Comments on a paper by Straub, Borkovec, and Berne

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The paper referred to in the title, in J. Chem. Phys. **84**, 1788 (1986), presented results of computer simulations of non-Markovian barrier crossing dynamics, and compared these results with various theoretical predictions. One comment made here is that the observed limited applicability of the Grote–Hynes theory can be explained by singular perturbation theory. The other comment concerns the importance of a second constant of the motion when the non-Markovian friction has a very long relaxation time.

Straub, Borkovec, and Berne[1] (SBB) recently presented the results of a large-scale numerical simulation of a non-Markovian barrier crossing problem. They compared their results with the predictions of several theories, and concluded that the energy diffusion theory[2] worked well at very small friction, the Grote–Hynes (GH) theory[3] worked well for a limited intermediate range of friction, and the observed behavior at very large friction was not predicted correctly by any current theory. (The precise meaning of "very large friction" will be discussed later.)

Two comments about their conclusions are made here. First, it is argued that the GH theory is expected to be valid only for the limited range of intermediate friction in which SBB actually find agreement with their simulations. The argument is based on use of singular perturbation theory to find the smallest eigenvalue of the Fokker–Planck equation that describes the computer simulations. Second, it is observed that in the very large friction region where none of the standard theories work, the simulated system should be treated by a diffusion equation involving two variables, the energy and another dynamical quantity, both of which are constants of the motion in their "infinite friction" limit.

SBB studied Brownian motion in a potential $U(x)$ having two wells separated by a high barrier. They simulated non-Markovian friction and noise by means of a Markovian three-variable system (suggested by Marchesoni and Grigolini[4]) involving the coordinate x, the velocity v, and an auxiliary variable z,

$$\frac{dx}{dt} = v\,,$$

$$\frac{dv}{dt} = -U'(x) + z\,,$$

$$\frac{dz}{dt} = -(1/\alpha)v - [1/(\alpha\gamma)]z + \xi(t)\,.$$

The Gaussian noise $\xi(t)$ is delta correlated,

$$\langle \xi(0)\xi(t)\rangle = [2/(\alpha^2\beta\gamma)]\delta(t)\,.$$

This set of three equations is, of course, equivalent to the more familiar non-Markovian two-variable Langevin equation

$$\frac{dx}{dt} = v\,,$$

$$\frac{dv(t)}{dt} = -U'[x(t)] - \int_0^t dt'\zeta(t-t')v(t') + R(t)\,,$$

in which the friction memory function $\zeta(t)$ is given by

$$\zeta(t) = (1/\alpha)\exp[-t/(\alpha\gamma)]\,.$$

Then γ is the static friction constant and $\alpha\gamma$ is the correlation time of the nonwhite noise $R(t)$.

While nonlinear Langevin equations are quite easy to use for computer simulations, they are very hard to treat analytically. For mathematical analysis, it is usually much more practical to use the corresponding Fokker–Planck equation. The three-variable Langevin equation used by SBB is Markovian, so that it is easy to write down the corresponding Fokker–Planck equation (referred to in the following as FP3) for the probability density $f(x,v,z;t)$:

$$\frac{\partial f}{\partial t} = -v\frac{\partial f}{\partial x} + [U'(x) - z]\frac{\partial f}{\partial v} + \frac{1}{\alpha}v\frac{\partial f}{\partial z} + \frac{1}{\alpha^2\beta\gamma}\frac{\partial}{\partial z}\left(\frac{\partial f}{\partial z} + \beta\alpha z f\right),$$

or, in brief, $\partial f/\partial t = \mathcal{L}f$.

This should be contrasted with the more familiar FP2 for a two-variable Markovian Langevin equation,

$$\frac{\partial f}{\partial t} = -v\frac{\partial f}{\partial x} + U'(x)\frac{\partial f}{\partial v} + \gamma kT\frac{\partial}{\partial v}\left(\frac{\partial f}{\partial v} + \beta v f\right).$$

Attempts to eliminate the variable z from FP3 lead to a non-Markovian form of FP2 that can be trusted only in very limited circumstances. This is analogous to the familiar problem of going from a Markovian FP2 to the corresponding non-Markovian Smoluchowski or diffusion equation. It seems best to stay with the three-variable equation.

The reaction rate associated with barrier crossing can be related to eigenvalues of FP3. The (right) eigenfunctions are solutions of

$$\mathcal{L}\psi_j = -\lambda_j\psi_j\,.$$

The eigenvalues are ordered so that increasing j corresponds to increasing magnitude of λ_j. The equilibrium solution

$$f_e(x,v,z) = \exp\{-\beta[v^2/2 + U(x) + \alpha z^2/2]\}$$

is in fact stationary to $\mathcal{L}$, and is therefore the eigenfunction ψ_0 with eigenvalue $\lambda_0 = 0$. Because FP3 is not self-adjoint, one needs also the left eigenfunctions of FP3, denoted here by φ_j. The two sets $\{\psi_j\}$ and $\{\varphi_j\}$ are biorthogonal, with the inner product $(,)$,

$$(\varphi_j,\psi_k) = \int \varphi_j\psi_k = \delta_{jk}\,,$$

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where $\int$ denotes an integral over x, v, and z. They provide a basis for expanding general solutions of FP3. In particular, the time evolution of any arbitrary initial distribution $f(0) = f(x,v,z;t=0)$ is given by the expansion

$$f(t) = \sum_j e^{-\lambda_j t} \psi_j [\varphi_j f(0)] .$$

Under suitable circumstances, the lowest nonzero eigenvalue λ_1 is directly related to a reaction rate. First, define the "species test function" $S(x) = \text{sign}(x)$. The time dependent average of S is the net difference between reactants $[x<0]$ and products $[x>0]$. This average is given by the expansion

$$\langle S(t) \rangle = \sum_j e^{-\lambda_j t} (s,\psi_j) [\varphi_j, f(0)] .$$

The term with $j=0$ vanishes because $S(x)$ is odd and ψ_0, the equilibrium distribution, is even. If the relaxation of $\langle S \rangle$ is to be regarded as a "good" chemical process, the term $j=1$ should dominate the whole expansion; the other terms should describe, at most, small early transients. Further, $j=1$ should dominate the decay of the time correlation function of $S(x)$, which is frequently used[5] to define a rate constant. Whether or not there is a sufficiently large separation between λ_1 and λ_j for $j>1$, so that the first eigenfunction dominates the decay, is not known in general. (Very little is known about eigenvalues of Fokker–Planck equations; the equations usually are not self-adjoint, and standard theorems may not apply.)

An alternative and popular procedure for obtaining rate constants is by the calculation of first passage times. For the problem discussed here, these are intimately related to the dominant eigenvalue.

Larson and Kostin[6] have calculated eigenvalues for the Markovian two-variable FP2, for high barriers, by means of singular perturbation theory. They do find that there is a significant gap between λ_1 and λ_j for $j>1$, and that the eigenfunction ψ_1 is quite close to $S(x) f_e(x,v)$.

Dygan, Matkowsky, and Schuss[7] (DMS) used the singular perturbation method to find first passage times for FP3. (Actually, they looked at the more general n-variable FPn.) On combining the method used by Larson and Kostin to get eigenvalues with the method used by DMS to get first passage times, one finds that the reciprocal of the eigenvalue λ_1 is the average of the first passage times from the right- and the left-hand side of the barrier. The resulting rate constant is exactly what was predicted by Grote and Hynes.

This suggests that the Grote–Hynes theory ought to apply generally for high barriers. However, there is a further test, of internal consistency, that must be made. The eigenvalue is computed from an integral that is quadratic in the eigenfunction. The eigenfunction is an error function of an argument containing the variables x, v, and z. In calculating the eigenvalue, first one integrates out v and z, and then the x integral is performed. The integrand is approximately Gaussian, with a width that depends on the friction coefficient γ. For singular perturbation theory to be applicable, there should be no appreciable contribution to the integral from x in the neighborhood of the potential minima. This requirement limits the range of friction in which singular perturbation theory can be trusted, on both the low and high friction sides, to roughly $0.04 < \gamma < 10$. This is essentially the range in which SBB observe good agreement with the Grote–Hynes theory. (The meaning of "neighborhood" is somewhat arbitrary, especially when the potential has a very flat minimum. Perhaps one should require the integrand to become negligible halfway up the potential well. In any case, the only really satisfactory way to test the validity of singular perturbation theory is to do a better calculation.)

Because the GH theory completely ignores the presence of potential minima, having been developed solely for an inverted parabolic potential, it is not surprising that the above limitation does not appear in that theory.

Hanggi[8] arrived at similar constraints on γ by means of quite different arguments.

The other comment to be made here is concerned with the unexpected behavior observed by SBB at large friction. First, one should note that there is some ambiguity in the way "very large friction" is to be interpreted. The frictional memory function $\zeta(t)$ is specified by two parameters, α and γ. Large friction can mean large γ at fixed $\alpha\gamma$ or it can mean large γ at fixed α. In the first case, the limit of very large friction at constant correlation time, the dynamical behavior of the system was shown by DMS to be well described by a Smoluchowski equation. But the SBB simulations are performed at constant α, and not at constant $\alpha\gamma$, and the large friction is associated with a long correlation time. In this case, the DMS argument leading to a Smoluchowski equation fails, and one should not expect a spatial diffusion theory to apply.

In this second case, there are *two* dynamical quantities that are almost constants of the motion. From the three-variable Langevin equation, the last two terms in dz/dt are small: the noise term is of the order of $\gamma^{-1/2}$, and the frictional term is of order γ^{-1}. In the limit of infinite correlation times, at fixed α, these terms can be dropped. The resulting three equations have two conserved quantities, the total energy

$$H = v^2/2 + U(x) + \alpha z^2/2$$

and another variable,

$$W = z + x/\alpha .$$

On combining these two quantities, one finds that the motion of the coordinate is governed by the effective potential

$$U_{\text{eff}} = U(x) + \alpha(W - x/\alpha)^2/2 .$$

SBB commented on the importance of this potential for the special case $W=0$. When α is fixed and γ is very large, both H and W will drift slowly in time; there can be many oscillations in the effective potential during a time of the order of $\alpha\gamma$. SBB did in fact observe this behavior. It is important, however, to note that not only the energy, but also the effective potential will change because W is drifting. This suggests the importance of following the simultaneous diffusion of both H and W. A modification of the energy diffusion theory is required to account for the large friction results.

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