 - e^{-\tau}. \tag{9c}$$

Simulations were conducted using time steps ranging from 0.01 to 100. Each method produced trajectories whose average properties were in excellent agreement with the analytic results. Table I shows the results from two simulations in which Eqs. (7) and (8) were used and the time step was $\Delta\tau = 0.5$. Each simulation was run for a total of 100,000 trajectories.

TABLE I

	$\langle u(\tau) \cdot u(0) \rangle$			$\langle u(\tau) \cdot [x(\tau) - x(0)] \rangle$			$\langle [x(\tau) - x(0)]^2 \rangle$		
τ	I[a]	II[b]	III[c]	I	II	III	I	II	III
0.0	1.000	1.001	0.998	0.000	0.000	0.000	0.000	0.000	0.000
0.5	0.607	0.607	0.605	0.393	0.394	0.393	0.213	0.213	0.213
1.0	0.368	0.368	0.366	0.632	0.633	0.632	0.736	0.736	0.736
1.5	0.223	0.221	0.221	0.777	0.779	0.778	1.446	1.448	1.447
2.0	0.135	0.134	0.134	0.865	0.866	0.864	2.271	2.274	2.272
2.5	0.082	0.080	0.079	0.918	0.917	0.914	3.164	3.168	3.163
3.0	0.050	0.048	0.047	0.950	0.949	0.947	4.100	4.103	4.095
3.5	0.030	0.028	0.027	0.970	0.968	0.965	5.060	5.061	5.051
4.0	0.018	0.019	0.018	0.982	0.983	0.979	6.037	6.037	6.025
4.5	0.011	0.011	0.009	0.989	0.986	0.985	7.022	7.022	7.007
5.0	0.007	0.007	0.006	0.993	0.994	0.994	8.013	8.014	7.996
5.5	0.004	0.004	0.005	0.996	0.999	0.999	9.008	9.001	8.992
6.0	0.002	0.003	0.003	0.998	1.001	1.000	10.00	10.01	9.993
6.5	0.002	0.001	0.000	0.998	0.999	0.995	11.00	11.01	10.99
7.0	0.001	0.000	0.000	0.999	0.996	0.995	12.00	12.01	11.99
7.5	0.001	0.001	0.001	0.999	0.994	0.987	13.00	13.00	12.98
8.0	0.000	0.001	0.004	1.000	0.997	0.996	14.00	14.00	13.97

[a] I—Analytic results from Eqs. (9).
[b] II—Simulation results using Eqs. (7).
[c] III—Simulation results using Eqs. (8).

3. Generalized Langevin Equation

3.1. *Use of Memory Functions*

A more general form of the Langevin equation is obtained through the use of a memory function in the friction force term [9]. In this formalism, the friction force is proportional to a weighted average of the particle velocity taken over its past history with the weighting factor given by the memory function. The ordinary Langevin equation is the special case where the memory function is proportional to the Dirac delta function.

Using the memory function approach, the generalized Langevin equation is

$$m\dot{\mathbf{v}} = \mathbf{F} - m\int_{-\infty}^{t} M(t - t')\,\mathbf{v}(t')\,dt' + \mathbf{X}, \qquad t > -\infty, \tag{10a}$$

where m, t, $\mathbf{v}(t)$, and $\mathbf{F}(\mathbf{r}, t)$ are as defined in Eq. (2), $M(t)$ is the memory function, and $\mathbf{X}(t)$ is the random force. Equation (10a) is the stationary form of the generalized Langevin equation with the lower limit of the friction force integral extended to minus infinity rather than set equal to a specific initialization time. The autocorrelation function of the random force is related to the memory function by the fluctuation–dissipation theorem

$$\langle \mathbf{X}(t) \cdot \mathbf{X}(0) \rangle = 3mkTM(t) \tag{10b}$$

and the memory function is normalized so that

$$\int_0^\infty dt\, M(t) = \beta. \tag{10c}$$

Assuming that the statistical properties of the random force are governed by a Gaussian distribution function, then Eq. (10b) uniquely defines the properties of the random force.

Integrating Eq. (10a) by the method of Fourier–Laplace transforms yields the following equations for the particle velocity and position.

$$\mathbf{v}(t) = \frac{1}{m} \int_{-\infty}^{t} dt'\, \psi(t - t')\{\mathbf{F}(\mathbf{r}, t') + \mathbf{X}(t')\}, \tag{11a}$$

$$\mathbf{r}(t) = \mathbf{r}(-\infty) + \frac{1}{m} \int_{-\infty}^{t} dt'\, \phi(t - t')\{\mathbf{F}(\mathbf{r}, t') + \mathbf{X}(t')\}. \tag{11b}$$

In these equations $\psi(t) = \mathscr{L}^{-1}[(s + M\{s\})^{-1}]$, $M\{s\} = \mathscr{L}[M(t)]$, and $\phi(t) = \int_0^t dt'\, \psi(|\, t' \,|)$ where $|\, t \,|$ is the absolute value of t, $\mathscr{L}$ is the Laplace transform operator defined to be

$$\mathscr{L}[M(t)] = \int_0^\infty dt\, e^{-st} M(t), \tag{12}$$

and $\mathscr{L}^{-1}$ is the inverse Laplace transform operator.

The statistical properties of the free particle ($\mathbf{F} = 0$) dynamic behavior can be calculated from Eqs. (11a) and (11b) and the properties of the random force given by Eq. (10b) and (10c). For example, the velocity autocorrelation function is found to be (see Ref. [9])

$$\langle \mathbf{v}(t') \cdot \mathbf{v}(t'') \rangle = (3kT/m)\, \psi(|\, t' - t'' \,|). \tag{13a}$$

The displacement–velocity correlation function is

$$\langle \Delta r(t'; t) \cdot \mathbf{v}(t'') \rangle = (3kT/m)[\phi(t' - t'') - \phi(t' - t'' - t)] \tag{13b}$$

and the displacement autocorrelation function is

$$\langle \Delta\mathbf{r}(t';t)\cdot\Delta\mathbf{r}(t'';t)\rangle = (3kT/m)[\chi(t'-t''+t)-2\chi(t'-t'')+\chi(t'-t''-t)], \tag{13c}$$

where

$$\Delta\mathbf{r}(t';t)=\mathbf{r}(t')-\mathbf{r}(t'-t) \qquad \text{and} \qquad \chi(t)=\int_0^t dt'\,\phi(t').$$

The particle diffusion coefficient is [10]

$$D=\frac{1}{3}\int_0^\infty dt\langle \mathbf{v}(t)\,\mathbf{v}(0)\rangle = \frac{kT}{m\beta}. \tag{13d}$$

3.2. *Simulation Equations*

When the particle experienes additional interactions, it may not be possible to calculate the particle properties analytically and a numerical simulation becomes useful. As was the case with the ordinary Langevin equation, a velocity and displacement equation is sought which is restricted in the length of the time step only by the rate of change in the external force **F**.

Equations (11a) and (11b) provide a set of equations from which the particle trajectory through phase space can be calculated. Letting the time step be t and using the notation $\mathbf{v}_n=\mathbf{v}(nt)$ and $\Delta r_n=\mathbf{r}_n-\mathbf{r}_{n-1}$, the following equations are obtained for the velocity and displacement:

$$\mathbf{v}_n=\frac{t}{m}\sum_{i=-\infty}^{n-1}\psi_{n-i}\mathbf{F}_i+\mathbf{V}_n, \tag{14a}$$

$$\Delta\mathbf{r}_n=\frac{t}{m}\left\{\phi_1\mathbf{F}_{n-1}+\sum_{i=-\infty}^{n-2}\Delta\phi_{n-i}\mathbf{F}_i\right\}+\mathbf{R}_n, \tag{14b}$$

where $\mathbf{V}_n$ and $\mathbf{R}_n$ are Gaussian random deviates and the difference operator $\Delta\phi_n=\phi_n-\phi_{n-1}$ has been used in Eq. (14b). In obtaining these equations it was assumed that the force F could be considered to be constant during each time step.

The sequence of velocity and displacement random deviates $\{\mathbf{V}_n\}$ and $\{\mathbf{R}_n\}$ are described by a multivariate probability distribution. Their variance and covariance can be obtained from Eqs. (13a)–(13c) and are found to be

$$\langle\mathbf{V}_i\rangle=\langle\mathbf{R}_i\rangle=0, \tag{15a}$$

$$\langle\mathbf{V}_i\cdot\mathbf{V}_j\rangle=(3kT/m)\,\psi_{i-j}, \tag{15b}$$

$$\langle\mathbf{R}_i\cdot\mathbf{V}_j\rangle=(3kT/m)\,\Delta\phi_{i-j}, \tag{15c}$$

$$\langle\mathbf{R}_i\cdot\mathbf{R}_j\rangle=(3kT/m)\,\Delta^2\chi_{i-j}, \tag{15d}$$

where the difference operator $\Delta^2x_n=\chi_{n+1}-2\chi_n+\chi_{n-1}$ was used in Eq. (15d).

The random deviates $\mathbf{V}_n$ and $\mathbf{R}_n$ for any given time step are seen to be statistically correlated to the deviates at all other time steps. As a matter of convenience, it is desirable to express $\mathbf{V}_n$ and $\mathbf{R}_n$ in terms of statistically independent Gaussian random deviates. This can be done by using the weighted sums

$$\mathbf{V}_n = \sum_{i=-\alpha}^{n} \sigma_{n-i}\mathbf{Y}_i \,, \tag{16a}$$

$$\mathbf{R}_n = \sum_{i=-\infty}^{n} \{\rho_{n-i}\mathbf{Y}_i + \zeta_{n-i}\mathbf{Z}_i\}, \tag{16b}$$

where

$$\begin{aligned} \langle \mathbf{Y}_i \rangle &= \langle \mathbf{Z}_i \rangle = \langle \mathbf{Y}_i \cdot \mathbf{Z}_j \rangle = 0, \\ \langle \mathbf{Y}_i \cdot \mathbf{Y}_j \rangle &= \langle \mathbf{Z}_i \cdot \mathbf{Z}_j \rangle = \delta_{ij} \,, \end{aligned} \tag{17}$$

and δ_{ij} is the Dirac delta function. The weighting parameters $\{\sigma_n\}$, $\{\rho_n\}$, and $\{\zeta_n\}$ are defined by the following sets of equations:

$$\frac{3kT}{m}\psi_i = \sum_{j=0}^{\infty} \sigma_j\sigma_{i+j} \,, \qquad i = 0, \infty; \tag{18a}$$

$$\frac{3kT}{m}\Delta\phi_i = \sum_{j=0}^{\infty} \sigma_j\rho_{i+j} \,, \qquad i = 0, \infty; \tag{18b}$$

$$\frac{3kT}{m}\Delta^2\chi_i = \sum_{j=0}^{\infty} \{\rho_j\rho_{i+j} + \zeta_j\zeta_{i+j}\}, \qquad i = 0, \infty. \tag{18c}$$

The infinite sums in Eqs. (14), (16), and (18) present a computational difficulty to a numerical simulation. This obstacle can be overcome if it can be assumed that the velocity autocorrelation function $\psi(t)$ is essentially zero for sufficiently large values of t. Letting $\psi_i = 0$ for $i \geqslant N$, then $\sigma_i = 0$ for $i \geqslant N$ and $\Delta\phi_i = \Delta^2\chi_i = \rho_i = \zeta_i = 0$ for $i > N$. The remaining values of σ_i, ρ_i, and ζ_i can be calculated form Eq. (18) and the velocity and displacement can be calculated from Eqs. (14) and (16) with the summations limited to the weighting parameters with nonzero values.

The method for simulating the generalized Langevin equation is similar to the method previously presented for the ordinary Langevin equation except for the initialization conditions. In addition to defining the initial velocity, position, and external force on the particle, the values of these parameters at the previous N time steps must also be defined in order to calculate the new velocity and position. Calculation of the new coordinates can be done by specifying the initial $N + 1$ values of the random deviates Y_i and Z_i (see Eq. (16)) and the force F_i, and then retaining the past $N + 1$ values of these parameters as the simulation proceeds.

The approach described above presents a method for simulating the particle trajectory through phase space. However, if the force F and the desired particle

properties can be calculated from the particle trajectory in position space, it is not necessary to have knowledge of the time history of the particle velocity. In this case, the particle displacement can be calculated from the equation

$$\Delta \mathbf{r}_n = \frac{t}{m}\left\{\phi_1 \mathbf{F}_{n-1} + \sum_{i=n-N}^{n-2} \Delta\phi_{n-i}\mathbf{F}_i\right\} + \sum_{i=n-N}^{N} \sigma_{n-i}\mathbf{Z}_i\,, \tag{19}$$

where

$$\langle Z_i \rangle = 0,$$
$$\langle Z_i Z_j \rangle = \delta_{ij}\,,$$

and

$$\frac{3kT}{m}\Delta^2\chi_i = \sum_{j=0}^{N-i} \sigma_j \sigma_{i+j}\,, \qquad i = 0, N,$$

and the velocity can be neglected since it is not explicitly contained in Eq. (19). Using this approach will reduce the storage requirements by about a third of that required for a simulation in phase space and will also reduce the number of calculations per time step.

4. Exponential Memory Function Model

A numerical simulation of the generalized Langevin equation with any desired memory function can be accomplished by the general method presented in the previous section. Here another method is presented for the exponential memory function model. In this method the exponential memory function kernel is handled by introducing the acceleration as another stochastic variable [2, 11]. Consequently, the new coordinate values (**r**, **v**, **a**) depend only on the values at the previous time step as was the case with the ordinary Langevin equation.

The generalized Langevin equation with an exponential memory function can be obtained from Eq. (10) by setting $M(t) = \alpha\beta e^{-\alpha t}$. The random force can be conveniently expressed as

$$\mathbf{X}(t) = \alpha\beta m \int_{-\infty}^{t} dt'\, e^{-\alpha(t-t')}\mathbf{Y}(t'), \tag{20a}$$

where $\mathbf{Y}(t)$ is also a Gaussian random function whose autocorrelation function is

$$\langle \mathbf{Y}(t') \cdot \mathbf{Y}(t'') \rangle = 6\,\frac{kT}{m\beta}\,\delta(t' - t''). \tag{20b}$$

Using this expression for the random force and introducing the acceleration as another stochastic variable, the Langevin equation can be written as

$$\dot{\mathbf{a}}(t_0 + t) = \dot{\mathbf{a}}(t_0)\, e^{-\alpha t} + (1/m)[\mathbf{F}(\mathbf{r}, t_0 + t) - F(\mathbf{r}, t_0)\, e^{-\alpha t}]$$
$$- \alpha\beta \int_0^t dt'\, e^{-\alpha(t-t')}[\mathbf{v}(t_0 + t') - \mathbf{Y}(t_0 + t')]. \tag{20c}$$

The $\mathbf{a}(t_0)$ and $\mathbf{F}(\mathbf{r}, t_0)$ terms have been used to replace the integral from minus infinity to t_0 so that the acceleration is independent of its past history prior to the time t_0. The free particle ($\mathbf{F} = 0$) properties of the exponential memory function model have been described by Berne *et al.* [12] and Friedman [13] who points out the relation to certain measurable coefficients. The velocity autocorrelation function is

$$\langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle = \frac{3kT}{m}\, e^{-(\alpha/2)t} \left[\cos(\gamma t) + \frac{\alpha}{2\gamma} \sin(\gamma t)\right], \tag{21}$$

where $\gamma^2 = \alpha\beta - \alpha^2/4$ and $t \geqslant 0$.

An equation for the particle velocity in terms of the random force and the initial velocity, acceleration, and external force is obtained by integrating Eq. (20c) using Laplace transforms and by assuming that the external force is essentially constant during the period of the time step. A second integration yields an equation for the particle displacement. The acceleration equation is obtained by differentiating the velocity equation. From these three equations, the trivariate distribution function $W(\mathbf{r}, \mathbf{v}, \mathbf{a}, t)$ can be derived using Markoff's method [1, 14, 15]. This function governs the probability that a particle, initially located at $\mathbf{r}_0$, with velocity $\mathbf{v}_0$, while accelerating at the rate $\mathbf{a}_0$, and experiencing the external force $\mathbf{F}_0$, will be located at $\mathbf{r}$ with velocity $\mathbf{v}$ and acceleration $\mathbf{a}$ at time $\mathbf{t}$.

W($\mathbf{r}$, $\mathbf{v}$, $\mathbf{a}$, t) is Gaussian and therefore is uniquely defined by the moments

$$\langle \mathbf{A} \rangle = \langle \mathbf{V} \rangle = \langle \mathbf{R} \rangle = 0,$$

$$\langle A^2 \rangle = \epsilon \int_0^t dt'\, \psi^2(t'), \qquad \psi(t) = \alpha\beta e^{-(\alpha/2)t} \left[\cos(\gamma t) - \frac{\alpha}{2\gamma} \sin(\gamma t)\right],$$

$$\langle V^2 \rangle = \epsilon \int_0^t dt'\, \phi^2(t'), \qquad \phi(t) = \int_0^t dt'\, \psi(t'),$$

$$\langle R^2 \rangle = \epsilon \int_0^t dt'\, \chi^2(t'), \qquad \chi(t) = \int_0^t dt'\, \phi(t'), \tag{22}$$

$$\langle \mathbf{A} \cdot \mathbf{V} \rangle = \epsilon \int_0^t dt'\, \psi(t')\, \phi(t'),$$

$$\langle \mathbf{A} \cdot \mathbf{R} \rangle = \epsilon \int_0^t dt'\, \psi(t')\, \chi(t'),$$

$$\langle \mathbf{V} \cdot \mathbf{R} \rangle = \epsilon \int_0^t dt'\, \phi(t')\, \chi(t'),$$

where

$$\mathbf{A} = \mathbf{a} - \frac{1}{\alpha\beta}\,\mathbf{a}_0\psi(t) + \mathbf{v}_0\phi(t) - \frac{1}{m\beta}\,\mathbf{F}_0\phi(t),$$

$$\mathbf{V} = \mathbf{v} - \mathbf{v}_0[1 - \chi(t)] - \frac{1}{\alpha\beta}\,\mathbf{a}_0\phi(t) - \frac{1}{m\beta}\,\mathbf{F}_0\chi(t),$$

$$\mathbf{R} = \mathbf{r} - \mathbf{r}_0 - \frac{1}{\alpha\beta}\,\mathbf{a}_0\chi(t) - \mathbf{v}_0[t - \Omega(t)] + \frac{1}{m\beta}\,\mathbf{F}_0\Omega(t),$$

and $\epsilon = 6kT/m\beta$ and $\Omega(t) = \int_0^t dt'\,\chi(t')$. The notation of Section 2 is used here so tjat a subscript 0 on the variablies $\mathbf{r}_0$, $\mathbf{v}_0$, $\mathbf{a}_0$, and $\mathbf{F}_0$ indicates that it is evaluated at time t_0 and the lack of a subscript 0 indicates that it is evaluated at time $t_0 + t$.

Equations (22) provide the information for simulating the particle acceleration, velocity, and position. The new coordinate values ($\mathbf{a}$, $\mathbf{v}$, $\mathbf{r}$) are seen to be functions of the initial coordinate values ($\mathbf{a}_0$, $\mathbf{v}_0$, $\mathbf{r}_0$) and the time step t, and therefore are independent of the particle's history prior to the initial time t_0.

5. Conclusion

A Monte Carlo simulation technique was presented for solving the generalized Langevin equation for a Brownian particle in the presence of an arbitrary external force. The method is sufficiently general so as to be independent of the choice of the memory function used to described the friction and random forces. The particle trajectory in phase space is simulated by a sequence of randomly chosen changes in the particle velocity and position. The method also allows the possibility of a simulation solely in position space without ever having to calculate the particle velocity.

Special attention was given to the Dirac delta (ordinary Langevin equation) and the exponential memory function models. Simulation techniques were derived for these models which require less information storage than does the general simulation method. In these methods the new particle coordinates depend only on the coordinate values at the previous time step and not on the entire past history of the particle trajectory in phase space.

All of the simulation techniques presented in this paper allow considerable freedom in selecting the size of the time step. The length of the time step between successive displacements is restricted only by the rate of change in the external force. Consequently, within the constraints due to the external force and the specific needs of the desired solution, the time step may be chosen to be any size relative to the free particle velocity autocorrelation function decay time.

Acknowledgments

One of us (D.L.E.) is grateful to Dr. C. Moser, Director of the Centre Européen de Calcul Atomique et Moléculaire, for an invitation to the CECAM workshop on models for protein dynamics (Orsay,

France, May–July 1976) where this study was initially conducted. This work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore Laboratory under Contract W-7405-ENG-48.

REFERENCES

1. S. CHANDRASEKHAR, *Rev. Mod. Phys.* **15** (1943), 1.
2. M. C. WANG AND G. E. UHLENBECK, *Rev. Mod. Phys.* **17** (1945), 323.
3. J. M. HAMMERSLEY AND D. C. HANDSCOMB, "Monte Carlo Methods," Wiley, New York, 1964.
4. N. P. BUSLENKO, D. I. GOLENKO, YU. A. SHREIDER, I. M. SOBAL, AND V. G. SRAGOVICH, "The Monte Carlo Method" (English edition, Yu. A. Shreider, Ed.), Pergamon, New York, 1966.
5. P. TURQ, F. LANTELME, AND H. L. FRIEDMAN, *J. Chem. Phys.* **66** (1977), 3039.
6. J. H. WEINER AND R. E. FORMAN, *Phys. Rev. B* **10** (1974), 315.
7. D. L. ERMAK, *J. Chem. Phys.* **62** (1975), 4189, 4197.
8. J. D. DOLL AND D. R. DION, *Chem. Phys. Lett.* **74** (1975), 386.
9. R. KUBO, *Rep. Progr. Phys.* **29** (1966), 255.
10. F. REIF, "Fundamentals of Statistical and Thermal Physics," pp. 488, 576, McGraw–Hill, New York/London, 1965.
11. M. SHUGARD, J. C. TULLY, AND A. NITZAN, *J. Chem. Phys.* **66** (1977), 2534.
12. B. J. BERNE, J. P. BOON, AND S. A. RICE, *J. Chem. Phys.* **45** (1966), 1086.
13. H. L. FRIEDMAN, *J. Chim. Phys.* (19° RCP) (1969), 75.
14. A. A. MARKOFF, *Wahrscheinlichkeitsrechnung*, para. 16 and 33, Leipzig, 1912.
15. A. ISIHARA, "Statistical Physics," p. 184, Academic Press, New York/London, 1971.