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Reactive flux method for numerical evaluation of rate constants is generalized to arbitrary underlying dynamics. The feasibility of the method is illustrated by numerically evaluating rate constants for a one-dimensional jump process and a diffusion process. In both cases, we find excellent agreement with exact results known in these cases.

I. INTRODUCTION

Decay of metastable states plays an important role in a wide variety of fields such as chemical kinetics, reaction networks, diffusion in solids and glasses, kinetics of first order phase transitions, quantum optics, and electronics.[1-8] On the theoretical side, there exist only very few models for which exact rate expressions are available. However, many problems can be asymptotically solved in the limit of a large barrier separating the considered metastable state from other locally stable states.[9-11] Of course, the presence of a barrier is vital for the notion of metastability and the feasibility of a rate description. For these purposes, a barrier height Q of already a few $k_B T$ will suffice to separate the decay time being of the order of $\tau_m e^{\beta Q}$ ($1/\beta = k_B T$) from the fast time scale τ_m on which the deterministic processes take place within the part of state space bordered by the barrier. In the above mentioned asymptotic theories $1/(\beta Q)$ itself, rather than $e^{-\beta Q}$, enters as a small parameter. Therefore, these theories do not cover the whole range of parameters where a rate description is appropriate. Especially the presence of other small or large parameters than the barrier height may push the range of applicability of the asymptotic laws towards extremely low temperatures.[12] Unfortunately, also the numerical evaluation of rate constants is plagued by problems which originate in the wide separation of time scales. For example, in a simulation of stochastic trajectories with initial values near the metastable state being sampled from equilibrium distribution, almost any trajectory will stay near this state for an extremely long time until it escapes. Among various numerical approaches,[13,14] only the reactive flux method[15,16] is able to circumvent this difficulty by starting trajectories at the barrier top and to extract the long time behavior from data available on the short time scale.

So far, however, the reactive flux method has only been formulated for systems with a rather special underlying dynamics, namely in situations where the velocity is noiseless. As a consequence, many important rate problems cannot be tackled using this method. A Markovian jump process describing a dissociating molecule,[17] the incoherent energy transport by excitons in a molecular crystal,[2,18] and the diffusion of small particles in a liquid[4] are but a few examples.

In the present article, we shall extend the reactive flux method to cases with arbitrary Markovian dynamics. The paper is organized as follows: In the next section, we present the generalized reactive flux method. In Sec. III, the classical reactive flux theory is obtained as a special case of the general theory, and in Sec. IV, the general theory is applied to Markovian jump and diffusion processes. Section V provides a summary.

II. FORMAL DEVELOPMENT

Consider a Markovian process $x(t)$ in a d-dimensional state space with a metastable state x_0. The probability density $P(x,t)$ satisfies the time evolution equation

$$\partial P(x,t)/\partial t = LP(x,t), \tag{2.1}$$

where L is the forward operator characterizing the process. We assume that a stationary probability density $p_{st}(x)$ is known which satisfies[19]

$$LP_{st}(x) = 0. \tag{2.2}$$

After a transient on a microscopic time scale τ_m, the decay rate constant of the metastable state governs the time behavior of the correlation function

$$C(t) = \frac{\langle f(x(0))\chi(x(t))\rangle}{\langle f(x(0))\rangle} \simeq e^{-kt} \tag{2.3}$$

where $\langle\cdot\rangle$ denotes the equilibrium average. We have introduced the characteristic function $\chi(x)$ of the domain of attraction of the considered metastable state and $f(x)$ being of similar nature as $\chi(x)$, namely $f(x)$ essentially equals unity inside the domain of attraction and zero outside, but in contrast to $\chi(x)$, it may show a smooth transition from these extreme values.[20] In order to avoid back reactions, regions far away from the domain of attraction must be absorbing.

The time derivative of Eq. (2.3) yields a time-dependent expression

$$k(t) = -\frac{dC(t)}{dt} = \frac{\langle \dot{f}(x(0))\chi(x(t))\rangle}{\langle f(x(0))\rangle} \simeq ke^{-kt}, \tag{2.4}$$

which for intermediate times $\tau_m \ll t \ll k^{-1}$, equals the rate constant k. We have introduced the time derivative of $f(x)$ by

$$\dot{f}(x) = L^* f(x), \tag{2.5}$$

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where

$$L^{*}\cdot = -P_{st}^{-1}L(P_{st}\cdot). \tag{2.6}$$

Note, that in the case of a process with detailed balance, the operator $-L^{*}$ coincides with the backward operator of the time-reversed process.[13]

It is convenient to split the time-dependent rate constant into its initial value $k(0)$ and a transmission coefficient $\kappa(t)$:

$$k(t) = k(0)\kappa(t). \tag{2.7}$$

The initial value of the reactive flux $k(0)$ is given by

$$k(0) = \lim_{t\to 0^{+}} k(t) = \frac{\langle \dot{f}(x(0))\chi(x(0^{+}))\rangle}{\langle f(x(0))\rangle}. \tag{2.8}$$

The initial value of the transmission coefficient $\kappa(t)$ is unity and for general $t>0$, it can be written as

$$\kappa(t) = \langle \chi(x(t))\rangle_{+} - \langle \chi(x(t))\rangle_{-}, \tag{2.9}$$

where we have introduced nonstationary ensemble averages

$$\langle\cdot\rangle_{+} = \frac{\langle \chi(x(0^{+}))\dot{f}(x(0))\cdot\rangle}{\langle \chi(x(0^{+}))\dot{f}(x(0))\rangle} \tag{2.10}$$

and

$$\langle\cdot\rangle_{-} = \frac{\langle [1-\chi(x(0^{+}))]\dot{f}(x(0))\cdot\rangle}{\langle [1-\chi(x(0^{+}))]\dot{f}(x(0))\rangle}. \tag{2.11}$$

In the derivation of Eq. (2.11), we have used the fact that due to the presence of the absorbing states, the backward operator L^{+} acting on unity yields a negligible contribution of $O(k)$.

The usefulness of the present generalization depends crucially on a proper choice of the function $f(x)$. The best choice would be the eigenfunction of L^{*} with the smallest nonvanishing eigenvalue $\lambda = k$. In that case, the initial value of the reactive flux $k(0)$ would already determine the exact rate constant. In general, however, this eigenfunction is not known exactly. An approximate eigenfunction of L^{*} might still serve the purpose, provided that $k(0)$ is well defined and the nonstationary ensemble averages $\langle\cdot\rangle_{\pm}$ contain proper nonnegative probability densities. Any choice of $f(x)$ that interpolates unity in the reactant state and zero in the product state and fulfills the above requirements may be used to evaluate either analytically or numerically $k(0)$ and the plateau value κ of $\kappa(t)$ which yields the rate constant by $k = k(0)\kappa$.

III. CLASSICAL REACTIVE FLUX

In the classical case, the reaction coordinate $q(x)$ depends only on the configuration coordinates $\mathbf{r}$, but not on the velocities $\mathbf{v} = \dot{\mathbf{r}}$, i.e., $q(x)$ is positive in the reactant state and vanishes on the barrier. In that case, one may choose $f(x) = \chi(x) = \theta(q(x))$, where $\theta(q)$ is the Heaviside step function. Inserting into Eq. (2.8), we obtain with

$$\dot{f}\chi(x(0^{+})) = \dot{q}\delta(q)\theta(\dot{q}) \tag{3.1}$$

the result of transition state theory[1,15]

$$k(0) = \frac{\langle \delta(q)\dot{q}\theta(\dot{q})\rangle}{\langle \theta(q)\rangle}. \tag{3.2}$$

The nonstationary ensemble averages Eqs. (2.10) and (2.11) are given by

$$\langle\cdot\rangle_{\pm} = \frac{\langle \delta(q)(\pm\dot{q})\theta(\pm\dot{q})\cdot\rangle}{\langle \delta(q)(\pm\dot{q})\theta(\pm\dot{q})\rangle}. \tag{3.3}$$

In a stochastic simulation, one generates trajectories $x(t)$ with initial conditions sampled from the distributions (3.3) and Eq. (2.9) gives the plateau value of the reactive flux. This method has been applied in a variety of situations with success.[3,15,16]

IV. GENERALIZED REACTIVE FLUX

In the following, we shall demonstrate that in several other situations a meaningful choice of $f(x)$ is possible. We shall focus on a Markovian jump process and a small step diffusion process.[2,13,21] Neither problem can be approached numerically using the classical reactive flux method since the initial value $k(0)$ diverges, due to the fact that the velocity $\dot{x}$ is ill defined. In order to demonstrate the applicability of the present method, we shall evaluate rate constants in one dimension where a comparison with exact results is possible. In both situations, the extension of the method to many-dimensional cases is straightforward.

A. Markovian jump process

Consider a molecule undergoing a dissociation reaction in a dilute gas. The energy E of the molecule as a function of time is a continuous jump process described by a Master equation

$$\frac{\partial P(E,t)}{\partial t} = LP(E,t) = \int_{0}^{\infty} dE'[K(E,E')P(E',t) - K(E',E)P(E,t)], \tag{4.1}$$

where $P(E,t)$ is the time-dependent probability density of E and $K(E',E)$ the transition rate from E to E' obeying the detailed balance relation

$$K(E,E')P_{st}(E') = K(E',E)P_{st}(E). \tag{4.2}$$

Let us evaluate the rate constant for infinitely rapid dissociation at $E>Q$ using the reactive flux formalism. Again, we choose $f(E) = \chi(E) = \theta(Q-E)$ and obtain

$$\dot{f}(E) = L^{*}f(E) = \int_{0}^{\infty} dE'\,K(E',E)[f(E') - f(E)]. \tag{4.3}$$

Inserting Eq. (4.3) into Eq. (2.8), the initial value becomes

$$k(0) = \int_{Q}^{\infty} dE' \int_{0}^{Q} dE\,K(E',E)P_{st}(E), \tag{4.4}$$

which is the strong collision approximation of unimolecular rate theory.[2,17] The transmission coefficient (2.9) simplifies to

$$\kappa(t) = \langle \theta(Q - E(t))\rangle_{+}, \tag{4.5}$$

since $E>Q$ is perfectly absorbing. Note that the absorbing boundary method[21] is exact in the present example. The initial distribution entering Eq. (2.9)is proportional to

$$\theta(Q-E)\int_{Q}^{\infty} dE'\,K(E,E')P_{st}(E'). \tag{4.6}$$

In order to test the present algorithm for numerical evalua-

tion of the rate constant, consider the exactly soluble exponential model[22]

$$K(E',E) = \frac{\alpha}{a+b} \begin{cases} e^{-(E-E')/a} & \text{for } E' < E \\ e^{-(E'-E)/b} & \text{for } E' > E \end{cases} \quad (4.7)$$

with $1/b - 1/a = \beta$ and $P_{st}(E) \propto e^{-\beta E}$ and α being the collision rate. The asymptotic low temperature result ($\beta Q \ll 1$) for the rate constant is[22]

$$k = \alpha \beta^2 b^2 e^{-\beta Q}. \quad (4.8)$$

Let us evaluate this rate constant numerically using the reactive flux method. The initial value of the reactive flux (4.4) becomes

$$k(0) = \alpha\beta \frac{ab}{a+b} e^{-\beta Q}. \quad (4.9)$$

The transmission coefficient κ can be evaluated from Eq. (4.5) using a stochastic simulation. We generate energy trajectories $E(t)$ by sampling numerically transition probabilities[25] according to Eq. (4.7) and the initial distribution Eq. (4.6) which simplifies with Eq. (4.7) to

$$\theta(Q-E)e^{(Q-E)/a}. \quad (4.10)$$

We average 10^4 trajectories and the plateau value is reached after 10^2–10^5 collisions. The simulation requires few minutes on a VAX-8800. Numerical results for different values of βb are summarized in Table I. Calculated transmission coefficients are compared with the theoretical value

$$\kappa = \beta \frac{b}{a}(a+b) \quad (4.11)$$

and show excellent agreement.

B. Diffusion process

As a second example, consider the diffusive motion of a Brownian particle of unit mass with a damping rate γ in a symmetric double well potential $U(x)$ which is governed by the Smoluchowski equation

$$\frac{\partial P(x,t)}{\partial t} = LP(x,t)$$

$$= \frac{1}{\gamma}\frac{\partial}{\partial x}\left(U'(x)P(x,t) + \frac{1}{\beta}\frac{\partial}{\partial x}P(x,t)\right), \quad (4.12)$$

where $U' = dU/dx$. The exact rate constant of escape is[1]

$$k = \frac{1}{\beta\gamma}\left[\int_{-x_0}^{x_0} dx\, e^{\beta U(x)} \int_{-\infty}^{x} dx'\, e^{-\beta U(x')}\right]^{-1}, \quad (4.13)$$

where $\pm x_0$ denote the positions of the wells.

Again let us apply the reactive flux formalism to evaluate the rate constant in this case. We choose $\chi(x) = \theta(x)$, but the same choice in $f(x)$ would lead to a diverging $k(0)$ because of the presence of the second derivative in

$$f(x) = L^* f(x) = \frac{1}{\gamma}\left(U'\frac{\partial f}{\partial x} - \frac{1}{\beta}\frac{\partial^2 f}{\partial x^2}\right). \quad (4.14)$$

In the case of a parabolic barrier, the most convenient choice for $f(x)$ is

$$f(x) = \left(\frac{\beta}{2\pi}\right)^{1/2} \int_{-\infty}^{\lambda x} ds\, e^{-\beta s^2/2}. \quad (4.15)$$

We insert this relation in Eqs. (2.8) and (4.14) and obtain

TABLE I. Numerical results for rate constants $\kappa = k/k(0)$ obtained by the present generalization of the reactive flux method (num.) compared to the exact values (ex.). We apply the method to the exponential Markovian jump process (left) and to diffusive motion in a double well potential (right). In both cases, the classical reactive flux method is not applicable. The error bars correspond to 90% confidence level (Ref. 3).

Exponential model			Diffusion		
βa	κ(ex.)	κ(num.)	ω_b/ω_0	κ(ex.)	λ(num.)
3.00	0.937	0.936 ± 0.005	5.0	0.869	0.862 ± 0.009
1.00	0.750	0.751 ± 0.007	7.5	0.709	0.708 ± 0.012
0.30	0.408	0.411 ± 0.010	10.0	0.580	0.586 ± 0.012
0.10	0.174	0.174 ± 0.006	12.5	0.485	0.492 ± 0.011
0.03	0.057	0.054 ± 0.004	15.0	0.415	0.411 ± 0.010

$$k(0) = \frac{\lambda\omega_0}{2\pi\gamma} e^{-\beta Q}, \quad (4.16)$$

where $Q = U(0) - U(x_0)$ is the barrier height and ω_0 the well frequency. The initial distribution entering Eq. (2.10) turns out to be

$$P_+(x) \propto \theta(x) V'(x) e^{-\beta V(x)}, \quad (4.17)$$

where

$$V(x) = U(x) + \tfrac{1}{2}\gamma^2 x^2. \quad (4.18)$$

In order that Eq. (4.17) defines a proper probability density, $V'(x)$ must not be negative for all $x \geqslant 0$. In view of Eq. (4.16), the minimal value of λ is favorable, fixing uniquely its best value. In the frequently occurring case of a potential which is convex without the barrier contribution, i.e., $U''(x) + \omega_b^2 \geqslant 0$, where ω_b is the barrier frequency, $\lambda = \omega_b$ represents the optimal choice.

In that case $k(0)$ turns out to coincide with the low temperature limit of the exact rate expression (4.13),

$$k(0) = \frac{\omega_0\omega_b}{2\pi\gamma} e^{-\beta Q}. \quad (4.19)$$

The transmission coefficient κ now incorporates finite temperature corrections of Eq. (4.16). Due to the symmetry of $U(x)$, Eq. (2.9) simplifies to

$$\kappa(t) = 2\langle\theta(x(t))\rangle_+ - 1. \quad (4.20)$$

Numerical results for a piecewise harmonic potential are obtained from a stochastic simulation of diffusive motion satisfying the equation of motion

$$\dot{x} = \frac{1}{\gamma}U'(x) + \left(\frac{2}{\beta\gamma}\right)^{1/2}\xi, \quad (4.21)$$

where ξ is Gaussian noise with $\langle\xi(t)\rangle = 0$ and $\langle\xi(t)\xi(s)\rangle = \delta(t-s)$. Trajectories $x(t)$ are generated by discretizing Eq. (4.21) using the Euler method[23] with a time step of $\Delta t\omega_b^2/\gamma \simeq 10^{-2}$. Initial conditions are sampled from Eq. (4.20) using a Monte Carlo procedure. The plateau value κ is reached after 10^3–10^4 time steps. Again, we average 10^4 trajectories which requires approximately half an hour central processing unit (CPU) time. The transmission coefficients κ are calculated for a fixed barrier height $\beta Q = 15$ and different ω_b/ω_0. The results are presented in Table I. The

exact rate constant is obtained by a numerical integration of Eq. (4.13). Again, we find excellent agreement between numerical and exact transmission coefficients.

V. CONCLUSION

We have shown how to generalize the powerful reactive flux method for numerical evaluation of rate constants to cases of arbitrary underlying Markovian dynamics. We have illustrated the feasibility of the method by performing reactive flux calculations for a one-dimensional exponential jump process and a diffusion process in a double well potential. The numerical results obtained are in excellent agreement with exact results known in these cases. The present formulation is easily generalized to more dimensional jump and diffusion processes and allows numerical studies of such rate problems with tractable computational effort. We expect that other situations may be successfully approached within the same spirit as e.g., discrete jump processes or nonequilibrium situations. Also the present ideas might offer an interesting alternative to the absorbing boundary method[24] in order to estimate very small transmission coefficients. Replacing the step function by a smooth dividing function could yield a lower initial value of the reactive flux and lead to a larger transmission coefficients. Finally, using the present formation, one might be able to generalize the concept of a transition state and transition state theory to arbitrary Markovian dynamics.

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