Solution of Kramers–Moyal equations for problems in chemical physics

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We derive asymptotic solutions of Kramers–Moyal equations (KMEs) that arise from master equations (MEs) for stochastic processes. We consider both one step processes, in which the system jumps from x to $x + \epsilon$ or $x - \epsilon$ with given probabilities, and general transitions, in which the system moves from x to $x + \epsilon \xi$, where ξ is a random variable with a given probability distribution. Our method exploits the smallness of a parameter ϵ, typically the ratio of the jump size to the system size. We employ the full KME to derive asymptotic expansions for the stationary density of fluctuations, as well as for the mean lifetime of stable equilibria. Thus we treat fluctuations of arbitrary size, including large fluctuations. In addition we present a criterion for the validity of diffusion approximations to master equations. We show that diffusion theory can not always be used to study large deviations. When diffusion theory is valid our results reduce to those of diffusion theory. Examples from macroscopic chemical kinetics and the calculation of chemical reaction rates ("Kramers" models) are discussed.

I. INTRODUCTION

In the last decade, considerable effort was dedicated to the study of chemical systems by the methods of stochastic processes. Much of this work is summarized in Refs. 1–6. In general, the problems of interest involve a system with discrete states (e.g., numbers of species or energy levels) or a mixture of discrete and continuous states, that evolve in time. Such systems are best described by master equations (ME) that characterize quantitites of interest in terms of the probabilities of transitions between states. Master equations are, unfortunately, very hard to solve. One approach, following Kramers[8] and Moyal,[7] is to expand the ME and obtain an infinite order differential equation called the *forward Kramers–Moyal equation* (FKME), which is equivalent to the ME. Since the FKME is also difficult to solve, it is usually truncated after two terms, yielding a diffusion approximation. Although this diffusion approximation provides equations that are often solvable, the validity of such an approximation has not yet been made clear. In order to study the validity on the diffusion approximation, one must be able to solve both the FKME and the diffusion approximation to it. In this paper, we will show how to construct solutions of the FKME.

We are concerned with processes that on the average have one or more stable equilibrium points. For such systems we calculate the density of small and large fluctuations about the stable states and the mean lifetime of such states. These lifetimes are often related to quantities of physical interest. For example, the mean lifetime of a molecule at energy levels below the dissociation energy is essentially the reciprocal of the dissociation rate.

We use the FKME to calculate the stationary or quasi-steady-state density of fluctuations. For the calculation of the mean lifetime we introduce the *backward Kramers–Moyal equation* (BKME). We construct asymptotic solutions to the FKME and the BKME in terms of a small parameter ϵ that measures the distance between neighboring states. That is, we consider problems characterized by small jumps in which the process hits the boundary as it exits a specified region. For example, for one step chemical processes in which the reaction mechanism leads to changes of ± 1 molecule, the concentration changes by $\epsilon = \pm 1/V$, where V is the volume of the system. Thus ϵ may be viewed as the reciprocal of some measure of the size of the system. It should be noted that our expansion is fundamentally different from Van Kampen's Ω expansion, in that we retain all the terms in the Kramers–Moyal equation, and the leading term in our expansion of the solution is shown to depend on all of these terms.

We employ a WKB approach to the FKME. This ap-

proach was employed by Kubo *et al.*[5] For the analysis of the BKME we adapt the approach of Matkowsky and Schuss[14] which is based on the methods of boundary layer theory and matched asymptotic expansions. We thus obtain a more complete description of the process than that given by Kubo *et al.*

In Sec. II we present a number of examples from macroscopic chemical kinetics and the microscopic theory of chemical reaction rates. We also show how the master equation and the forward and backward Kramers–Moyal equations are derived. In Sec. III, we show how to obtain asymptotic solutions of the FKME and BKME. In Sec. IV, we discuss a model for dissociation of a molecule with two degrees of freedom. This leads to a two dimensional problem that we fully analyze. In Sec. V, we provide some concluding comments, as well as compare our work with other recent approaches to the master equation–Fokker Planck equation modeling issue.

II. EXAMPLES AND DERIVATION OF THE ME AND KME

The first example described in this section pertains to macroscopic chemical kinetics.[10–13] The second example is a generalization[9] of the model proposed by Kramers[8] for the calculation of chemical reaction rates.

A. One step processes in chemical kinetics

In order to help fix ideas and introduce notation, we begin with a relatively simple problem (harder ones will follow). Imagine a single macroscopic variable $X(t)$ that measures the concentration of a chemical species. The reaction mechanism leads to changes of ± 1 molecule per reactive collision. If $x(t) = X(t)/V$ is a concentration variable, so that V is the volume of the system, it is often possible to model the evolution of $x(t)$ as follows. Let $\epsilon = 1/V$, so that $x(t)$ changes by $\pm \epsilon$ per reactive collision, and assume that

$$\text{Prob}\{\Delta x = \epsilon | x(t) = x\} = r(x)\Delta t,$$
$$\text{Prob}\{\Delta x = -\epsilon | x(t) = x\} = l(x)\Delta t, \quad (2.1)$$
$$\text{Prob}\{\Delta x = 0 | x(t) = x\} = 1 - \{r(x) + l(x)\}\Delta t.$$

The FME and BME are derived the following way. Let $p(x,y,t)$ be the probability of reaching $x(t) = y$, given that $x(0) = x$. With respect to y, $p(x,y,t)$ satisfies the FME,

$$p(x,y,t) = p(x,y - \epsilon,t - \Delta t)r(y - \epsilon)\Delta t$$
$$\quad + p(x,y + \epsilon,t - \Delta t)l(y + \epsilon)\Delta t$$
$$\quad + p(x,y,t - \Delta t)(1 - r(y)\Delta t - l(y)\Delta t). \quad (2.2)$$

With respect to x, $p(x,y,t)$ satisfies the BME,

$$p(x,y,t) = p(x + \epsilon,y,t - \Delta t)r(x)\Delta t$$
$$\quad + p(x - \epsilon,y,t - \Delta t)l(x)\Delta t$$
$$\quad + p(x,y,t - \Delta t)[1 - r(x)\Delta t - l(x)\Delta t]. \quad (2.3)$$

Equations (2.2) and (2.3) are derived by applying the laws of conditional probability.

The FKME and BKME are obtained by subtracting $p(x,y,t - \Delta t)$ from both sides, dividing by Δt, letting $\Delta t \to 0$ [which gives the time derivative of $p(x,y,t)$], and then Taylor expanding in ϵ. When this is done, Eq. (2.2) gives the FKME,

$$\partial_t p = L_y^* p = \sum_{n=1}^{\infty} \frac{(-\epsilon)^n}{n!} [(\partial_y)^n \{r(y)p(x,y,t)\}]$$
$$\quad + \sum_{n=1}^{\infty} \frac{\epsilon^n}{n!} [(\partial_y)^n \{l(y)p(x,y,t)\}]. \quad (2.4)$$

Applying the same procedure to Eq. (2.3) gives the BKME,

$$\partial_t p = L_x p = r(x) \sum_{n=1}^{\infty} \frac{\epsilon^n}{n!} (\partial_x)^n p(x,y,t)$$
$$\quad + l(x) \sum_{n=1}^{\infty} \frac{(-\epsilon)^n}{n!} (\partial_x)^n p(x,y,t). \quad (2.5)$$

In these equations, ∂ denotes a partial derivative. Observe that L_x and L_x^* are formal adjoints,[15] a fact which will find considerable use later on.

If L_y^* is truncated after two terms, then Eq. (2.4) becomes the familiar Fokker–Planck equation. If it exists, the stationary density of fluctuations $v(y)$ satisfies $L_y^* v = 0$. We will not truncate Eq. (2.4) or (2.5). Rather, we will show how to obtain asymptotic solutions of these equations for small ϵ, but keeping all terms in Eqs. (2.4) or (2.5).

The operator L_x is used to determine the mean first passage time $\tau(x)$ out of a region R starting at a point x in R. It can be shown that $\tau(x)$ is the solution of [1]

$$L_x \tau(x) = -1 \quad \text{for } x \text{ in } R,$$
$$\tau(x) = 0 \quad \text{on the boundary of } R. \quad (2.6)$$

Generalizations of Eqs. (2.2)–(2.6) are obtained in a straightforward manner. For example, consider a two dimensional, one step process $x(t) = [x_1(t),x_2(t)]$ evolving according to

$$\text{Pr}\{\Delta x_1 = \epsilon,\Delta x_2 = 0 | x(t) = x\} = r_1(x_1,x_2)\Delta t,$$
$$\text{Pr}\{\Delta x_1 = 0,\Delta x_2 = \epsilon | x(t) = x\} = r_2(x_1,x_2)\Delta t,$$
$$\text{Pr}\{\Delta x_1 = -\epsilon,\Delta x_2 = 0 | x(t) = x\} = l_1(x_1,x_2)\Delta t,$$
$$\text{Pr}\{\Delta x_1 = 0,\Delta x_2 = -\epsilon | x(t) = x\} = l_2(x_1,x_2)\Delta t,$$
$$\text{Pr}\{\Delta x_1 = 0,\Delta x_2 = 0 | x(t) = x\} = 1 - [r_1(x_2,x_2)$$
$$\quad + r_2(x_1,x_2) + l_1(x_1,x_2) + l_2(x_1,x_2)]\Delta t, \quad (2.7)$$
$$\text{Pr}\{\text{any other transition}\} = 0.$$

The extension of Eq. (2.2) is the FME,

$$p(x_1,x_2,y_1,y_2,t) = p(x_1,x_2,y_1 - \epsilon,y_2,t - \Delta t)r_1(y_1 - \epsilon,y_2)\Delta t$$
$$\quad + p(x_1,x_2,y_1,y_2 - \epsilon,t - \Delta t)r_2(y_1,y_2 - \epsilon)\Delta t$$
$$\quad + p(x_1,x_2,y_1 + \epsilon,y_2,t - \Delta t)l_1(y_1 + \epsilon,y_2)\Delta t$$
$$\quad + p(x_1,x_2,y_1,y_2 + \epsilon,t - \Delta t)l_2(y_1,y_2 + \epsilon)\Delta t$$
$$\quad + p(x_1,x_2,y_1,y_2,t)\{1 - [r_1(y_1,y_2)$$
$$\quad + r_2(y_1,y_2) + l_1(y_1,y_2) + l_2(y_1,y_2)]\Delta t\}. \quad (2.8)$$

The FKME is found according to the same procedure that was used to obtain Eq. (2.4). It is

$$\partial_t p = L_y^* p$$
$$= \sum_{n=1}^{\infty} \frac{(-\epsilon)^n}{n!} ([(\partial_{y_1})^n \{r(y_1,y_2)p(x_1,x_2,y_1,y_2,t)\}]$$
$$\quad + [(\partial_{y_2})^n \{r(y_1,y_2)p(x_1,x_2,y_1,y_2,t)\}])$$
$$\quad + \sum_{n=1}^{\infty} \frac{\epsilon^n}{n!} ([(\partial_{y_1})^n \{l(y_1,y_2)p(x_1,x_2,y_1,y_2,t)\}]$$
$$\quad + [(\partial_{y_2})^n \{l(y_1,y_2)p(x_1,x_2,y_1,y_2,t)\}]). \quad (2.9)$$

Observe that the transition assumptions (2.7) model a two dimensional random walk in which changes in x_1 and x_2 are uncoupled. Such a model would be appropriate for energy migration on a lattice or uncoupled chemical reactions. For coupled chemical reactions, one could have, for example, the event $\Delta x_1 = \epsilon$, $\Delta x_2 = -\epsilon$ with a nonzero probability. Such modifications are easily taken into account. For purposes of clarity and expositional ease, until the last section we will concentrate on the one dimensional problems.

B. Chemical reaction rates

In 1940, Kramers[8] proposed the following model for calculating the rates of chemical reactions. Let $X(t)$ denote the reaction coordinate and assume that $X(t)$ satisfies the equations

$$\frac{dX}{dt} = V(t),$$

$$\frac{dV}{dt} = -U'(X) - \beta V + \tilde{f}(t). \tag{2.10}$$

Here $U(X)$ is the potential for the reaction coordinate, β is a friction coefficient, and $\tilde{f}(t)$ is Gaussian white noise, satisfying

$$\langle \tilde{f}(t) \rangle = 0,$$

$$\langle \tilde{f}(t)\tilde{f}(s) \rangle = \sigma^2 \delta(t-s), \tag{2.11}$$

where $\langle \ \rangle$ denotes an average, $\delta(t)$ is the Dirac delta function, and the constants σ^2 and β are connected via the fluctuation–dissipation theorem.

Kramers' method for calculating the rate of a reaction involves finding the mean time that it takes X to reach a certain level.[14,16] This model is generally called "Brownian motion in a field of force" and has received a great deal of attention in the past 40 years.

A model in the same spirit of Kramers is that of Il'in and Khasminskii[9] who go from a master equation formulation to a diffusion approximation. A simplified version of the model of Il'in and Khasminskii which captures the main ideas, is the following:

(1) Consider a particle of mass M whose motion between collisions with small particles of mass m (with $m \ll M$) is governed by the equations

$$\frac{dX}{dt} = V,$$

$$\frac{dV}{dt} = F(x), \tag{2.12}$$

where $F(x) = -U'(x)$ for some $U(x)$.

(2) The small particles have velocity $\pm \sqrt{(kT)/m}$ with probability $1/2$, where k is Boltzmann's constant and T is temperature. Consequently, if $\tilde{\xi}$ is the velocity of the small particles, then

$$\langle \tilde{\xi} \rangle = 0,$$

$$\langle \tilde{\xi}^2 \rangle = kT/m. \tag{2.13}$$

We show in the next section that the result is independent of the particular distribution of $\tilde{\xi}$, for all distributions satisfying Eq. (2.13). We choose Eq. (2.13) to match the first two moments of the Maxwell Boltzmann distribution.

(3) Upon a collision, the value of V changes according to the law of an elastic collision. Thus, if ΔV is the change in velocity,

$$\Delta V = (\tilde{\xi} - V)\frac{2m}{M+m}. \tag{2.14}$$

Here $2m/(M+m) \approx 2m/M$ is the reduced mass for the collision. The probability density for the time between collisions follows an exponential distribution with parameter $\alpha = M\beta/m$, so that β is a measure of "viscosity." In order to use this model to calculate reactions rates, we imagine that the potential $U(x)$ has two stable equilibria, $x = A,B$, separated by an unstable equilibrium $x = C$. In the $(x,v = \dot{x})$ phase plane, there exists a trajectory (the separatrix) that divides the phase plane into two domains of attraction, D_A and D_B, of the stable equilibria $(A,0)$ and $(B,0)$. The Kramers picture of reaction rates is based on finding the mean time $\tau(x,v)$ for a particle starting at a point (x,v) near $(A,0)$ to reach the separatrix. The reaction rate is then inversely proportional to this mean time. Using $2m/M$ as the reduced mass the BME is

$$\frac{\partial p}{\partial t} = F(x)\frac{\partial p}{\partial v} + v\frac{\partial p}{\partial x} + \frac{1}{4}\frac{M\beta}{m}$$

$$\times \left\{ p\left[x,v + \frac{2m}{M}\left(\sqrt{\frac{kT}{m}} - v\right)\right] \right.$$

$$\left. + p\left[x,v + \frac{2m}{M}\left(-\sqrt{\frac{kT}{m}} - v\right)\right] - 2p(x,v) \right\}. \tag{2.15}$$

Setting $\epsilon^2 = 2m/M$ and expanding Eq. (2.15) in a Taylor series about $\epsilon = 0$, gives the BKME,

$$\frac{\partial p}{\partial t} = F(x)\partial_v p + v\partial_x p + \frac{\beta}{4\epsilon^2}$$

$$\times \left[\sum_{n=1}^{\infty} (2\epsilon)^n \frac{1}{n!}\left(\sqrt{\frac{kT}{M}} - \epsilon v\right)^n (\partial_v)^n p \right.$$

$$\left. + \sum_{n=1}^{\infty} (-2\epsilon)^n \frac{1}{n!}\left(\sqrt{\frac{kT}{M}} + \epsilon v\right)^n (\partial_v)^n p \right]. \tag{2.16}$$

The Kramers-like models for diffusion in a field of force are valid if the diffusion approximation to Eq. (2.16) (i.e., truncating after $n = 2$) is valid on a time scale comparable to $\tau(x,v)$. In Sec. III we show that this is the case for the model under consideration.

We now discuss a model for the calculation of reaction rates similar to those of Montroll and Shuler[17] and Kim.[18] Imagine a particle moving in a bath and experiencing collisions. Let E_n denote the energy of the particle after the nth collision with a bath molecule.

For the time being, we consider E_n to be a single variable. In Sec. IV, we will discuss an example in which the energy is represented by a vector (e.g., rotational and vibrational energies). We assume that the dynamics of E_n are described by

$$E_{n+1} = E_n + \epsilon \xi_n(E_n,\epsilon). \tag{2.17}$$

Here $\xi_n(E_n,\epsilon)$ represents a random process characterizing

all the possible transitions from energy level E_n, and ϵ measures the average distance between adjacent energy levels. The distribution of $\xi_n(E_n, \epsilon)$ may be determined from quantum statistics, but the mean number of collisions $n(x)$ to reach a dissociation energy starting at $E_0 = x$ needs to be computed. For example, in Refs. 19 kinetic equations for desorption are considered. Using perturbation theory, the authors are able to calculate transition probabilities from bound states to bound or continuum states. These transition rates then specify the distribution of $\epsilon_n(E_n, \epsilon)$. More specifically, we denote

$$w(z,x) = \Pr(\xi_n = z | E_n = x).$$

Extending the reasoning that led to Eq. (2.6) to continuous jump densities, one can show that $n(x)$ satisfies

$$\hat{L}_x n \equiv E_x \left\{ \sum_j \frac{\xi_n^j \epsilon^j}{j!} (\partial_x)^j n(x) \right\}$$

$$= -1, \tag{2.18}$$

$n(E_d) = 0$, where E_d is the dissociation energy. Here E_x denotes the expectation, conditioned on the level x, so that

$$E_x\{f(\xi_n)\} = \int \{f(z)\} w(z,x) dz \tag{2.19}$$

for any function f. Once the mean number $n(x)$ is known, we can find the mean time to reaction by multiplying $n(x)$ by the mean time κ between collisions. If κ is state dependent, then one must work with physical time directly, rather than numbers of collisions (see, e.g., Refs. 20 and 22).

III. ASYMPTOTIC SOLUTION OF THE KRAMERS–MOYAL EQUATIONS

In the next three sections, we will describe a new, asymptotic method for the solution of Kramers–Moyal equations. The method is completely general; that is, it can be used for problems with any number of dimensions. In this section, however, we will concentrate on one dimensional problems that are familiar. This allows us to concentrate on the new method and show why the standard diffusion approximation fails. In Sec. IV, we do a two dimensional example, to show the ease with which the new method can be used.

In this section we construct the solution to the stationary FKME,

$$L_x^* v(x) = 0 \tag{3.1}$$

and

$$\hat{L}_x^* v(x) = 0,$$

where L_x^* is given by Eq. (2.4), and $\hat{L}_x^*$ is the formal adjoint of $\hat{L}_x$ given by Eq. (2.18). The solution of Eq. (3.1) gives the *exact* stationary density of fluctuations in cases where it exists.

The quantities $\tau(x)$ and $n(x)$ are determined from

$$L_x \tau(x) = -1 \tag{3.2}$$

and

$$\hat{L}_x n(x) = -1, \tag{3.3}$$

respectively, with L_x given by Eq. (2.5) and $\hat{L}_x$ given by Eq. (2.18). The solution of Eq. (3.2), with the boundary condition given in Eqs. (2.6) and (2.18), respectively, allows us to find rates for one step processes. We also give a criterion for the validity of diffusion approximations (i.e., truncation of the KME). Finally, we discuss Eq. (2.16) and show that the approach of Il'in and Khaminskii is correct. Additional examples and calculations are in Ref. 20.

A. The stationary distribution of fluctuations

For a one step process, Eq. (3.1) takes the form

$$L^* v = \sum_{n=1}^{\infty} \left(\frac{(-\epsilon)^n}{n!} \left[(\partial_x)^n \{ r(x) v(x) \} \right] \right.$$

$$\left. + \frac{\epsilon^n}{n!} \left[(\partial_x)^n \{ l(x) v(x) \} \right] \right) = 0, \tag{3.4}$$

where $r(x)$, $l(x)$ are known and $v(x)$ is normalized by $\int v \, dx = 1$. We assume that $x[l(x) - r(x)] > 0$ for $x \neq 0$, and $l(0) = r(0)$. Then $x = 0$ is a stable equilibrium point. Since the stationary distribution of x_n is concentrated near $x = 0$, we employ the WKB method and seek a solution of Eq. (3.4) in the form

$$v(x) \sim e^{-\psi(x)/\epsilon} [K_0 + K_1 + \cdots]. \tag{3.5}$$

Substituting Eq. (3.5) into Eq. (3.4) and equating the coefficient of each power of ϵ to zero, to leading order we obtain the following equation for $\psi(x)$:

$$r(x) e^{\psi_x} + l(x) e^{-\psi_x} - [l(x) + r(x)] = 0. \tag{3.6}$$

Here $\psi_x = \partial \psi / \partial x$. Equation (3.6) is a nonlinear first order partial differential equation. It is analogous to the eikonal equation[14,21] that arises in the asymptotic solution of Fokker–Planck equations. In fact, if ψ_x is small, and Eq. (3.6) is Taylor expanded, one obtains the eikonal equation for the diffusion approximation. One solution of Eq. (3.6) is $\psi(x) = $ constant which is rejected because it is not normalizable, and the other solution is

$$\psi(x) = \int_0^x \log\left[\frac{l(s)}{r(s)} \right] ds. \tag{3.7}$$

We also find that K_0 satisfies

$$[r(x) e^{\psi_x} - l(x) e^{-\psi_x}] K_{0,x} + \{ \tfrac{1}{2} [r(x) e^{\psi_x} + l(x) e^{-\psi_x}] \psi_{xx}$$

$$+ r_x(x) e^{\psi_x} - l_x(x) e^{-\psi_x} \} K_0 = 0. \tag{3.8}$$

The solution of Eq. (3.8) is

$$K_0(x) = \frac{c_1}{\sqrt{l(x) r(x)}}, \tag{3.9}$$

where c_1 is a normalization constant. Thus the leading term in the asymptotic solution of Eq. (3.4) is given by

$$v(x) \sim \frac{c_1}{\sqrt{l(x) r(x)}} \exp\left\{ -\frac{1}{\epsilon} \int_0^x \log\left[\frac{l(s)}{r(s)} \right] ds \right\}. \tag{3.10}$$

Before continuing, we pause to make three observations about the solution (3.5)–(3.10). The first is that one can obtain the eikonal equation and equation for K_0 directly from the FME.

The stationary FME in this case is

$$r(x - \epsilon)v(x - \epsilon) + l(x + \epsilon)v(x + \epsilon)$$
$$- v(x)[r(x) + l(x)] = 0. \tag{3.11}$$

Using the WKB form (3.5) in Eq. (3.11) gives

$$r(x - \epsilon)e^{-\psi(x - \epsilon)/\epsilon}[K_0(x - \epsilon) + O(\epsilon)]$$
$$+ l(x + \epsilon)e^{-\psi(x + \epsilon)/\epsilon}[K_0(x + \epsilon) + O(\epsilon)]$$
$$- [r(x) + l(x)]e^{-\psi(x)/\epsilon}[K_0(x) + O(\epsilon)] = 0. \tag{3.12}$$

As $\epsilon \to 0$, a Taylor expansion of $\psi(\cdot)$ and $K_0(\cdot)$ give Eqs. (3.6) and (3.8). It will be seen, however, that the method for the calculation of exit times requires the use of the FKME.

The second observation concerns the extension of Eqs. (3.5)–(3.10) to two dimensional problems. For example, if the WKB form is used in the stationary version of Eq. (2.9), we obtain the following equation for $\psi(x_1, x_2)$:

$$r_1(x_1, x_2)e^{\psi_{x_1}} + l_1(x_1, x_2)e^{-\psi_{x_1}} + r_2(x_1, x_2)e^{\psi_{x_2}}$$
$$+ l_2(x_1, x_2)e^{-\psi_{x_2}} - [r_1(x_1, x_2) + l_1(x_1, x_2) \tag{3.13}$$
$$+ r_2(x_1, x_2) + l_2(x_1, x_2)] = 0.$$

This equation can be solved by the method of characteristics.[15] The evaluation of $K_0(x_1, x_2)$ is not much more difficult. The third observation is a comparison of Eq. (3.10) with the solution derived from the diffusion approximation, obtained by truncating Eq. (3.4) after two terms. The diffusion equation is given by

$$\frac{\epsilon}{2}\frac{\partial^2}{\partial x^2}\{[r(x) + l(x)]v(x)\} - \frac{\partial}{\partial x}\{[r(x) - l(x)]v(x)\} = 0. \tag{3.14}$$

Using Eq. (3.5) with $\psi(x)$ replaced by $\hat{\psi}(x)$, we obtain from Eq. (3.14),

$$\tfrac{1}{2}[r(x) + l(x)]\hat{\psi}_x^2 + [r(x) - l(x)]\hat{\psi}_x = 0. \tag{3.15}$$

Hence

$$\hat{\psi}(x) = 2\int_0^x \frac{l(s) - r(s)}{r(s) + l(s)}\,ds. \tag{3.16}$$

Clearly, Eqs. (3.16) and (3.7) are, in general, not equal. We observe that $\psi(x) > \hat{\psi}(x)$ for $x \neq 0$. Thus the density of fluctuations predicted by the diffusion approximation has higher tails than the density of the random walk. That is, the process obtained from the diffusion approximation is more diffuse than the random walk, so that the probability of large deviations of the diffusion process from equilibrium is greater than that of the underlying random walk. However, near the stable equilibrium point $x = 0$, $\psi(x)$ and $\hat{\psi}(x)$ have the same leading term in their Taylor expansions. Near $x = 0$ Eq. (3.15) is obtained by truncating Taylor's expansion of the exponentials in Eq. (3.6). Thus, the diffusion approximation can be used only for the description of small fluctuations about $x = 0$.

If $r(x) - l(x)$ has more than one zero, there may be metastable equilibrium points as well as a stable equilibrium. In such a case, there is a finite domain of attraction $\mathscr{D}$ for the metastable equilibrium point. The probability density of a particle in $\mathscr{D}$ relaxes to a quasi-steady-state distribution on a time scale much faster than the decay to equilibrium. The decay rate to equilibrium, often exponentially small, depends upon the mean time to escape from $\mathscr{D}$. The quasi-

steady-state distribution is the solution to Eq. (3.1), and thus has the same structure as Eqs. (3.5)–(3.10).

The mean exit time from an interval is computed by solving the BKME. In particular, let $\tau(x)$ be the expected exit time from (A,B), with $A < 0 < B$, given that $x(0) = x$. Then $\tau(x)$ satisfies

$$L_x\tau(x) = r(x)\sum_{n=1}^{\infty}\frac{\epsilon^n}{n!}(\partial_x)^n\tau(x) + l(x)\sum_{n=1}^{\infty}\frac{(-\epsilon)^n}{n!}(\partial_x)^n\tau(x)$$
$$= -1, \quad A < x < B \tag{3.17}$$

with

$$\tau(x) = 0 \quad \text{for } x \notin (A,B).$$

We again consider the specific case in which $r(x) = l(x)$ at exactly one point, $x = 0$ say, which is stable in the sense described above.

Since $x = 0$ is stable, $\tau(x)$ is large. We seek a solution of Eq. (3.17) in the form

$$\tau(x) = C(\epsilon)\sum_{j=0}^{\infty}\epsilon^j\tau_j(x), \tag{3.18}$$

where $C(\epsilon)$ is a constant that goes to infinity as $\epsilon \to 0$, and the $\tau_j(x)$ are to be determined. Substituting Eq. (3.18) into Eq. (3.17) yields[14,20]

$$[r(x) - l(x)]\frac{d}{dx}\tau_0(x) \sim 0. \tag{3.19}$$

From Eq. (3.19), we conclude that $\tau_0(x)$ is a constant. Without loss of generality, we set $\tau_0(x) = 1$. Consequently, $\tau(x) \sim C(\epsilon)$. Since this solution can not satisfy the boundary conditions, boundary layer corrections are needed near $x = A$ and $x = B$. We determine these boundary layer corrections and match them to the interior solution $C(\epsilon)$ by the method of matched asymptotic expansions.[23] Thus near $x = B$, we introduce the stretching transformation $\eta = B - x/\epsilon$, set $\tau(x) = U(\eta)$, and seek a solution $U(\eta)$ with $U(0) = 0$, $U(\eta) \to C(\epsilon)$ as $\eta \to \infty$. To leading order, Eq. (3.17) becomes

$$r(B)\sum_{n=1}^{\infty}\frac{(-1)^n}{n!}(\partial_\eta)^nU + l(B)\sum_{n=1}^{\infty}\frac{1}{n!}(\partial_\eta)^nU \sim 0. \tag{3.20}$$

We consider only the case $r(B) < l(B)$ and $r(A) > l(A)$. Other possibilities are discussed in Ref. 20. We seek a solution of Eq. (3.20) in the form

$$U(\eta) \sim C(\epsilon)[1 - e^{-\beta\eta}], \tag{3.21}$$

where the constant β is to be determined. Substituting Eq. (3.21) into Eq. (3.20) we find that β satisfies

$$r(B)e^{\beta} + l(B)e^{-\beta} = l(B) + r(B). \tag{3.22}$$

This equation has a unique positive solution under the above assumptions. A similar expansion is constructed near $x = A$. The uniform expansion is given by[20]

$$\tau(x) \sim C(\epsilon)[1 - e^{\alpha(x - A)/\epsilon} - e^{-\beta(B - x)/\epsilon}], \tag{3.23}$$

where α is the negative solution of Eq. (3.22) with B replaced by A. To find the unknown constant $C(\epsilon)$ we follow the method of Matkowsky and Schuss.[14] We multiply the equation

$$L_x\tau = -1 \tag{3.24}$$

by a solution of $L_x^*v = 0$ and integrate to obtain

$$\int_A^B vL_x\tau\, dx = -\int_A^B v\, dx. \tag{3.25}$$

Then we use the Lagrange identity[15]

$$\int_A^B vL_x\tau\, dx = \mathscr{B}(\tau,v)\Big|_A^B \tag{3.26}$$

with $\mathscr{B}(\tau,v)$ given by[20]

$$\mathscr{B}(\tau,v) = \sum_{n=0}^{\infty} \frac{\epsilon^n}{n!}\left\{\sum_{k=0}^{n-1}(-1)^k\,[(\partial_x)^k rv]\,[(\partial_x)^{n-k-1}\tau]\right\}$$
$$+ \sum_{n=1}^{\infty}\frac{(-\epsilon)^n}{n!}\left\{\sum_{k=0}^{n-1}(-1)^k\,[(\partial_x)^k lv]\,[(\partial_x)^{n-k-1}\tau]\right\}. \tag{3.27}$$

We note that $v(x)$ is already known [Eq. (3.10)]. We use Eqs. (3.10), (3.23), and (3.27) in Eq. (3.25) to obtain an asymptotic formula for $C(\epsilon)$. It is given by

$$C(\epsilon)\sim\frac{\{2\pi\epsilon/r(0)[l\,'(0)-r'(0)]\}^{1/2}}{\epsilon\left\{\dfrac{e^{-\psi(x)/\epsilon}}{\sqrt{r(x)l\,(x)}}[l\,(x)-r(x)]\right\}\Big|_A^B}. \tag{3.28}$$

Note that Eq. (3.28) is valid for one step processes. Thus we see that $\tau(x) = O\,(e^{\psi(x)/\epsilon}|_A^B)$. In contrast the exit time according to the diffusion approximation (3.14) is given by $\tau^d(x) = O\,(e^{\tilde\psi(x)/\epsilon}|_A^B)$, so that $\tau^d \ll\tau$. This is a result of the fact that the density of fluctuations predicted by the diffusion approximation has higher tails than those of the random walk. Thus large deviations are more likely in the diffusion approximation, and the expected time to exit is exponentially shorter.

Now we generalize our analysis to process with a general transition density

$$P(\xi_n = z|E_n = x) = w(z,x),$$

where E_n is the energy level of a molecule after the nth collision. The stationary FKME is given by

$$\widehat{L}_x^* v = \sum_{m=1}^{\infty}\partial_x^m E_x\xi_n^m\frac{v(x)(-\epsilon)^m}{m!} = 0. \tag{3.29}$$

Written in terms of the density $w(z,x)$ this equation is

$$0 = \int \sum_{n=1}^{\infty}\frac{z^n(-\epsilon)^n}{n!}(\partial_x)^n\{w(z,x)v(x)\}dz. \tag{3.30}$$

We assume that $x = 0$ is a stable equilibrium point of the averaged equation

$$\dot x = E_x(\xi_n)\equiv m_1(x).$$

That is, we asusme that $m_1(0) = 0$ and $xm_1(x) < 0$ if $x\neq 0$.

We again seek a solution of Eq. (3.27) in the WKB form

$$v\sim K(x)e^{-\psi(x)/\epsilon}. \tag{3.31}$$

In order to collect terms according to powers of ϵ, the following identity is useful[20]:

$$(\partial_x)^n[w(z,x)K(x)e^{-\psi/\epsilon}] = e^{-\psi(x)/\epsilon}$$
$$\times\left[\frac{K(x)w(z,x)(-\psi_x)^n}{\epsilon^n} + \frac{T_n}{\epsilon^{n-1}} + O(\epsilon^{-n+2})\right], \tag{3.32}$$

where

$$T_n = \frac{n(n-1)}{2}(\psi_x)^{n-2}(\psi_{xx})(Kw) + n(Kw)_x(-\psi_x)^{n-1}. \tag{3.33}$$

Substituting into Eq. (3.27) and setting the coefficient of each power of ϵ to zero, to leading order we obtain the equation for $\psi(x)$,

$$\int(e^{z\psi_x} - 1)w(z,x)dz = 0. \tag{3.34}$$

We can rewrite Eq. (3.34) in the form

$$E_x\{e^{\xi_n\psi_x}\} = 1. \tag{3.35}$$

This equation was derived by Kubo *et al.*[5] If the moment generating function for ξ_n is known, then we can write Eq. (3.35) explicitly. For example, if the distribution of ξ_n given, $E_n = x$, is normal with mean $b\,(x)$ and variance $\sigma^2(x)$, then Eq. (3.35) becomes[24]

$$\frac{1}{\sqrt{2\pi}\sigma(x)}\int_{-\infty}^{\infty}\exp\left\{-\frac{1}{2}\left[\frac{z-b\,(x)}{\sigma(x)}\right]^2\right\}e^{z\psi_x}dz = 1$$

with the solution

$$\psi(x) = -2\int_0^x\frac{b\,(u)}{\sigma^2(u)}du.$$

The $O(\epsilon)$ term in the asymptotic solution of Eq. (3.30) yields the equation

$$\frac{\partial}{\partial x}\left[KE_x(\xi_n e^{\xi_n\psi_x})\right] = \frac{K}{2}E_x\{\xi_n^2 e^{\xi_n\psi_x}\psi_{xx}\}. \tag{3.36}$$

The solution of Eq. (3.36) is given by

$$K(x)$$
$$= \frac{C_1\exp\left\{\dfrac{1}{2}\displaystyle\int_0^x\left[E_{x'}\{\xi_n^2 e^{\xi_n\psi_{x'}}\psi_{x'x'}\}/E_{x'}\{\xi_n e^{\xi_n\psi_{x'}}\}\right]dx'\right\}}{\left|E_x\{\xi_n e^{\xi_n\psi_x}\}\right|}. \tag{3.37}$$

For the normal distribution we have

$$K(x) = \frac{C_1}{\sigma^2(x)}\exp\left\{\frac{1}{2}\int_0^x\left[\frac{b\,(u)}{\sigma^2(u)}\right]'b\,(u)du\right\}.$$

If the variance $\sigma(x)$ is a constant, this expression reduces to

$$K(x) = \frac{C_1}{\sigma^2}\exp\left[\frac{1}{4\sigma^2}b^2(x)\right].$$

A simple extension of our methods can be used to determine the mean lifetime for an arbitrary process ξ_n,[20] or for a multidimensional problem (as will be done in Sec. V).

Next, we reexamine models for reaction rates based on Brownian motion. To do this, we study the BKME (2.16). Observe that, physically, two things occur in Eq. (2.16) as ϵ decreases to zero. The collision rate β/ϵ^2 increases and simultaneously the velocity change per collision ΔV decreases. The backward equation (2.16) can be written in the form

$$\frac{\partial p}{\partial t} = F(x)\partial_v p + v\partial_x p$$
$$+ \frac{\beta}{4\epsilon^2}\left\{2\epsilon\left[\sqrt{\frac{kT}{M}} - \epsilon v - \left(\sqrt{\frac{kT}{M}} + \epsilon v\right)\right]\partial_v p\right.$$

$$+ 2\epsilon^2 \left[\left(\sqrt{\frac{kT}{M}} - \epsilon v \right)^2 \right.$$

$$\left. + \left(\sqrt{\frac{kT}{M}} + \epsilon v \right)^2 \right] \partial_v^2 p + O(\epsilon^3) \right\}. \tag{3.38}$$

After simplification, this equation becomes

$$\frac{\partial p}{\partial t} = F(x)\partial_v p + v\partial_x p - \beta v\partial_v p + \frac{\beta kT}{M}\partial_v^2 p + O(\epsilon). \tag{3.39}$$

In the limit $\epsilon \to 0$, Eq. (3.39) becomes the backward diffusion (Kolmogorov) equation associated with Kramers model (2.12).

The key observation is that by scaling the collision rate properly and choosing a symmetric (i.e., zero mean) distribution for the velocity of the small particle, Il'in and Khasminskii force the coefficients of $\partial_v p$ and $\partial_v^2 p$ to be the same order in ϵ. This allows one to write a diffusion approximation to the KME. If this scaling and symmetry did not occur, then the diffusion equation would not be valid. The example in the next section shows a case where the boundary conditions play a crucial role as well.

The Il'in–Khasminskii models leads to the general question about the validity of diffusion approximations for KME. Consider the BKME given by

$$p_t = \sum_{k=1}^{\infty} \frac{m_k(x;\epsilon)}{k!}(\partial_x)^k p. \tag{3.40}$$

In this equation, $m_k(x;\epsilon)$ is the k th moment of the transition density for the process under consideration. We assume that $m_k(x;\epsilon)/m_2(x;\epsilon) \to 0$ as $\epsilon \to 0$ for $k \geqslant 3$, and want to consider the validity of the diffusion approximation given by

$$p_t^d = m_1(x;\epsilon)p_x^d + \tfrac{1}{2}m_2(x;\epsilon)p_{xx}^d. \tag{3.41}$$

Our results show that Eq. (3.41) is a valid approximation to Eq. (3.40) if Eq. (3.41) is not a singular perturbation problem as $\epsilon \to 0$. In that case, the derivatives of p^d with respect to x are bounded as $\epsilon \to 0$ and one can seek a solution of Eq. (3.40) in the form

$$p \sim p^d + o(1). \tag{3.42}$$

The higher order terms in Eqs. (3.42) and (3.40) are small and thus the diffusion approximation is valid. On the other hand, if Eq. (3.41) is a singular perturbation problem [so that $m_1(x;\epsilon)/m_2(x;\epsilon)$ is unbounded as $\epsilon \to 0$], then the partial derivatives of p^d are unbounded as $\epsilon \to 0$. This means that the higher order terms in Eq. (3.40) may not be small and the expansion (3.41) not valid.

IV. A TWO DIMENSIONAL EXAMPLE

We now consider a more complicated model for dissociation, which is two dimensional. It is similar to Troe's model.[25,26] Let x and y denote the energy levels of two degrees of freedom of the molecule (e.g., vibrational and rotational energy) and let $E(x,y)$ be the total energy associated with them. We will assume that x and y are measured relative to the dissociation energy E_D. We assume that the dynamics of x and y satisfy the stochastic difference equations

$$x_{n+1} = x_n + \epsilon \xi_n(x_n,y_n),$$
$$y_{n+1} = y_n + \epsilon \eta_n(x_n,y_n). \tag{4.1}$$

In Eq. (4.1), $\epsilon = kT/E_D$. We will set $E/kT = \psi(x,y)/\epsilon$ so that $\psi(x,y) < 1$. We wish to compute the mean number of transitions before $E(x,y) = E_D$ [or $\psi(x,y) = 1$]. Associated with Eq. (4.1) is a joint transition density $w(z_1,z_2,x,y)$ defined by

$$w(z_1,z_2,x,y) = \Pr\{\xi_n = z_1, \eta_n = z_2 | x_n = x, y_n = y\}. \tag{4.2}$$

The moment generating function, $\Phi_{x,y}(t_1,t_2)$, associated with Eq. (4.2) is defined by

$$\Phi_{x,y}(t_1,t_2) = \int\int e^{t_1 z_1 + t_2 z_2} w(z_1,z_2,x,y) dz_1 dz_2. \tag{4.3}$$

We assume that the process (x_n, y_n) has a steady state energy distribution $v(x,y) \propto e^{-\psi(x,y)/\epsilon}$. It is easy to see that the steady state distribution satisfies

$$\Phi_{x,y}(\psi_x,\psi_y) = 1 \tag{4.4}$$

[Eq. (4.4) is the extension of Eq. (3.35) to two dimensions]. Equation (4.4) is equivalent to

$$\sum_{i+j>1} \frac{m_{ij}(x,y)}{i!j!} \psi_x^i \psi_y^j = 0, \tag{4.5}$$

where the moments $m_{ij}(x,y)$ are given by

$$m_{ij}(x,y) = \int\int z_1^i z_2^j w(z_1,z_2,x,y) \, dz_1 dz_2. \tag{4.6}$$

We assume that $x = 0$ and $y = 0$ are reflecting boundaries. We also assume as in Ref. 25 that the process (x_n, y_n) hits the boundary as it exits. In general, this will not be true and the solutions must be corrected to take into account jumps over the boundary. Consequently, the dissociation rate is found by solving for the mean exit time $n(x,y)$ of the process (x_n, y_n) from the domain $\mathscr{D} = \{\psi(x_n,y_n) < 1, x_n > 0, y_n > 0\}$ given that $x_0 = x$, $y_0 = y$. This exit time is a solution of the BKME,

$$\sum_{i+j>1} \frac{\epsilon^{i+j}}{i!j!} m_{ij}(x,y)\frac{\partial^{i+j}}{\partial x^i \partial y^j}n(x,y) = -1 \tag{4.7}$$

$$\text{for } (x,y)\in\mathscr{D}$$

with the associated boundary conditions

$$n(x,y) = 0 \quad \text{for} \quad S:\psi(x,y) = 1,$$

$$\frac{\partial n}{\partial y}(x,0) = \frac{\partial n}{\partial x}(0,y) = 0. \tag{4.8}$$

Following the procedure of Sec. III, we set $n(x,y) = C(\epsilon)N(x,y)$ where $N(x,y)$ is picked so that $\max_{\mathscr{D}} N(x,y) = 1$.

We begin by constructing a boundary layer solution for $N(x,y)$, valid near $S: \psi(x,y) = 1$. To do this, introduce local coordinates v and s, where $v = -[\psi(x,y) - 1]/\epsilon$ is a scaled distance to S and s is arc length along $\mathscr{S}$. When this is done, Eq. (4.7) becomes (to leading order in ϵ)

$$\sum_{i+j>1} \frac{m_{ij}}{i!j!}\psi_x^i \psi_y^j \frac{\partial^{i+j}}{\partial v^{i+j}} N(v,s) = 0. \tag{4.9}$$

The boundary condition for Eq. (4.9) is $N(0,s) = 0$ and the matching condition is $\lim_{v\to\infty} N(v,s) = 1$. The solution of Eq. (4.9) that satisfies these conditions is

$$N(x,y) = 1 - e^{-v} = 1 - e^{[\psi(x,y) - 1]/\epsilon}. \tag{4.10}$$

In obtaining Eq. (4.10), we used Eq. (4.5).

Next, multiply Eq. (4.7) by the Boltzmann density $e^{-\psi(x,y)/\epsilon}$ and integrate over $\mathscr{D}$. Using Green's formula gives

$$n(x,y) = \frac{-\iint_{\mathscr{D}} \exp[-\psi(x,y)/\epsilon] dx\, dy}{\oint_{\partial\mathscr{D}} G\, ds}. \tag{4.11}$$

In Eq. (4.11), $\partial\mathscr{D}$ denotes the boundary of $\mathscr{D}$ and G is given by

$$G = \sum_{i+j>1} \frac{\epsilon^{i+j}}{i!j!} \left\{ \left[\sum_{k=0}^{j-1} (-1)^k v_2 \frac{\partial^k e^{-\psi/\epsilon} m_{ij}}{\partial y^k} \right. \right.$$

$$\left. \times \frac{\partial^{i+j-k-1}(1 - e^{(\psi-1)/\epsilon})}{\partial x^i \partial y^{j-k-1}} \right]$$

$$+ \left[\sum_{k=0}^{i-1} (-1)^{k+j} v_1 \frac{\partial^{j+k} e^{-\psi/\epsilon} m_{ij}}{\partial x^k \partial y^j} \right.$$

$$\left. \left. \times \frac{\partial^{i-k-1}(1 - e^{(\psi-1)/\epsilon})}{\partial x^{i-k-1}} \right] \right\}, \tag{4.12}$$

where (v_1, v_2) is the outer unit normal. On S, the outer unit normal is given by

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$$v_1 = \psi_x / |\nabla\psi|,$$

$$v_2 = \psi_y / |\nabla\psi|. \tag{4.13}$$

Using Eqs. (4.8) and (4.13) we find that the contributions to the boundary integral from the segments $x = 0$, $\psi \leqslant 1$ and $y = 0$, $\psi \leqslant 1$ are lower order in ϵ. Thus,

$$\oint_{\substack{\psi=1 \\ x,y>0}} G\, ds \sim \epsilon e^{-1/\epsilon} \int_{\substack{\psi=1 \\ x,y>0}}$$

$$\times \frac{\psi_x \Phi_{t_1}(\psi_x, \psi_y) + \psi_y \Phi_{t_2}(\psi_x, \psi_y)}{|\nabla\psi|} ds \equiv \epsilon e^{-1/\epsilon} \gamma. \tag{4.14}$$

For the numerator in Eq. (4.11), the main contribution comes from a vicinity of the minimum of $\psi(x,y)$, which occurs at (0,0). Near (0,0), $\psi(x,y) = x + y + O(x^2 + y^2)$, so that

$$\iint_{\mathscr{D}} e^{-\psi(x,y)/\epsilon} dx\, dy = \epsilon^2 [1 + o(1)] \quad \text{as } \epsilon \to 0. \tag{4.15}$$

Combining Eqs. (4.14) and (4.15) we find that the dissociation rate is, to leading order in ϵ, given by

$$\kappa \sim \gamma(E_D/kT) e^{-E_D/kT}. \tag{4.16}$$

For $d \geqslant 3$ dimensions, we find

$$\kappa \sim \gamma_d (E_D/kT)^{d-1} e^{-E_D/kT}, \tag{4.17}$$

where γ_d is similar to γ in Eq. (4.14).

As an example, consider the following exponential jump distribution (see, e.g., Refs. 25 and 26)

$$w(z_1, z_2, x, y) = \begin{cases} \dfrac{1}{(a+b)(c+d)} & e^{z_1/b} e^{z_2/d} & \begin{cases} -x/\epsilon < z_1 < 0 \\ -y/\epsilon < z_2 < 0 \end{cases} \\[12pt] \dfrac{1}{(a+b)(c+d)} & e^{-z_1/a} e^{z_2/d} & \begin{cases} z_1 \geqslant 0 \\ -y/\epsilon < z_2 < 0 \end{cases} \\[12pt] \dfrac{1}{(a+b)(c+d)} & e^{z_1/b} e^{-z_2/c} & \begin{cases} -x/\epsilon < z_1 < 0 \\ z_2 > 0 \end{cases} \\[12pt] \dfrac{1}{(a+b)(c+d)} & e^{-z_1/a} e^{-z_2/c} & z_1, z_2 > 0 \end{cases} \tag{4.18}$$

---

for $x,y > 0$, with reflection at $x = 0$ and $y = 0$. The requirement of detailed balance implies that

$$(1-a)(1+b)(1-c)(1+d) = 1. \tag{4.19}$$

We will assume that $(1-a)(1+b) = (1-c)(1+d) = 1$ and that $a < b$, $c < d$. This insures that the ground state is stable. For the transition rate (4.18), the Boltzmann distribution is given

$$\rho(x,y) = (1/\epsilon^2) e^{-(x+y)/\epsilon}, \quad x,y \geqslant 0 \tag{4.20}$$

(so that $\psi = x + y$) and γ is given by

$$\gamma = ab + cd \tag{4.21}$$

[assuming that $(1-a)(1+b) = (1-c)(1+d) = 1$]. Thus, the dissociation rate is completely determined.

Troe,[26] in a similar problem, assumed that the dissociation level is given by $x + \alpha y = 1$, with $0 < \alpha \leqslant 1$. A similar analysis leads to

$$\gamma = \frac{ab\beta v_1}{1 - \beta v_2}, \tag{4.22}$$

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where $v_1 = 1/\sqrt{1+\alpha^2}$, $v_2 = \alpha/\sqrt{1+\alpha^2}$, and β is the smallest positive root of the equation

$$(1 + \beta v_1)(1 + d\beta v_2)(1 - a\beta v_1)(1 - c\beta v_2) = 1. \tag{4.23}$$

Observe that if $\alpha = 1$, then Eq. (4.22) reduces to Eq. (4.21).

V. CONCLUSION

We derived asymptotic expansions of solutions of Kramers–Moyal equations, by exploiting the smallness of the increments in the stochastic process of interest. We do not approximate the master equation or KME. Rather we consider the full forward and backward equations and approximate their solutions. In this way, our work is fundamentally different from approaches that "expand" the master equation.[2] Most expansions of the master equation are fundamentally small deviation theories, since they require an expansion about the deterministic path. In contrast, our theory can be used to study problems where large deviations are of interest. In addition, our method extends directly to

multidimensional stochastic processes. It is important to note that while other approaches have employed the forward equation to find both the stationary distribution and the first passage time, we have employed the backward equation to derive an expression for the first passage time. Our results, based on this approach, appear to be more general. We also note that the first nonzero eigenvalue, λ_1, of the transition matrix in the master equation is the reciprocal of the first passage time. Thus, we have derived results for λ_1 as well. We observe that it is exponentially small in $1/\epsilon$, and that the usual methods were capable of finding only the eigenvalues whose magnitude is $O(1)$ in ϵ.

In recent work, Hanggi and his collaborators[27–30] compare relaxation times computed by master equations and Fokker Planck equations (FPE). Their methods and approach differ from ours; but many of the conclusions are in the same spirit. They recognize that mean first passage times can not be calculated by the Fokker Planck equation obtained by truncating the ME.[27] Rather than treating the entire ME, they construct "effective" Fokker Planck equations. In Ref. 29 the following procedure is used. Let the stationary solution of the FME be denoted by

$$v(x) = c \exp - \left\{ \frac{\phi_0(x)}{\epsilon} - \phi_1(x) \right\}, \tag{5.1}$$

where c is a normalization constant. $\phi_0(x)$ and $\phi_1(x)$ are determined as in Sec. III of this paper. Hanggi *et al.*[29] propose the effective FPE,

$$\partial_t v^e = - \partial_x [M_1(x)v^e] + \tfrac{1}{2}\partial_x^2 [M_2(x)v^e], \tag{5.2}$$

where

$$M_1(x) = - L(x)\left\{ \frac{\partial \phi_0}{\partial x} + \frac{\epsilon \partial \phi_1}{\partial x} \right\} + \epsilon \frac{\partial L}{\partial x},$$

$$M_2(x) = m_2(x) + \sum_{n=1}^{\infty} \frac{1}{(n+1)!} m_{n+2}(x)\left[\frac{\partial \phi_0}{\partial x}\right]^n,$$

and $\qquad\qquad\qquad\qquad\qquad\qquad$ (5.3)

$$L(x) = \frac{1}{2}\left\{ \sum_{n=0}^{\infty} \frac{1}{(n+1)!} m_{n+2}(x)\left[\frac{\partial \phi_0}{\partial x}\right]^n + m_2(x) \right\}.$$

Here $m_j(x)$ is the jth moment of the transition density function. They show that Eq. (5.2) leads to first passage times that agree with those predicted by using the full ME. Thus Hanggi *et al.* provide another solution to the problem that we discuss in this paper. Their method, however, requires the solution of the eigenvalue problem associated with Eq. (5.2). The method described in Secs. III–IV of this paper, which utilizes the BKME, is simpler to use than the eigenvalue methods.

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