Interrelations between the Langevin, generalized Langevin, and Fokker–Planck dynamics

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Abstract

The phenomenological description of the statistical dynamics of a physical system in terms of stochastic models is very familiar. The main advantage of this approach is that it allows one to reduce infinite-dimensional problems to much more tractable few-dimensional problems. The aim of this short review is to outline the interrelations between four mesoscopic kinetic equations underlying many (if not most) stochastic models. These are the Langevin equation (LE), generalized Langevin equation (GLE), Fokker–Planck equation (FPE), and Smoluchowski equation (SE).

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I. INTRODUCTION

The importance of solvent effects on the kinetics of chemical reactions is the topic of particular interest in chemical physics. Much of the theoretical work on these effects relies on stochastic models,[1–3] the most successfully and extensively used being the Langevin model. These models prove to be especially useful in the case of systems of high complexity, where the explicit consideration of all particles would demand very costly resources, because they allow simulations of solute trajectories without any explicit consideration of the solvent. In the Langevin approach, the reactive event is idealized by the classical motion of a Brownian particle in phase space, under the influence of a one-dimensional potential of mean force $U(x)$. The crossing of the particle over the barrier in the potential, followed by subsequent localization in the opposite well, constitutes reaction. This approach was originally proposed by Kramers[4] for systems where the dynamics of the solvent is much faster than that of the solute. The latter condition, however, is not always met in experiments or molecular dynamics simulations. Therefore, GLE's proposed by Zwanzig[5] and Mori[6] have been introduced to include the important case of comparable time scales.[7] Lastly, since both LE's and GLE's are rather difficult to treat because of their stochastic nature, an alternative approach to the statistical dynamics based on the Fokker–Planck description has also been actively used.[1]

II. LANGEVIN EQUATION FOR ONE-DIMENSIONAL MARKOVIAN BROWNIAN MOTION

In the simplest one-dimensional case, the classical motion of a Brownian particle, under the influence of a potential of mean force $U(x)$, is described by two coupled LE's that in mass-weighted variables read

$$\dot{x} = v, \qquad \dot{v} = -\gamma v - U'(x) + f(t). \tag{2.1}$$

Here the dot denotes the time derivative, and the prime the derivative with respect to the coordinate. The medium, which is modeled in this approach by a thermal bath, influences

the particle by a velocity-proportional damping force $-\gamma v$ and a Gaussian white random force $f(t)$, the former extracting and the latter supplying energy. The random force is normalized to

$$\langle f(t)\rangle = 0, \qquad \beta\langle f(t)f(s)\rangle = 2\gamma\delta(t-s), \tag{2.2}$$

where γ is the friction coefficient and β the inverse energy available from the thermal bath, $\beta^{-1} = k_B T$. Clearly, the dynamics governed by Eqs. (2.1) and (2.2) is Markovian. The latter means that the probability to find the particle at point (x, v) at time $t_0 + \Delta t$ is determined entirely by the knowledge of the most recent condition $(x(t_0), v(t_0))$, i.e., it does not depend on the prehistory.

In the limit of strong friction, the particle coordinate x undergoes an overdamped (creeping) motion, and the velocity v may be eliminated adiabatically from Eq. (2.1):

$$\dot{x} = -\gamma^{-1}U'(x) + \gamma^{-1}f(t). \tag{2.3}$$

In order for this equation to hold, Kramers[4] requires that $U'(x)$ be almost constant on the thermal length scale $1/(\gamma\sqrt{\beta})$.

III. FOKKER-PLANCK EQUATION FOR ONE-DIMENSIONAL MARKOVIAN BROWNIAN MOTION

As noted, compared to various well-established techniques available for integrating ordinary and partial differential equations, the methods for dealing with Langevin dynamics are considerably less well developed because of the stochastic nature of Eqs. (2.1) and (2.2). Therefore, a stochastically equivalent Fokker–Planck description of the Markovian Langevin dynamics, Eqs. (2.1) and (2.2), has been used to avoid this problem. The description is based on a two-dimensional FPE, which governs the time evolution of the probability density of finding the particle at time t at the phase space point $x,\ v$

$$\partial_t P(x,v,t) = \left[-v\partial_x + U'(x)\partial_v + \gamma\partial_v\left(v + \beta^{-1}\partial_v\right)\right] P(x,v,t). \tag{3.1}$$

Due to detailed balance the stationary solution of the Fokker-Planck operator is given by the Maxwell-Boltzmann distribution

$$P_{\rm eq}(x,v) = (\beta/2\pi)^{1/2} Z^{-1} \exp\left\{-\beta\left[\tfrac{1}{2}v^2 + U(x)\right]\right\}, \tag{3.2}$$

with Z being the partition function

$$Z = \int_{-\infty}^{\infty} dx \ \exp\left[-\beta U(x)\right]. \tag{3.3}$$

Next, in the strong friction limit where the reduced description in terms of Eq. (2.3) is justified, the time evolution of the corresponding reduced probability

$$P(x,t) = \int_{-\infty}^{\infty} dv \ P(x,v,t) \tag{3.4}$$

is governed by the SE

$$\partial_t P(x,t) = \gamma^{-1}\partial_x \left[U'(x) + \beta^{-1}\partial_x\right] P(x,t). \tag{3.5}$$

Higher-order corrections to the SE in powers of γ^{-1} have also been derived.[3] For the lowest-order correction one still obtains a SE but with an effective, γ-dependent potential and an x- and γ-dependent diffusion term,

$$\partial_t P(x,t) = \gamma^{-1}\partial_x \left[1 + \gamma^{-2}U''(x)\right]\left[U'(x) + \beta^{-1}\partial_x\right] P(x,t). \tag{3.6}$$

Note that the next correction is of order γ^{-5} and contains derivatives whose degree is higher than second order, thereby breaking the Fokker–Planck form.

IV. GENERALIZED LANGEVIN EQUATION

For many important applications in physics and chemistry, the Markovian assumption of white noise and instantaneous friction is not adequate. This happens when the motion of the particles of the system depends on the history of the system, and not just on the instantaneous values of position and velocity. In such a case, the conventional Brownian picture based on Eqs. (2.1) and (2.2) should be replaced by the generalized Langevin

description, which takes into account the microscopic time scales of the bath. The GLE dynamics is characterized by a finite correlation function of the random force and a memory kernel, i.e. by a retarded, instead of the instantaneous, friction force of an ordinary LE, thus allowing a flexible description of the influence of an environment in thermal equilibrium that may have a long memory.

In the simplest one-dimensional case, the GLE has the form[5]

$$\dot{x} = v, \qquad \dot{v} = -U'(x) - \int_0^t ds\ \gamma(t-s)v(s) + f(t), \tag{4.1}$$

where the time-dependent friction kernel or memory function $\gamma(t)$ represents the response of the thermal bath (solvent) from the past to the present. This kernel is directly related to the correlation function of the Gaussian zero mean random force $f(t)$ by the second fluctuation dissipation theorem reading

$$\gamma(t-s) = \beta\langle f(t)f(s)\rangle. \tag{4.2}$$

The latter property ensures that the equilibrium distribution will be of the standard Maxwell–Boltzmann form, Eq. (3.2). Last, the static friction coefficient γ, which characterizes the overall magnitude of the solvent damping, is defined by the zero-frequency Laplace transform of $\gamma(t)$:

$$\gamma = \int_0^\infty dt\ \gamma(t). \tag{4.3}$$

Both the friction kernel $\gamma(t)$ and the potential of mean force $U(x)$ are typically determined either from experiment[8] or by analysis of full molecular dynamics simulations.[9,10] Note that the memory friction must be a positive definite function, i.e., it must have a positive Fourier transform (Wiener–Khinchin theorem). In all other respects it may be an arbitrary function. In theoretical calculations $\gamma(t)$ is often assumed to have an exponential

$$\gamma(t) = (\gamma/\tau)\exp(-t/\tau), \tag{4.4}$$

or a Gaussian form

$$\gamma(t) = (2\gamma/\sqrt{\pi}\tau)\exp(-t^2/\tau^2), \tag{4.5}$$

with τ being the correlation time of the random force.

Finally we note that in the strong friction limit, the non-Markovian dynamics, Eq. (4.1), can be reduced to the Smoluchowski dynamics, Eq. (2.3), whatever the particular form of the friction kernel is. However, the latter holds true if the time scale on which $\gamma(t)$ decays to zero (τ in both above examples) is independent of the static friction γ. Otherwise, large deviations between the non-Markovian and Smoluchowski dynamics may be observed even in the limit $\gamma \to \infty$ (see, e.g. a series of papers by Straub, Borkovec, and Berne[11]).

V. THREE DIFFERENT REPRESENTATIONS OF THE GLE INCLUDING THOSE BASED ON THE LANGEVIN AND FOKKER-PLANCK DYNAMICS

Unfortunately, the GLE is just a compact (purely formal) representation of the non-Markovian dynamics in the sense that there is no direct method for treating Eq. (4.1). The main difficulty is the sampling of the random force $[f(t)]$ such that it obeys the fluctuation dissipation relation, Eq. (4.2). The only way to overcome this obstacle is to transform the GLE to a stochastically equivalent form which is simpler to treat. There have been several approaches to this, three of which will be specifically discussed in the following.

A. The Hamiltonian representation of the GLE

The first approach, which was put forward by Rice,[12] involves expanding the random force in a Fourier series. The idea underlying this approach is the observation that the non-Markovian stochastic dynamics, Eq. (4.1), is equivalent to the dynamics of a system-bath Hamiltonian, which reads[5]

$$H = \frac{1}{2}p_x^2 + U(x) + \frac{1}{2}\sum_i \left[p_i^2 + (\omega_i y_i - g_i x/\omega_i)^2\right], \tag{5.1}$$

where the system coordinate x is linearly coupled to a bath of harmonic oscillators with mass-weighted coordinates y_i, frequencies ω_i, and coupling constants g_i. Hamilton's equations of

motion for the bath oscillators are easily solved analytically leading to Eq. (4.1) with the following identification:

$$\gamma(t) = \sum_i \frac{g_i^2}{\omega_i^2} \cos(\omega_i t) \tag{5.2}$$

and

$$f(t) = \sum_i a_i \cos(\omega_i t) + b_i \sin(\omega_i t), \tag{5.3}$$

where $a_i = g_i[y_i(0) - g_i x(0)/\omega_i^2]$ and $b_i = g_i p_i(0)/\omega_i$.

Equations (5.2) and (5.3) indicate how one can sample the random force $[f(t)]$ for a given memory friction $[\gamma(t)]$. If the friction kernel $\gamma(t)$ is a periodic function with period T, then Eq. (5.2) is just its cosine Fourier expansion. The frequencies ω_i are integer multiples of the fundamental frequency, $\omega_i = 2\pi i/T$, and the expansion coefficients g_i are just the appropriate Fourier expansion coefficients. Accordingly, the random force can be replaced by uncorrelated random initial conditions for each oscillator with the Fourier expansion coefficients, a_i and b_i, sampled from independent Gaussian distributions whose widths are determined from the Fourier cosine transform of the friction kernel.[12] The advantage of this approach is that it can be applied equally well to any memory function for which $f(t)$ is a Gaussian stationary random variable. A difficulty lies in the fact that the friction kernel $\gamma(t)$ appearing in Eq. (4.1) is not periodic but is rather a decaying function. Therefore care must always be taken not to extend the dynamics beyond the chosen value of the period T, because beyond this time one is following the dynamics of a system which is considerably different from the continuum limit, Eq. (4.1).

Numerical integration of the GLE using the above-mentioned algorithm consists of two steps. In the first step, we divide the time interval T into N discrete time steps Δt, truncate the Fourier series representation of $f(t)$ at $i = N$, and generate a sequence of values $\{f_i\}$ at the corresponding times $\{i\Delta t\}$. High efficiency is achieved by making use of the fast Fourier transform.[14] In the second step of the calculation, we include the particular realization of $f(t)$ in a finite difference representation of the GLE (usually using some version of a Verlet

algorithm[9]) to integrate the equation of motion. This approach has been used by many authors,[13–18] though it has its limitations. Integrators so constructed are at most of the second order in Δt and hence do not offer the virtue of good stability for moderately large time steps. The latter means that even when a relatively small number N of the bath oscillators are involved accurate results with these integrators may be obtained only over very short times. Additionally, for large bath correlation times ($\tau \gg 1$) as well as in both limits of weak ($\gamma \ll 1$) and strong ($\gamma \gg 1$) damping where calculations over long times are generally required, one needs to use an increasingly larger set of oscillators, and at some point it becomes prohibitively expensive.

An alternative to the Fourier expansion method for generating a random force sequence has been suggested by Smith and Harris.[19] Within its scope the random force is modeled as an autoregressive process of order N with a Gaussian white noise source. A set of N autoregressive parameters are obtained from the friction kernel by inverting a set of Yule–Walker equations. However, this method is formally equivalent to and more difficult to implement than the Fourier expansion method.

B. The Langevin representation of the GLE

Another way of dealing with a non-Markovian (GLE) process is to add a sufficient number of supplementary variables such that the resulting process is Markovian in the enlarged phase space.[20] In the case of the GLE with the exponential memory kernel (4.4), this is achieved by introducing just one additional variable,[11]

$$y = -\int_0^t ds\ \gamma(t-s)v(s) + f(t), \tag{5.4}$$

and rewriting the random force as

$$f(t) = \tau^{-1}\int_0^t ds\ e^{-(t-s)/\tau}F(s). \tag{5.5}$$

Now the new random force $F(t)$ is white, that is,

$$\langle F(t)F(s)\rangle = 2\gamma\beta^{-1}\delta(t-s), \tag{5.6}$$

thus resulting in a set of Markovian LE's

$$\begin{aligned} \dot{x} &= v, \\ \dot{v} &= -U'(x) + y, \\ \tau\dot{y} &= -\gamma v - y + F(t). \end{aligned} \tag{5.7}$$

In the case of an arbitrary friction kernel, the GLE can be transformed to a hierarchy of LE's using Mori's technique.[6] Within its scope the Laplace transform of the friction kernel, $\hat{\gamma}(z)$, is assumed to have a continued fraction expansion

$$\hat{\gamma}(z) = \int_0^\infty dt\ e^{-tz}\gamma(t) = \frac{\eta_1}{z+\gamma_1+}\ \frac{\eta_2}{z+\gamma_2+}\cdots\frac{\eta_m}{z+\gamma_m+}\cdots, \tag{5.8}$$

where the parameters satisfy $\eta_i > 0,\ \gamma_i \geq 0$. Truncation of the continued fraction after its first m terms yields an approximation to the friction kernel which is a sum of m exponentials. Then, introducing m auxiliary variables $\mathbf{y} = (y_1, \ldots, y_m)$, the one-dimensional non-Markovian process (4.1) is approximated by a $(m+2)$-dimensional Markov process reading[20]

$$\begin{aligned} \dot{x} &= v, \\ \dot{v} &= -U'(x) + y_1, \\ \dot{y}_1 &= -\eta_1 v - \gamma_1 y_1 + y_2 + F_1(t), \\ \dot{y}_2 &= -\eta_2 y_1 - \gamma_2 y_2 + y_3 + F_2(t), \\ &\cdots \\ \dot{y}_m &= -\eta_m y_{m-1} - \gamma_m y_m + F_m(t). \end{aligned} \tag{5.9}$$

The random forces $F_1, \ldots, F_m$ appearing in Eq. (5.9) are uncorrelated zero mean Gaussian white noises

$$\langle F_i(t)F_j(0)\rangle = 2\beta^{-1}\delta_{ij}\gamma_i\pi_i\delta(t), \tag{5.10}$$

where δ_{ij} stands for the Kronecker symbol and

$$\pi_i = \prod_{j=1}^{i} \eta_j. \tag{5.11}$$

The principal advantage of this approach over the Fourier series expansion method is that it allows one to efficiently treat situations when the friction kernel can be presented by a finite sum of exponentials. In such a case, the number of auxiliary variables, m, is not related to the number of time steps required, N, and calculations over arbitrarily long times can be performed. Unfortunately, for arbitrary friction kernels, one needs to choose m very large to obtain accurate results at long times, although accurate results can still be obtained over short times with a relatively small value of m.

Numerical solution of Eq. (5.9) is straightforward. At each integration step one generates via a random number generator the Gaussian random forces and include them into a finite difference representation of the LE's based on a Verlet algorithm.[9] Clearly, integrators of this kind all have flaws that are inherent to low order algorithms. An alternative is to construct a higher order propagation scheme by integrating Eq. (5.9) over the time step Δt and expanding the force term $-U'[x(t)]$ in a Taylor series about the prepoint. The resulting stochastic equations can then be solved iteratively to any desired order of accuracy in Δt.[21–24] Since the deterministic terms so obtained are just the Taylor expansion for the deterministic equations of motion, the integrator appears to be rather unstable. High stability is achieved by replacing the Taylor expansion for the deterministic part of the equations of motion by a corresponding order Runge–Kutta algorithm in the full iterative solution.[24]

The principal disadvantage of these high order integrators is that in the iterative procedure they introduce truncations in the expansion of the second cumulants of the random forces at orders higher than 1 which may become negative at a large time step. In order to overcome this obstacle, one must keep the time step Δt small enough such that the second cumulants of the random forces are positive for all reasonable $x(t)$. Otherwise, a drift will appear in calculated quantities, effectively reducing the accuracy of the integrator to first order.[23]

C. The Fokker–Planck representation of the GLE

An alternative to the Langevin representation of non-Markovian dynamics is the expanded variable FPE. For an exponential friction kernel [see Eq. (5.7)], the FPE for the joint probability distribution of the three variables $x,\ v$ and y can be written in an explicit form as

$$\partial_t P(x,v,y,t) = \left\{-v\partial_x + [U'(x)-y]\partial_v + \tau^{-1}\partial_y(\gamma v + y) + \gamma\tau^{-2}\beta^{-1}\partial_{yy}^2\right\} P(x,v,y,t). \quad (5.12)$$

Similarly, in the case of an arbitrary friction kernel, Eq. (5.9), the corresponding FPE reads

$$\frac{\partial}{\partial t}P(x,v,\mathbf{y},t) = LP(x,v,\mathbf{y},t), \quad (5.13)$$

where $P(x,v,\mathbf{y},t)$ is the probability density and

$$\begin{aligned} L = &-\frac{\partial}{\partial x}v + \frac{\partial}{\partial v}[U'(x)-y_1] \\ &+\frac{\partial}{\partial y_1}\left(\eta_1 v + \gamma_1 y_1 - y_2 + \beta^{-1}\gamma_1\pi_1\frac{\partial}{\partial y_1}\right) \\ &+\frac{\partial}{\partial y_2}\left(\eta_2 y_1 + \gamma_2 y_2 - y_3 + \beta^{-1}\gamma_2\pi_2\frac{\partial}{\partial y_2}\right) + \cdots \\ &+\frac{\partial}{\partial y_m}\left(\eta_m y_{m-1} + \gamma_m y_m + \beta^{-1}\gamma_m\pi_m\frac{\partial}{\partial y_m}\right) \end{aligned} \quad (5.14)$$

denotes the Fokker–Planck operator. Since the noise in the GLE (4.1) obeys the fluctuation dissipation theorem, Eq. (4.2), the above-mentioned FPE possesses the following Boltzmann-type equilibrium distribution (within a normalization constant)

$$P_{\rm eq}(x,v,\mathbf{y}) \propto \exp[-\beta\varphi(x,v,\mathbf{y})], \quad (5.15)$$

$$\varphi(x,v,\mathbf{y}) = U(x) + \tfrac{1}{2}\left(v^2 + y_1^2/\pi_1 + \cdots + y_m^2/\pi_m\right),$$

which reduces, after integration over the additional variables y_i, to the standard Maxwell–Boltzmann form, Eq. (3.2).

Traditional methods of mathematical physics such as basis set expansion and distribution function propagation schemes have proven to be extremely valuable for treating FPE's.

These methods are unconditionally stable and do not suffer from statistical errors. However, their storage requirements and execution time grow exponentially with the number of auxiliary variables needed to represent the system. With the present day computers, the utility of the standard techniques is restricted to $m \leq 2$; while for systems with $m > 2$ some approximations must be involved. An exception to this rule of thumb can be achieved if one uses a short time propagator[22,25] in conjunction with Monte Carlo integration[26] and it is on this type of approach that we have recently based our new integrator.[27] The most appealing feature of this approach, which falls in the category of path integral methods, is that it avoids using high-dimensionality transition matrices and distribution function vectors and thus allows one to treat multidimensional Fokker–Planck processes without introducing uncontrolled approximations.

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