Asymptotic solution of the Kramers-Moyal equation and first-passage times for Markov jump processes

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(Received 6 January 1984)

We calculate the activation rates of metastable states of general one-dimensional Markov jump processes by calculating mean first-passage times. We employ methods of singular perturbation theory to derive expressions for these rates, utilizing the full Kramers-Moyal expansions for the forward and backward operators in the master equation. We discuss various boundary conditions for the first-passage-time problem, and present some examples. We also discuss the validity of various diffusion approximations to the master equation, and their limitations.

I. INTRODUCTION

Transitions between metastable states of physical systems described by Markov jump processes have been of continuing interest for many years.[1–15] The decay rates or mean lifetimes of these metastable states have attracted much attention because they represent important quantities such as dissociation rates or other activation rates. The calculation of these rates for Markov jump process has been based on the analysis of master equations. The general discrete time Markov jump process $\{x_n\}$ is described by

$$x_{n+1}=x_n+\epsilon\xi_n\ , \tag{1.1}$$

where ξ_n is a sequence of independent random variables, and $\epsilon\xi_n$ represents the jump size. The conditional jump density, which we assume to be stationary, is given by

$$\text{Prob}(\xi_n=z\mid x_n=x)=w(z,x)\ , \tag{1.2}$$

and whose moments are given by

$$m_k(x)=\int_{-\infty}^{\infty}z^k w(z,x)dz\quad (k=1,2,\ldots)\ . \tag{1.3}$$

The small parameter ϵ typically represents the ratio of the mean jump size to the system size. For example $\epsilon=1/\Omega$ were Ω is the total number of states.[3] A metastable state for the process $\{x_n\}$ at $x=0$ with domain of attraction $[-A,B]$ exists in the drift

$$m_1(x)=\int_{-\infty}^{\infty}zw(z,x)dz \tag{1.4}$$

satisfies $m_1(0)=0$ and

$$xm_1(x)<0\quad\text{for } x\in(-A,B),\ \ A,B>0,\ \ x\neq 0\ . \tag{1.5}$$

Outside the interval $[-A,B]$, the drift carries the process away from the metastable state $x=0$. We assume the process hits the boundary in finite time, with probability one. Various types of boundaries may be considered. For example, (i) noncharacteristic boundary points B, i.e., $m_1(B)\neq0$, and (ii) characteristic boundary points, i.e., $m_1(B)=0$. We will consider problems with one boundary point which is absorbing (characteristic or noncharacteristic), and the other which is either absorbing, reflecting or is partially absorbing (i.e., sticky). We refer to the latter case as type (iii) (see, e.g., Secs. IV and V). The transition density function

$$p(x,y,n)=\text{Prob}\{x(n)=y\mid x(0)=x\}$$

satisfies the master equation (ME)

$$p(x,y,n+1)-p(x,y,n)=L_y^*p\equiv\int_{-\infty}^{\infty}[p(x,y-\epsilon z,n)w(z,y-\epsilon z)-p(x,y,n)w(z,y)]dz\ . \tag{1.6}$$

The Kramers-Moyal expansion[16,17] of (1.6) is given by the forward Kramers-Moyal equation (FKME)

$$p(x,y,n+1)-p(x,y,n)=L_y^*p=\sum_{k=1}^{\infty}\frac{(-\epsilon)^k}{k!}\frac{\partial^k}{\partial y^k}[m_k(y)p]\ . \tag{1.7}$$

Constructing the solutions of (1.6) or (1.7) is, in general, difficult, so that approximate techniques have been developed. The method of approximating the jump process $\{x_n\}$ by a diffusion process has been widely used in the literature.[3,16,17] In this approximation, the master equation (1.6) or the Kramers-Moyal equation (1.7) is approximated by a Fokker-Planck equation. The standard method consists in truncating (1.7) after two terms, to obtain

$$p_t = -[m_1(y)p]_y + \tfrac{1}{2}\epsilon[m_2(y)p]_{yy} . \quad (1.8)$$

Here the discrete time is replaced by the continuous time variable $t = \epsilon n$. This procedure is useful for small deviations from the metastable state $x = 0$, but it has been shown to lead to erroneous results in many cases[3,4,8,18] (see Sec. III). In fact, this approximation may lead to decay rates which differ by many orders of magnitude from those obtained from the master equation (1.6). Another method, proposed by Van Kampen,[3] employs the system size expansion (Ω expansion) which reduces the master equation (1.6) locally to a diffusion process of the Ornstein-Uhlenbeck type

$$p_t = -[m_1'(0)zp]_z + \tfrac{1}{2}[m_2(0)p]_{zz} . \quad (1.9)$$

Here $z = y/\sqrt{\epsilon}$ is defined locally near the metastable state and t is the continuous time variable described above. Van Kampen's method is useful only for describing small deviations from the metastable state $x = 0$. Thus, neither approximation (1.8) nor (1.9) allows the determination of global properties such as the probability of large fluctuations or the decay rates of metastable states.

A third method has recently been proposed, which is an important step in the analysis of large deviations.[8] This method is based on the Wentzel-Kramers-Brillouin (WKB) solution for the stationary density $p(y)$ of (1.6) or (1.7) (cf. Kubo *et al.*[4])

$$p(y) = A^{-1}\exp\left[-\frac{1}{\epsilon}(\psi_0 + \epsilon\psi_1 + \cdots)\right] , \quad (1.10)$$

where A is a normalization constant. An effective diffusion approximation is constructed by the Fokker-Planck equation

$$p_t = -(\{m_1(y) + \epsilon[L'(y) - L(y)\psi_1'(y)]\}p)_y + \epsilon[L(y)p]_{yy} , \quad (1.11)$$

where

$$L(y) = \tfrac{1}{2}\left[m_2(y) + \sum_{k=1}^{\infty}\frac{m_{k+2}(y)}{(k+1)!}(\psi_0')^k\right] . \quad (1.12)$$

It is shown, by means of a birth-death process example, that this diffusion approximation gives the correct decay rate to leading order in ϵ, for boundaries of type (ii). Unfortunately, this approximation does not apply directly to boundary conditions of type (iii) as in the Montroll-Shuler model (cf. Sec. V.) We also note that in order to obtain higher-order terms in the expansion with respect to ϵ, the drift and diffusion coefficients in (1.11) would have to be corrected by terms which are $O(\epsilon^2)$.

Our purpose in this paper is to present an asymptotic theory of large deviations using the full master equation. We calculate the decay rates or mean lifetimes of metastable states of both discrete and continuous time jump processes. We relate the decay rate to the first-passage time for the process to escape from the domain of attraction of the metastable state. Rather than analyzing the forward master equation (1.6) and computing the time dependent fluxes, we introduce and analyze below an equation for the mean first-passage time derived from its Kramers-Moyal expansion.

Let $\tilde{n}(x)$ be the first (random) time the process $\{x_n\}$ leaves the interval $(-A,B)$, given that $x_0 = x$. The mean first-passage time or mean lifetime

$$\bar{n}(x) \equiv E[\tilde{n} \mid x_0 = x] = \sum_n \int_{-A}^{B} p(y,x,n)\,dy \quad (1.13)$$

satisfies the equation[19]

$$L\bar{n} \equiv \int_{-\infty}^{\infty}[\bar{n}(x+\epsilon z) - \bar{n}(x)]w(z,x)\,dz = 1 , \quad x \in (-A,B) \quad (1.14)$$

subject to the condition

$$n(x) = 0 \quad \text{for } x \notin (-A,B) . \quad (1.15)$$

The operator L in (1.14) is the formal adjoint of L^* which appears in the forward master equation (1.6). As before, we can replace (1.14) by its Kramers-Moyal expansion to obtain the equation[16,17]

$$L\bar{n} = \sum_{k=1}^{\infty}\frac{\epsilon^k}{k!}m_k(x)n^{(k)}(x) = -1 . \quad (1.16)$$

We analyze (1.16) by adapting the asymptotic method of Matkowsky and Schuss.[20–28] Our main results are the following explicit expressions for the mean lifetimes $\bar{n}(0)$ of the metastable state $x = 0$. For a boundary of type (i)

$$\bar{n}(0) \sim \frac{[\pi m_2(0)/\epsilon]^{1/2}}{-m_1'(0)} \Bigg/ \sum_{x=-A,B} K(x)e^{-\psi(x)/\epsilon}\,|\phi_x'(\psi'(x))| , \quad (1.17)$$

where the moment generating function $\phi_x(t)$ is defined by

$$\phi_x(t) = \int_{-\infty}^{\infty} e^{zt}w(z,x)\,dx , \quad (1.18)$$

the "eikonal" function $\psi(x)$ is the solution of the first-order equation

$$\phi_x(\psi') = 1 , \quad (1.19)$$

and the "amplitude" function $K(x)$ is given by

$$K(x) = \frac{\exp\left[-\tfrac{1}{2}\int_0^x\left[\int_{-\infty}^{\infty} z\frac{\partial w}{\partial z}(z,x)e^{z\psi'(x)}dz \Big/ \int_{-\infty}^{\infty} ze^{z\psi'(x)}w(z,x)\,dz\right]dx\right]}{\left[\int_{-\infty}^{\infty} ze^{z\psi'(x)}w(z,x)\,dz\right]^{1/2}} . \quad (1.20)$$

For case (ii)

$$\bar{n}(0) \sim \frac{\pi}{\epsilon} \frac{\sqrt{m_2(0)}}{-m_1'(0)} \Bigg/ \sum_{x=-A,B} K(x) e^{-\psi(x)/\epsilon} \sqrt{|m_1'(x) m_2(x)|} \ . \tag{1.21}$$

The above discussion was for discrete time Markov processes. Continuous time problems are also cast in the form of Kramers-Moyal equations, which are then solved asymptotically as in the case of discrete time problems.

Formulas (1.17) and (1.21) can also be derived from the approximation (1.11). Thus (1.11) is valid not only for the calculation of the leading terms of the probability of large deviations, and of the decay rates of metastable states, for the birth-death example with type (ii) boundary, as shown in Ref. 8, but for general jump processes of the form (1.1), with boundary conditions of types (i) and (ii). In Sec. III we specialize our results to birth-death processes. We also present criteria for the validity of the standard diffusion approximation to the Kramers-Moyal equation (master equation). In Sec. IV we consider the Ising-Weiss[29] mean-field model for ferromagnetism, and in Sec. V we consider the Montroll-Shuler[2] model for dissociation. In each of the problems in Secs. IV and V, type (iii) boundaries arise. For the dissociation problem, we calculate the relaxation rate $\alpha(1/\bar{\tau})$ where the mean lifetime $\bar{\tau}$ is given by our formula (4.16). Thus we are able to give an analytical expression for the exponential constant δ which was not computed in Ref. 1. We observe that the mean lifetime is inversely proportional to the first positive eigenvalue of the transition matrix of the master equation. Thus our calculation of $\bar{\tau}$ yields this eigenvalue, which is exponentially small in ϵ. This eigenvalue was not computed in Refs. 4 and 5, where only the eigenvalues 0(1) and larger were computed. Finally we remark that generalizations of our method to higher dimensions will be presented in a forthcoming paper.

II. MEAN FIRST-PASSAGE TIMES

We consider the process $\{x_n\}$ defined above, on an interval $[-A,B]$ with $A,B>0$, that satisfies the stochastic difference equation

$$x_{n+1} = x_n + \epsilon \xi_n \ . \tag{2.1}$$

Here ξ_n is a Markov process, whose conditional jump density, assumed to be stationary, is given by

$$\text{Prob}(\xi_n = z \mid x_n = x) = w(z,x) \ , \tag{2.2}$$

and whose moments are given by

$$m_k(x) = \int_{-\infty}^{\infty} z^k w(z,x) dz \ . \tag{2.3}$$

We assume that the drift $m_1(x)$ satisfies

$$x m_1(x) < 0, \quad x \in (-A,B), \quad x \neq 0 \ , \tag{2.4}$$

so that the mean (deterministic) flow has a single stable equilibrium at $x=0$. Let $\tilde{n}(x)$ be the first time the process x_n leaves the interval $(-A,B)$, i.e., $x_{n(x)} \notin (-A,B)$ and $x_{\tilde{n}(x)-1} \in (-A,B)$. The mean first-passage time

$$\bar{n}(x) = E(\tilde{n} \mid x_0 = x)$$

satisfies (Ref. 19)

$$\int_{-\infty}^{\infty} [\bar{n}(x+\epsilon z) - \bar{n}(x)] w(z,x) dz = -1 \tag{2.5}$$

$$\text{for } x \in (-A,B)$$

and

$$\bar{n}(x) = 0 \quad \text{for } x \notin (-A,B) \ . \tag{2.6}$$

Equation (2.5) is equivalent to the Kramers-Moyal expansion[16,17]

$$L\bar{n}(x) \equiv \sum_{k=1}^{\infty} \frac{\epsilon^k}{k!} m_k(x) \bar{n}^{(k)}(x) = -1 \ , \tag{2.7}$$

obtained from (2.5) by expanding about $\epsilon=0$. We construct an asymptotic expansion of the solution of (2.7) and (2.6), and consequently of (2.5) and (2.6), by adopting the method of Matkowsky and Schuss.[20–28] It is clear from (2.4) that $\bar{n}(x) \to \infty$ as $\epsilon \to 0$. Thus we assume, for x bounded away from the boundary, that $\bar{n}(x)$ is of the form

$$\bar{n}(x) \sim C(\epsilon) v(x) \ , \tag{2.8}$$

where $C(\epsilon) \to \infty$ as $\epsilon \to 0$, and

$$\max_{-A \le x \le B} \{v(x)\} = 1 \ . \tag{2.9}$$

The function $v(x)$ then satisfies

$$Lv \sim 0 \tag{2.10}$$

as $\epsilon \to 0$, for x bounded away from the boundary, and

$$v(x) = 0 \text{ for } x \notin (-A,B) \ . \tag{2.11}$$

We seek the outer expansion of (2.10) in the form

$$v \sim v_0 + \epsilon v_1 + \epsilon^2 v_2 + \cdots \ , \tag{2.12}$$

whose leading term satisfies

$$m_1(x) v_0'(x) = 0 \ . \tag{2.13}$$

Hence by (2.9), $v_0(x) \equiv 1$. Since $v_0(x)$ does not satisfy the boundary condition (2.11), it is necessary to construct boundary layer corrections[30] near $x=-A$ and $x=B$.[20] In this section we consider two types of boundaries: (i) the boundary is noncharacteristic, i.e., $m_1(-A) m_1(B) \neq 0$, and (ii) the boundary is characteristic, i.e., $m_1(-A) = m_1(B) = 0$. Other cases can be treated similarly.

For type (i) boundaries, we introduce the stretched variable

$$\zeta = (B - x)/\epsilon \tag{2.14}$$

into (2.10), and find that the leading term in the boundary layer expansion of the solution $V = v(B - \epsilon\zeta)$ satisfies

$$\sum_{k=1}^{\infty} \frac{(-1)^k m_k(B)}{k!} V^{(k)}(\zeta) = 0 \ . \tag{2.15}$$

The boundary and matching conditions are

$$V(0)=0 \text{ and } V(\infty)=1 , \tag{2.16}$$

respectively. The function $V(\zeta)=1-e^{-\beta\zeta}$ is a solution of (2.15) and (2.16), where β is the unique positive root of the equation

$$\sum_{k=1}^{\infty} \frac{\beta^k m_k(B)}{k!}=0 , \tag{2.17}$$

or equivalently

$$\phi_B(\beta)=1 , \tag{2.18}$$

where

$$\phi_x(t)=E(e^{t\xi_n} \mid x_n=x)$$

is the moment generating function of the process ξ_n, conditioned on $x_n=x$ (see the discussion in the Appendix). A similar analysis near $x=-A$ leads to the uniform expansion

$$v_{\rm nc}(x)\sim 1-e^{-\beta(B-x)/\epsilon}-e^{-\alpha(x+A)/\epsilon} , \tag{2.19}$$

where α is the unique positive root of

$$\phi_{-A}(-\alpha)=1 \tag{2.20}$$

and the subscript nc denotes the noncharacteristic case (i).

For type (ii) boundaries we assume that

$$m_1(x)=m_1'(B)(x-B)+\cdots \tag{2.21}$$

with $m_1'(B)>0$. We introduce the stretched variable

$$\eta=(B-x)/\sqrt{\epsilon} \tag{2.22}$$

into (2.10), and obtain the boundary layer equation

$$m_1'(B)\eta V_\eta+\frac{m_2(B)}{2}V_{\eta\eta}=O(\epsilon^{1/2}) , \tag{2.23}$$

and the boundary and matching conditions (2.16). The solution of (2.23) and (2.16) is given by

$$V(\eta)=\int_0^\eta \exp\left[-\frac{m_1'(B)}{m_2(B)}s^2\right]ds \Big/ \left[\frac{1}{2}\left[\frac{\pi m_2(B)}{m_1'(B)}\right]^{1/2}\right]$$
$$=\operatorname{erf}\left[\eta\left[\frac{m_1'(B)}{m_2(B)}\right]^{1/2}\right] . \tag{2.24}$$

The uniform expansion of $v(x)$ is now given by

$$v_c(x)\sim \operatorname{erf}\left[\frac{B-x}{\sqrt{\epsilon}}\left[\frac{m_1'(B)}{m_2(B)}\right]^{1/2}\right] +\operatorname{erf}\left[\frac{x+A}{\sqrt{\epsilon}}\left[\left|\frac{m_1'(-A)}{m_2(-A)}\right|\right]^{1/2}\right]-1 \tag{2.25}$$

where the subscript c denotes the characteristic case (ii).

To find the as yet undetermined constant $C(\epsilon)$ in (2.8), we multiply[20] (2.7) by the solution $u(x)$ of the stationary FKME

$$L^*u\equiv \sum_{k=1}^{\infty}\frac{(-\epsilon)^k}{k!}[m_k(x)u(x)]^{(k)}=0 , \tag{2.26}$$

and integrate by parts to obtain

$$\int_{-A}^{B} u(x)L\bar{n}(x)=\sum_{k=2}^{\infty}\frac{\epsilon^k}{k!}\sum_{j=0}^{k-2}(-1)^j[m_k(x)u(x)]^{(j)}\bar{n}^{(k-j-l)}(x)\Big|_{-A}^{B}$$
$$\equiv C(\epsilon)\mathscr{B}(u,V) , \tag{2.27}$$

where we have used $\bar{n}=C(\epsilon)V$. Using (2.7), (2.8), and (2.27), we obtain

$$C(\epsilon)\sim\frac{-\int_{-A}^{B}u(x)dx}{\mathscr{B}(u,V)} . \tag{2.28}$$

We now construct $u(x)$ in the WKB form

$$u(x)\sim K(x)e^{-\psi(x)/\epsilon}[1+O(\epsilon)] . \tag{2.29}$$

Employing (2.29) in (2.26), we find that $\psi(x)$ satisfies the eikonal equation[4]

$$\int_{-\infty}^{\infty}(e^{z\psi'(x)}-1)w(z,x)dz=0 \tag{2.30}$$

or

$$\phi_x(\psi'(x))=1 \tag{2.31}$$

or

$$\sum_{k=1}^{\infty}\frac{(\psi'(x))^k m_k(x)}{k!}=0 . \tag{2.32}$$

We observe that (2.31) is identical to (2.18) and (2.20), so that $\beta=\psi'(B)$ and $\alpha=-\psi'(-A)$. At the next order in ϵ, we find that $K(x)$ satisfies the "transport" equation[4]

$$\int_{-\infty}^{\infty}\left[\frac{\partial}{\partial x}[w(z,x)K(x)]+\frac{zw(z,x)K(x)}{2}\psi''(x)\right]e^{z\psi'(x)}z\,dz=0 , \tag{2.33}$$

whose solution is given by

$$K(x)=\frac{\exp\left\{-\frac{1}{2}\int_0^x\left[\int_{-\infty}^{\infty}z\left[\frac{\partial}{\partial x}w(z,x)\right]e^{z\psi'(x)}dz\Big/\int_{-\infty}^{\infty}ze^{z\psi'(x)}w(z,x)dz\right]dx\right\}}{\left[\int_{-\infty}^{\infty}ze^{z\psi'(x)}w(z,x)dz\right]^{1/2}}\ . \tag{2.34}$$

For small x, $\psi'(x)$ and $K(x)$ behave as

$$\psi'(x)\sim\frac{-2m_1'(0)}{m_2(0)}x+\cdots\ ,$$

and

$$K(x)\sim\frac{1}{\sqrt{-m_1'(0)}}\ .$$

Returning to (2.28), we evaluate the integral in the numerator asymptotically for small ϵ by Laplace's method[31] in which the major contribution comes from the point $x=0$, where $\psi(x)$ has an absolute minimum in $(-A,B)$, as shown in the Appendix. We find that

$$\int_{-A}^{B}u(x)dx\sim\frac{\sqrt{\pi\epsilon m_2(0)}}{-m_1'(0)}\ . \tag{2.35}$$

Now, using (2.17) in (2.27) for case (i), we obtain

$$\begin{aligned}\mathscr{B}(u,V)\,|_{x=B}&=-\epsilon\sum_{k=2}^{\infty}\frac{\beta^{k-1}}{k!}\sum_{j=0}^{k-2}m_k(B)K(B)e^{-\psi(B)/\epsilon}\\&=-\epsilon\int_{-\infty}^{\infty}zw(z,B)e^{z\psi'(B)}dz\,K(B)e^{-\psi(B)/\epsilon}\\&=-\epsilon K(B)e^{-\psi(B)/\epsilon}\,|\,\phi_B'(\psi'(B))\,|\ .\end{aligned} \tag{2.36}$$

The expression at $x=-A$ is obtained by replacing B by $-A$ in (2.36). Thus, using (2.28), (2.35), and (2.36), we obtain the exit time for type (i) boundaries as

$$\bar{n}(x)=\left[\frac{[\pi m_2(0)/\epsilon]^{1/2}[-m_1'(0)]^{-1}}{\sum_{x=-A,B}K(x)e^{-\psi(x)/\epsilon}\,|\,\phi_x'(\psi'(x))\,|}\right]v_{\rm nc}(x)[1+O(\epsilon)]\ , \tag{2.37}$$

where $v_{\rm nc}(x)$ is given by (2.19). For type (ii) boundaries we employ (2.25) in (2.27) to obtain

$$\mathscr{B}(u,V)\,|_{x=B}\sim-\epsilon^{3/2}\frac{\sqrt{m_1'(B)m_2(B)}}{\sqrt{\pi}}\ . \tag{2.38}$$

Now, using (2.35), (2.38), and (2.28) we obtain the exit time for type (ii) boundaries as

$$\bar{n}(x)=\left[\frac{\frac{\pi}{\epsilon}\sqrt{m_2(0)}/[-m_1'(0)]}{\sum_{x=-A,B}K(x,0)e^{-\psi(x)/\epsilon}\sqrt{|\,m_1'(x)m_2(x)\,|}}\right]v_c(x)[1+O(\epsilon)]\ , \tag{2.39}$$

where $v_c(x)$ is given by (2.25). Note that if $w(z,x)$ depends on ϵ as

$$w(z,x)\sim w_0(z,x)+\epsilon w_1(z,x)+\cdots\ ,$$

the above analysis remains unchanged if $w(z,x)$ is replaced by $w_0(z,x)$ and $K(x)$ is replaced by

$$\tilde{K}(x)=K(x)\exp\int_0^x\left[\int_{-\infty}^{\infty}w_1(z,u)e^{z\psi'(u)}dz\Big/\int_{-\infty}^{\infty}zw_0(z,u)e^{z\psi'(u)}dz\right]du\ , \tag{2.40}$$

where $K(x)$ is given by (2.34) with $w(z,x)$ replaced by $w_0(z,x)$.

Next, we consider the continuous time jump process $x(t)$ defined by the stochastic equation

$$x(t+\Delta t)=\begin{cases}x(t)+b(x(t))\Delta t+o(\Delta t) & \text{with probability } 1-\frac{\lambda(x(t))}{\epsilon}\Delta t+o(\Delta t)\\ x(t)+b(x(t))\Delta t+\epsilon\xi & \text{with probability } \frac{\lambda(x(t))}{\epsilon}\Delta t+o(\Delta t)\ ,\end{cases} \tag{2.41}$$

where the conditional density of ξ is given by

$$\text{Prob}(\xi=z \mid x(t)=x)=\tilde{w}(z,x) . \quad (2.42)$$

We assume $b(0)=0$ and $b'(0)<0$ so that $x=0$ is a stable equilibrium of the averaged equation. The moments of ξ are denoted by

$$\tilde{m}_k(x)=E(\xi^k \mid x(t)=x)=\int_{-\infty}^{\infty} z^k \tilde{w}(z,x)dz , \quad (2.43)$$

and are assumed to be independent of t. We assume, without loss of generality, that $\tilde{m}_1(x)=0$ since $b(x)$ and $\lambda(x)\tilde{m}_1(x)$ can be combined [cf. (2.45) below]. Let τ be the first time that the process $x(t)$ leaves the interval $(-A,B)$. The mean first-passage time $\bar{\tau}(x)=E(\tau \mid x(0)=x)$ satisfies

$$b(x)\bar{\tau}'(x)+\frac{\lambda(x)}{\epsilon}\int_{-\infty}^{\infty}[\bar{\tau}(x+\epsilon z)-\bar{\tau}(x)]\tilde{w}(z,x)dz=-1 . \quad (2.44)$$

The Kramers-Moyal expansion of (2.44) is given by

$$\tilde{L}\,\bar{\tau}(x)\equiv b(x)\bar{\tau}'(x)+\frac{\lambda(x)}{\epsilon}\sum_{n=2}^{\infty}\frac{\epsilon^n}{n!}\tilde{m}_n(x)\bar{\tau}^{(n)}(x)=-1 \quad (2.45)$$

for $x\in(-A,B)$,

$$\bar{\tau}(x)=0 \quad \text{for } x\notin(-A,B) . \quad (2.46)$$

The eikonal equation for $\tilde{L}^*p=0$, where $\tilde{L}^*$ is the adjoint of $\tilde{L}$ in (2.45) is given by

$$b(x)\psi'(x)+\lambda(x)\int_{-\infty}^{\infty}(e^{z\psi'(x)}-1)\tilde{w}(z,x)dz=0 \quad (2.47)$$

and the transport equation is given by

$$[b(x)K(x)]'+\int_{-\infty}^{\infty}\left\{[\lambda(x)\tilde{w}(z,x)K(x)]_x+\lambda(x)\frac{z\tilde{w}(z,x)}{2}\psi''(x)K(x)\right\}\times z e^{z\psi'(x)}dz=0 . \quad (2.48)$$

Following the analysis for the discrete time case, we obtain

$$\bar{\tau}(x)=\left[\frac{\{[\pi\lambda(0)m_2(0)]\}^{1/2}[-b'(0)\epsilon]^{-1/2}}{\sum_{x=-A,B}K(x)e^{-\psi(x)/\epsilon}\phi_x'(\psi_x'(x))}\right]\times v_{\text{nc}}(x)[1+O(\epsilon)] , \quad (2.49)$$

where

$$\phi_x(t)=1+b(x)t+\lambda(x)\sum_{k=2}^{\infty}\tilde{m}_k(x)t/k! , \quad (2.50)$$

and $v_{\text{nc}}(x)$ is defined by (2.19). The characteristic boundary case can be treated by introducing the obvious modifications in (2.40).

If the jump rate is given by $\lambda(x)/\epsilon^2$, rather than $\lambda(x)/\epsilon$ as above, then (2.45) takes the form

$$b(x)\bar{\tau}'(x)+\tfrac{1}{2}\lambda(x)\tilde{m}_2(x)\bar{\tau}''(x)+O(\epsilon)=-1 . \quad (2.51)$$

Here we have assumed that $\tilde{m}_1(x)\equiv 0$. We seek an asymptotic solution in the form

$$\bar{\tau}\sim\bar{\tau}_0+\epsilon\bar{\tau}_1+\cdots , \quad (2.52)$$

where $\bar{\tau}_0$ satisifies[19]

$$L_0\bar{\tau}_0\equiv b(x)\bar{\tau}_0'(x)+\tfrac{1}{2}\lambda(x)\tilde{m}_2(x)\bar{\tau}_0''(x)=-1 , \quad x\in(-A,B) \quad (2.53)$$

$$\bar{\tau}_0(x)=0 \text{ for } x\notin(-A,B) . \quad (2.54)$$

The functions $\bar{\tau}_n(x)$ for $n\geq 1$ satisfy

$$L_0\bar{\tau}_n=-\lambda(x)\sum_{k=3}^{n+2}\frac{\tilde{m}_k(x)}{k!}\bar{\tau}_{n-k+2}^{(k)} . \quad (2.55)$$

Note that L_0 is the backward operator for the standard diffusion approximation.[3] We observe that Eq. (2.53) is not of singular perturbation type, as is the case if the jump rate is $\lambda(x)/\epsilon$. Thus the standard diffusion approximation is valid in this case.

III. A RANDOM WALK

As a simple illustrative example we consider the birth-death process defined by

$$x_{n+1}=x_n+\epsilon\xi_n , \quad (3.1)$$

where ϵ is a small parameter, and

$$\begin{aligned}&\text{Prob}(\xi_n=1 \mid x_n=x)=r(x) ,\\ &\text{Prob}(\xi_n=-1 \mid x_n=x)=l(x) ,\\ &\text{Prob}(\xi_n=0 \mid x_n=x)=1-r(x)-l(x) .\end{aligned} \quad (3.2)$$

This corresponds to

$$w(z,x)=r(x)\delta(z-1)+l(x)\delta(z+1)+[1-r(x)-l(x)]\delta(z) \quad (3.3)$$

in (2.2). We assume that $l(x)>r(x)$ for $0<x<B$, and $l(x)<r(x)$ for $-A<x<0$, $l(0)=r(0)\neq 0$, so that $x=0$ is a stable equilibrium point. The corresponding characteristic and noncharacteristic cases are $l(B)=r(B)$, $l(-A)=r(-A)$, and $l(B)>r(B)$, $l(-A)<r(-A)$, respectively. Then (2.5) becomes

$$r(x)\bar{n}(x+\epsilon)+l(x)\bar{n}(x-\epsilon)-[r(x)+l(x)]\bar{n}(x)=-1 \quad (3.4)$$

with boundary conditions

$$\bar{n}(x)=0 \quad \text{for } x\notin(-A,B) . \quad (3.5)$$

The Kramers-Moyal expansion of (3.4) is now

$$L\bar{n}(x)\equiv\sum_{k=1}^{\infty}\frac{\epsilon^k}{k!}[r(x)+(-1)^k l(x)]\bar{n}^{(k)}(x)=-1 . \quad (3.6)$$

Following the analysis of Sec. II, we seek the solution of the stationary (forward) KME (2.26), which in this case becomes

$$L^*u(x)=\sum_{k=1}^{\infty}\frac{\epsilon^k}{k!}\{[l(x)+(-1)^k r(x)]u(x)\}^{(k)}=0\ , \qquad (3.7)$$

in the WKB form

$$u(x)=K(x)e^{-\psi(x)/\epsilon}[1+O(\epsilon)]\ . \qquad (3.8)$$

Here the eikonal equation (2.30) for $\psi(x)$ reduces to

$$\phi_x(\psi'(x))\equiv r(x)e^{\psi'(x)}+l(x)e^{-\psi'(x)}+[1-r(x)-l(x)]=1\ . \qquad (3.9)$$

Thus

$$\psi(x)=\int_0^x \ln\frac{l(s)}{r(s)}ds\ . \qquad (3.10)$$

The transport equation (2.33) reduces to

$$[r(x)e^{\psi'(x)}-l(x)e^{-\psi'(x)}]K'(x)+\left[r'(x)e^{\psi'(x)}-l'(x)e^{-\psi'(x)}+\frac{\psi''(x)}{2}[r(x)e^{\psi'(x)}+l(x)e^{-\psi'(x)}]\right]K=0\ . \qquad (3.11)$$

Employing (3.10) in (3.11), we find that

$$K(x)=\frac{C_1}{\sqrt{r(x)l(x)}}\ , \qquad (3.12)$$

where C_1 is a normalization constant.

In the noncharacteristic boundary case, the mean exit time formula (2.38) becomes

$$\bar{n}(x)=\left[\frac{2\pi}{\epsilon r(0)[l'(0)-r'(0)]}\right]^{1/2} v_{\rm nc}(x)[1+O(\epsilon)]\Big/\left[\sum_{x=-A,B}\frac{|l(x)-r(x)|}{[r(x)l(x)]^{1/2}}e^{-\psi(x)/\epsilon}\right]\ , \qquad (3.13)$$

where

$$v_{\rm nc}(x)=-1-e^{-\beta(B-x)/\epsilon}-e^{-\alpha(x+A)/\epsilon}\ , \qquad (3.14)$$

with

$$\beta=\ln\frac{l(B)}{r(B)},\quad \alpha=\ln\frac{r(-A)}{l(-A)}\ .$$

In the characteristic boundary case, the mean exit time formula (2.40) becomes

$$\bar{n}(x)=\frac{\pi v_c(x)[1+O(\epsilon)]}{\epsilon\{r(0)[l'(0)-r'(0)]\}^{1/2}\sum_{x=-A,B}e^{-\psi(x)/\epsilon}[\,|l'(x)-r'(x)|\,/r(x)]^{1/2}} \qquad (3.15)$$

where

$$v_c(x)={\rm erf}\left[\frac{B-x}{\sqrt{\epsilon}}\left[\frac{r'(B)-l'(B)}{2r(B)}\right]^{1/2}\right]+{\rm erf}\left[\frac{A+x}{\sqrt{\epsilon}}\left[\frac{l'(-A)-r'(-A)}{2r(-A)}\right]^{1/2}\right]-1\ . \qquad (3.16)$$

We observe that our results (3.13) and (3.15) agree with the asymptotic expansion of the exact solution for types (i) and (ii) boundaries, respectively. The same is true for type (iii) boundaries as shown in Sec. V. In addition our results (3.15) agree with the result in Ref. 8, where the characteristic boundary case was treated.

We now compare our results for the mean exit time $\bar{n}(x)$ with the results obtained by the standard diffusion approximation to the random walk defined by (3.1) and (3.2). The backward operator for the standard diffusion operator is usually obtained from (3.6) by truncating the infinite series after two terms, to obtain

$$L_0u(x)=[r(x)-l(x)]u'+\frac{\epsilon}{2}[r(x)+l(x)]u''\ . \qquad (3.17)$$

In addition the discrete time is relaced by the continuous time variable $t=\epsilon n$. We note that the backward operator for the diffusion approximation is also obtained from (3.6) by introducing the scaling $\xi=x/\sqrt{\epsilon}$, in which case the Ornstein-Uhlenbeck approximation results. That is, one obtains (3.17) with $r(x)$ and $l(x)$ linearized about $x=0$. However, the linear coefficients are then usually replaced by general $r(x)$ and $l(x)$ so that (3.17) results. The mean exit time $\bar{\tau}(x)$ for the diffusion approximation to the process to exit the interval $(-A,B)$, satisfies

$$L_0\bar{\tau}(x)=-1\ ,$$
$$\bar{\tau}(-A)=\bar{\tau}(B)=0\ . \qquad (3.18)$$

The solution of (3.18) for small ϵ then yields

$$\bar{n}(x)=\frac{\bar{\tau}(x)}{\epsilon}=\left[\frac{2\pi}{\epsilon r(0)[l'(0)-r'(0)]}\right]^{1/2}\frac{v(x)}{2\sum_{x=-A,B}e^{-\hat{\psi}(x)/\epsilon}\{\,|l(x)-r(x)|\,/[l(x)+r(x)]\}}\ , \qquad (3.19)$$

where

$$\hat{\psi}(x)=2\int_0^x \frac{l(s)-r(s)}{l(x)+r(s)}ds \tag{3.20}$$

and

$$v(x)=1-\exp\left[-\frac{2[l(B)-r(B)]}{l(B)+r(B)}\frac{(B-x)}{\epsilon}\right]-\exp\left[-\frac{2[r(-A)-l(-A)]}{r(-A)+l(-A)}\frac{(x+A)}{\epsilon}\right] \tag{3.21}$$

for case (i). A similar analysis can be carried out for case (ii).

The function $\hat{\psi}(x)$ is the solution of the eikonal equation for the stationary Fokker-Planck (forward) equation

$$L_0^* p=0\ , \tag{3.22}$$

where L_0^* is the formal adjoint of L_0, and

$$p=Ke^{-\hat{\psi}/\epsilon}\ . \tag{3.23}$$

That is, $\hat{\psi}$ satisfies

$$\frac{r(x)+l(x)}{2}(\hat{\psi}'(x))^2+[r(x)-l(x)][\hat{\psi}'(x)]=0\ . \tag{3.24}$$

Clearly (3.20) and (3.10) are, in general, not equal. Indeed 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 probability of large deviations of the diffusion approximation, from equilibium, is greater than that of the underlying random walk, and consequently the mean first-passage time for the diffusion approximation is shorter than that of the random walk. Equation (3.24) can be obtained from (3.9) by expanding the exponentials in powers of ψ', and truncating terms higher than quadratic. Thus this diffusion approximation is valid only for x such that $\psi'(x)$ is small, which occurs near the equilibrium point $x=0$. For small deviations from equilibrium, either the standard diffusion approximation or the Ornstein-Uhlenbeck approximation can be used. However, for large deviations from equilibrium, neither can be used. In particular the Fokker-Planck equation (3.22) cannot be used to describe large fluctuations about equilibrium, in this random walk. In fact, the approximating diffusion process cannot be used to calculate first-passage times for deviations of order $\sqrt{\epsilon}$ or larger.

IV. THE ISING-WEISS MODEL OF FERROMAGNETISM

As an application which deals with a type (iii) boundary, we consider the mean-field model of ferromagnetism.[1,29] A system of N identical atoms, each with spin $\frac{1}{2}$, is subjected to a uniform magnetic field of strength H. The spins are further coupled to each other. This coupling is modeled by a molecular interaction field of strength J. We assume that initially there are N_+ spins which are aligned with the field, and $N_-=N-N_+$ with the opposite alignment. After each time increment Δt, the system undergoes one of two possible transitions. Either a spin is flipped or no change occurs. The probability that a spin parallel to H is flipped is given by[1]

$$P(N_+\to N_+-1)=\frac{2cN_+}{N}\exp\left[-\mu-\frac{\alpha(N_+-N_-)}{N}\right], \tag{4.1}$$

while the probability of the reverse transition is given by

$$P(N_+\to N_++1)=\frac{2cN_-}{N}\exp\left[\mu+\frac{\alpha(N_+-N_-)}{N}\right]. \tag{4.2}$$

Here $\mu\equiv\mu_0H/kT$ and $\alpha\equiv J/kT$, where μ_0 is the magnetic moment of the atom in question, k is Boltzmann's constant, T is the absolute temperature, and c is a normalization constant. Defining the parameter ϵ by

$$\epsilon\equiv\frac{2}{N}\ , \tag{4.3}$$

and the relative difference of parallel and antiparallel spins by

$$x\equiv\frac{N_+-N_-}{N}\ , \tag{4.4}$$

we obtain the following master equation for $p(x,t)$, the probability that at time t, there are N_+ parallel spins

$$p(x,t+\Delta t)-p(x,t)=c(x+1+\epsilon)e^{-\mu-\alpha(x+\epsilon)}p(x+\epsilon,t)+c(1-x+\epsilon)e^{\mu+\alpha(x-\epsilon)}p(x-\epsilon,t)-c[(1+x)e^{-\mu-\alpha x}+(1-x)e^{\mu+\alpha x}]p(x,t)\ . \tag{4.5}$$

This model corresponds to (3.1) and (3.2) with $r(x)$ and $l(x)$ given by

$$r(x)=(1-x)e^{\mu+\alpha x}\ , \tag{4.6}$$

$$l(x)=(1+x)e^{-\mu-\alpha x}\ . \tag{4.7}$$

Equations (3.8)—(3.12) give the stationary WKB distribution as

$$p(x,\infty)=\frac{A}{(1-x^2)^{1/2}}\frac{\exp\left[\frac{1}{\epsilon}(2\mu x+\alpha x^2)\right]}{[(x+1)^{(1+x)/\epsilon}(1-x)^{(1-x)/\epsilon}]}\ , \tag{4.8}$$

with A a normalization constant. For this problem, the stationary equation (4.5) can be solved exactly to yield the Boltzmann distribution

$$p(x,\infty)=\frac{B\Gamma(2/\epsilon+1)}{\Gamma((1+x)/\epsilon+1)\Gamma((1-x)/\epsilon+1)}\exp\left[\frac{1}{\epsilon}(2\mu x+\alpha x^2)\right]. \tag{4.9}$$

The equivalence as $\epsilon\to 0$ of (4.8) and (4.9) can be shown, upon an application of Stirling's formula for the asymptotic behavior of the gamma function Γ.[32]

The equilibrium points of the system are determined from $r(x)=l(x)$, and therefore satisfy

$$x=\tanh(\mu+\alpha x)\ . \tag{4.10}$$

We assume that

$$\alpha>1 \tag{4.11}$$

and

$$(\alpha^2-\alpha)^2>\mu+\ln(\sqrt{\alpha}+\sqrt{\alpha-1}) \tag{4.12}$$

so that (4.10) has three solutions $x_{A,B,C}$ satisfying

$$-1<x_A<x_C<0<x_B<1\ . \tag{4.13}$$

A local analysis shows that x_A and x_B are stable equilibria, while x_C is unstable. Equation (4.11) may be interpreted as the condition that the temperature is less than the Curie temperature of the substance. We now determine the mean relaxation time $\bar{\tau}(x)=\bar{n}(x)\Delta t$, from the state x_A to the state x_B, the latter being more stable due to the presence of the field H. Thus $\bar{n}(x)$ satisfies (3.4) with the boundary conditions

$$\bar{n}(x_C)=0 \tag{4.14}$$

and

$$\bar{n}(-1)=\bar{n}(-1+\epsilon)+\frac{e^{\alpha-\mu}}{2c}\ . \tag{4.15}$$

Condition (4.15) may either be obtained by simply setting $x=-1$ in equation (3.4) or can be reasoned as follows. Due to the underlying Markov property of the process at hand, the mean passage time from the interval $(-1,x_C)$, given that the process starts at $x=-1$ is the sum of the mean time of exit starting at $x=-1+\epsilon$ and the mean time it waits at $x=-1$. The latter quantity is computed by noting that the probability of a jump from $x=-1$ to $x=-1+\epsilon$ is $2ce^{\mu-\alpha}$ while the probability of no transition is $1-2ce^{\mu-\alpha}$. The mean waiting time is therefore $\sum_{m=1}^{\infty} m\ \Delta t Pr$ [system stays at $x=-1$ for $(m-1)$ time intervals and jumps on the mth]

$$\sum_{m=1}^{\infty} m\ \Delta t Pr=\Delta t\sum_{m=1} m(1-2ce^{\mu-\alpha})^{m-1}2ce^{\mu-\alpha}=\frac{\Delta t}{2c}e^{\alpha-\mu}\ .$$

Choosing $\Delta t=1$ we regain Eq. (4.15). A boundary layer analysis near $x=-1$ shows that condition (4.15) is unimportant in determining the mean exit time, since the contribution to the Lagrange identity (2.27) from $x=-1$ turns out to be much smaller than the contribution from $x=x_C$. However, in Sec. V, we show that a similar type of singular boundary condition can significantly affect the mean passage time.

Using (4.6)–(4.8) in (3.13), we obtain the mean passage time as

$$\bar{\tau}=\frac{\pi\Delta t}{2\epsilon c}\left[\frac{(1+x_C)^{(1+x_C)/\epsilon}(1-x_C)^{(1-x_C)/\epsilon}}{(1+x_A)^{(1+x_A)/\epsilon}(1-x_A)^{(1-x_A)/\epsilon}}\right]\frac{\exp\{-\mu-\alpha x_{A_e}-\epsilon^{-1}[2\mu(x_C-x_A)+\alpha(x_C^2-x_A^2)]\}}{\left[\left[\frac{1}{(1-x_A^2}-\alpha\right]\left[\frac{1}{1-x_C^2}-\alpha\right]\right]^{1/2}(1-x_A)}\ . \tag{4.16}$$

The result obtained in Ref. 1, for this model is given by

$$\bar{\tau}=\frac{\pi\Delta t}{2\epsilon c}[(1-x_A^2)^{-1}-\mu]^{1/2}[\mu(1-x_C^2)-1]^{-1/2}e^{\delta\mu/\epsilon}\ , \tag{4.17}$$

where $\mu=\alpha$. The constant δ, which represents the height of the barrier to be overcome (see Fig. 2 of Ref. 1) is not calculated. Our result (4.16) shows that the height of the barrier to be overcome in going from x_A to x_B is given by $\psi(x_C)-\psi(x_A)$ where

$$\psi(x)=(1+x)\ln(1+x)+(1-x)\ln(1-x)-2\mu x-\alpha x^2\ . \tag{4.18}$$

The function $\psi(x)$ in (4.18) was constructed in Ref. 4, but the rate $r\alpha(1/\bar{\tau})$ was not calculated.

V. THE MONTROLL-SHULER MODEL: A RANDOM WALK WITH A SINGULAR BOUNDARY

A simple model of dissociation of a gaseous diatomic molecule immersed in an inert gas was proposed and solved in Ref. 2. They consider a random walk of the energy levels

$$E_n=\hbar\omega(n+\tfrac{1}{2}),\quad n=0,1,2,\dots \tag{5.1}$$

of a harmonic oscillator. In this model the molecule dissociates when its energy reaches $E_D=(N_D+\frac{1}{2})\hbar\omega$. Defining $\epsilon\equiv 1/N_D$, and scaling $x_n=E_n/N_D$, the random walk is given by (3.1) with

$$\begin{aligned} r(x)&=\kappa(x+\epsilon)e^{-\theta}\,,\\ l(x)&=\kappa x\,, \end{aligned} \tag{5.2}$$

with $\theta=\hbar\omega/kT$, where k is Boltzmann's constant, T denotes absolute temperature, and κ is a rate constant.

The mean number of steps $\bar{n}(x)$ required for the molecule to dissociate starting at level x, satisfies the equation

$$\kappa(x+\epsilon)e^{-\theta}[\bar{n}(x+\epsilon)-\bar{n}(x)] -\kappa x[\bar{n}(x)-\bar{n}(x-\epsilon)]=-1,\quad 0<x<1\,. \tag{5.3}$$

The boundary conditions for (5.3) are

$$\begin{aligned} \bar{n}(1)&=0\,,\\ \bar{n}(0)&=\bar{n}(\epsilon)+\frac{e^{\theta}}{\epsilon\kappa}\,, \end{aligned} \tag{5.4}$$

so that we are again dealing with a type (iii) boundary. The second boundary condition in (5.4) is derived by using the same argument as in Sec. IV above. Equation (5.4) is a singular boundary condition in the sense that it cannot be expressed as a condition on finite number derivatives of $\bar{n}(x)$ at the origin, and all the derivatives $\bar{n}^{(m)}(0)$ contribute to the Lagrange identity (2.27). We therefore modify our procedure in a straightforward manner, by constructing a boundary-layer solution of the master equation (5.3), rather than of its Kramers-Moyal expansion. Near $x=1$, we obtain the boundary layer expansion as in Sec. IV

$$\bar{n}(x)\sim C(\epsilon)(1-e^{-\theta(1-x)/\epsilon})\,. \tag{5.5}$$

It is also the uniform asymptotic expansion of $\bar{n}(x)$ with $C(\epsilon)$ to be determined. The modification of our method begins with a local analysis of Eq. (5.3) near $x=0$. We introduce the stretched variable $\eta=x/\epsilon$, thus obtaining

$$e^{-\theta}(\eta+1)[V(\eta+1)-V(\eta)] -\eta[V(\eta)-V(\eta-1)]=-1\,, \tag{5.6}$$

where

$$V(\eta)=\frac{1}{\kappa\epsilon}\bar{n}(x)\,. \tag{5.7}$$

The second boundary condition (5.4) becomes

$$V(1)-V(0)=-e^{\theta}\,. \tag{5.8}$$

We also require that the solution to (5.6) matches with (5.5) for x fixed near $x=0$, i.e., in the overlap region where both representations are valid, as $\epsilon\to 0$. To leading order, in this limit

$$V(\eta)\sim C(\epsilon)\quad\text{as } \eta\to\infty\,. \tag{5.9}$$

A particular solution V_p of (5.6) satisfies

$$V_p(\eta+1)-V_p(\eta)=\frac{e^{\theta}}{e^{\theta}-1}\frac{1}{1+\eta}\,. \tag{5.10}$$

A solution of (5.10) is

$$V_p(\eta)=\frac{e^{\theta}}{e^{\theta}-1}\psi(\eta+1)\,,$$

where ψ is the digamma function.[32] The general solution to (5.6) is therefore given by

$$V(\eta)=V_p(\eta)+C_1+C_2\int_{-\infty}^{\theta}\frac{e^{s}(e^{s\eta}-1)}{e^{s}-1}ds\,, \tag{5.11}$$

where the two additional terms are solutions of the homogeneous problem. Employing the boundary condition (5.8) and (5.11) determines the constant C_2 as

$$C_2=\frac{-e^{\theta}}{e^{\theta}-1}\,, \tag{5.12}$$

and employing the matching condition (5.9) determines the constant C_1 as

$$C_1=C(\epsilon)\,. \tag{5.13}$$

Next, we note that an exact solution of the forward equation $L^{*}u=0$ is given by the unnormalized Boltzmann density

$$u(x)=e^{-\theta x/\epsilon}\,.$$

We multiply Eq. (5.3) by $u(x)$ and integrate from $x=\epsilon$ to $x=1-\epsilon$, rather than from 0 to 1, so that all quantities are defined, obtaining

$$\begin{aligned} -\int_{\epsilon}^{1-\epsilon}e^{-\theta x/\epsilon}dx&=\int_{\epsilon}^{1-\epsilon}(uL_x v-vL_x^{*}u)dx\\ &=\int_{\epsilon}^{1-\epsilon}e^{-\theta}e^{-\theta x/\epsilon}(x+\epsilon)[v(x+\epsilon)-v(x)]dx-\int_{\epsilon}^{1-\epsilon}e^{-\theta x/\epsilon}x[v(x)-v(x-\epsilon)]dx\\ &=\left[\int_{1-2\epsilon}^{1-\epsilon}+\int_{\epsilon}^{0}\right]\{e^{-\theta}e^{-\theta x/\epsilon}(x+\epsilon)[v(x+\epsilon)-v(x)]dx\}\,. \end{aligned} \tag{5.14}$$

Using (5.5) in the first integral on the right-hand side of (5.14) and employing (5.10)–(5.13) in the second integral we obtain

$$\bar{n}(x)\sim\frac{\epsilon}{\kappa}\frac{e^{\theta/\epsilon}}{(1-\hat{e}^{-\theta})^2}(1-e^{-(1-x)\theta/\epsilon})$$

which agrees with the Montroll-Shuler result.[2]

ACKNOWLEDGMENTS

This work was partially supported by the U.S. Air Force Office of Scientific Research under Grant No. AFOSR-83-0086, the U.S. Department of Energy under Grant No. DE-AC02-78-ERO-4650, and the National Science Foundation under Grant Nos. MCS-83-00562 and MCS-81-21659. One of us (B.M.J.) gratefully acknowledges the support of a John Simon Guggenheim Memorial Foundation Fellowship.

APPENDIX

In this appendix we discuss various properties of the eikonal function $\psi(x)$. First we show that a unique nonzero solution of the eikonal equation (2.31) exists under the condition $xm_1(x)<0$ for $x\neq 0$, and has an absolute minimum at $x=0$. Thus we also prove the existence of β in (2.18) and α in (2.20).

The moment generating function $\phi_x(t)$ is defined by

$$\phi_x(t)\equiv\int_{-\infty}^{\infty} e^{zt}w(z,x)dz \;. \tag{A1}$$

The condition

$$xm_1(x)<0 \quad \text{for } x\neq 0 \tag{A2}$$

implies that $x\phi_x'(0)<0$. Since $\phi_x''(t)>0$ and $\phi_x(0)=1$, the equation $\phi_x(t)=1$ has a unique nonzero solution $t(x)$ for $x\neq 0$, such that $xt(x)>0$. Since $m_1(0)=0$, the solution $t(0)=0$ is unique. Thus the function $\psi(x)=\int_0^x t(s)ds$ is well defined and has an absolute minimum at $x=0$. Condition (A2) is satisfied for all $x\neq 0$ in $[-A,B]$ for type (i) and type (iii) boundaries. For type (ii) boundaries, condition (A2) is satisfied for all $x\neq 0$ in $(-A,B)$, but not at the boundary. In this case the solution of $\phi_B(t)=1$ is given by $t(B)=0$. This defines $\psi'(x)$ as a continuous function in $[-A,B]$.

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