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A Singular Perturbation Approach to First Passage Times for Markov Jump Processes

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We introduce singular perturbation methods for constructing asymptotic approximations to the mean first passage time for Markov jump processes. Our methods are applied directly to the integral equation for the mean first passage time and do not involve the use of diffusion approximations. An absorbing interval condition is used to properly account for the possible jumps of the process over the boundary which leads to a Wiener–Hopf problem in the neighborhood of the boundary. A model of unimolecular dissociation is considered to illustrate our methods.

KEY WORDS: First passage time; Markov jump process; master equation; singular perturbation; asymptotic expansion.

1. INTRODUCTION

First passage times play an important role in applications such as rate processes in chemical physics (cf. other papers in this volume). In previous papers,[(1–27)] we introduced singular perturbation methods for constructing asymptotic approximations to the density of fluctuations about and the rate of transitions from deterministically stable states of the underlying dynamical systems. In particular, we computed the mean first passage time for diffusion processes (i.e., stochastically perturbed dynamical systems or Langevin equations),[(1–23)] and for Markov jump processes described by Master equations.[(24–27)] We considered both potential and nonpotential

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systems in one and higher dimensions, both smooth and sharp potential barriers, both state-dependent (multiplicative) and state independent (additive) noise, transitions from nonequilibrium as well as equilibrium steady states, and Markovian as well as non-Markovian processes. Our methods were successfully applied to a variety of applications including Kramers' model of chemical reactions, noise-induced transitions in Josephson junctions and DC squids, to name but a few.

When the underlying process is not a diffusion process, the mean first passage time is more difficult to construct and few reliable approximations are known. The purpose of this paper is to describe our method for constructing approximations to the mean first passage time for Markov jump processes.

We consider a Markov process $\{X_n\}$ defined by the stochastic difference equation

$$X_{n+1} = X_n + \varepsilon Z_n \tag{1.1}$$

where $\{Z_n\}$ is a process whose conditional jump density at time n is stationary, independent of the values of Z_k, $k < n$, and is given by

$$\frac{\partial}{\partial z} Pr\{Z_n \leqslant z \mid X_n = x, X_{n-1} = x_{n-1}, \ldots, X_0 = x_0\} = w(z, x) \tag{1.2}$$

Here ε is a small parameter, usually representing the ratio of the mean jump size to the size of the state space. We assume that the conditional moments of Z_n exist for all k and are given by

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

The scaling $t = \varepsilon n$ leads to the drift equation $x(t+\varepsilon) - x(t) = \varepsilon m_1(x) + O(\varepsilon^2)$, which corresponds to the ordinary differential equation

$$\dot{x}(t) = m_1(x) \tag{1.4}$$

where $m_1(x)$ is the conditional first moment of Z_n. For $\varepsilon \ll 1$, equation (1.4) qualitatively describes the evolution of the process. To simplify our presentation, we assume that there exists a unique stable equilibrium point of (1.4) at $x = 0$, i.e., $m_1(0) = 0$, $m_1'(0) < 0$.

We assume that the process $\{X_n\}$ is defined on $(-\infty, \infty)$ and define the first passage time, $\tilde{n}$, from the interval $(-\infty, B)$, $B > 0$, by

$$\tilde{n} = \min\{n\colon X_n \geqslant B\} \tag{1.5}$$

The mean first passage time, $n(x)$, from a point x in $(-\infty, B)$ is defined by

$$n(x) = E[\tilde{n} \mid X_0 = x] \tag{1.6}$$

where E denotes expectation. Then $n(x)$ satisfies

$$Ln(x) = \int_{-\infty}^{\infty} n(x + \varepsilon z)\, w(z, x)\, dz - n(x) = -1 \tag{1.7}$$

and the absorbing interval condition

$$n(x) = 0, \qquad x \geqslant B \tag{1.8}$$

Here L is the backward Kolmogorov operator.

We note that since the jump density $w(z, x)$ is defined for $-\infty < z < \infty$ for all x, the process $\{X_n\}$ can exit the interval $(-\infty, B)$ by jumping over the boundary point $x = B$ (cf. Fig. 1). As we shall see, this jump across $x = B$ gives rise to complications in the construction of $n(x)$. In particular, the mean first passage time $n(x)$ may have a jump discontinuity at $x = B$ (cf., e.g., Ref. 28).

In general, the exact solution of (1.7), (1.8) is not known, so that approximate techniques are needed. One technique is to replace the left side of (1.7) by a second-order differential equation. This diffusion approximation is equivalent to replacing the original process $\{X_n\}$ by a diffusion process. It is well known that diffusion approximations are not always good approximations to jump processes.[29–32] In addition, a second difficulty arises in using diffusion approximations for the mean first passage time problem (1.7), (1.8). Specifically there is the difficulty of choosing the proper boundary condition at $x = B$.[28,33] The diffusion process must hit the boundary point $x = B$ as it exists the interval $(-\infty, B)$. Thus, the boundary condition that is often employed is the absorbing boundary condition $n(B) = 0$ in which case no discontinuity can arise. Other types of boundary behavior have been studied for diffusion processes.[34] However, there appear to be no simple boundary conditions for diffusion equations that describe jumping over a boundary.

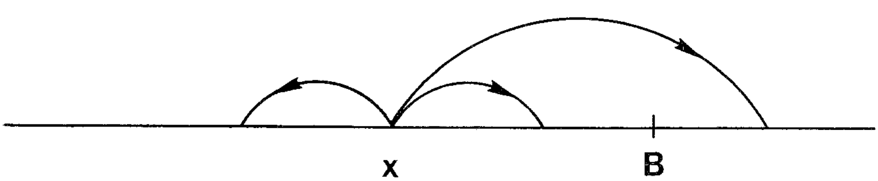

Fig. 1. An illustration of some possible jumps of the process X_n starting from the point x.

Our objective in this paper is to present a technique for constructing an asymptotic approximation of the mean first passage time $n(x)$ for the process $\{X_n\}$. Our methods are applied directly to (1.7) and do not involve the use of diffusion approximations. In addition, we properly account for the possible jumps of the process over the boundary $x = B$. Specifically we use condition (1.8) and do not replace it with an absorbing point condition. In previous work,[24–26] we constructed approximations to $n(x)$ for Markov jump processes that hit the boundary point as it exited. Thus a simple absorbing condition was used. This is the case, for example, in random walks with nearest-neighbor jumps where the boundary point is a lattice point.

In Section 2, we construct an asymptotic approximation to $n(x)$ for two types of boundary points at $x = B$. The first is the noncharacteristic boundary defined by $m_1(B) < 0$. Next we treat the characteristic boundary in which $m_1(B) = 0$, i.e., B is an unstable rest point of the drift equation (1.4). In particular, we show that $n(x)$ may have a jump discontinuity at $x = B$. Finally, in Section 3, we apply these methods to a model of unimolecular dissociation and compute the rate of dissociation. For this model, we also obtain an explicit, closed form solution of (1.7), (1.8) and verify that in fact our asymptotic solution is the leading term in the asymptotic solution of the exact solution. Finally, in the Appendix, we describe the WKB approximation to the stationary solution of the forward equation, which is used in the construction of $n(x)$.

We note that our methods have been extended to a wide variety of problems[27] including continuous time processes, problems with two exit boundaries, and partially reflecting or sticky boundary points. These were analyzed in the context of other applications such as queueing theory.[35]

2. MEAN FIRST PASSAGE TIME

We now construct an asymptotic solution of (1.7), (1.8) for small ε. We consider two types of boundary behavior. First, we consider the noncharacteristic boundary where $m_1(B) < 0$. Then, we treat the characteristic boundary in which $m_1(B) = 0$, i.e., B is an unstable rest point of the drift equation. Using the condition (1.8) in (1.7), we rewrite (1.7) as

$$\int_{-\infty}^{(B-x)/\varepsilon} n(x + \varepsilon z)\, w(z, x)\, dz - n(x) = -1 \tag{2.1}$$

For x bounded away from B, we extend the upper limit of integration to ∞

and use the Kramers–Moyal expansion of (2.1) to derive the outer solution. That is, we expand $n(x+\varepsilon z)$ in powers of ε to get

$$\sum_{k=1}^{\infty} \frac{\varepsilon^k m_k(x)}{k!} \frac{d^k}{dx^k} n(x) = -1 \tag{2.2}$$

Clearly, as $\varepsilon \to 0$, we expect $n(x)$ to become infinite. Thus we scale

$$n(x) = C(\varepsilon)\, u(x) \tag{2.3}$$

where $C(\varepsilon) \to \infty$ as $\varepsilon \to 0$ and $\sup_{x<B} u(x) = 1$. We obtain from (2.3) and (2.2)

$$\sum_{k=1}^{\infty} \frac{\varepsilon^k m_k(x)}{k!} u^{(k)}(x) \sim 0 \qquad \text{as} \quad \varepsilon \to 0 \tag{2.4}$$

Now we assume the regular expansion[24-27]

$$u(x) \sim u_0(x) + \varepsilon u_1(x) + \cdots \tag{2.5}$$

to obtain the reduced equation

$$m_1(x)\, u_0'(x) = 0 \tag{2.6}$$

It follows that $u_0(x) = 1$.

The approximate solution

$$n_0(x) = C(\varepsilon)\, u_0(x) = C(\varepsilon) \tag{2.7}$$

satisfies (2.1) asymptotically for x bounded away from B, that is, when the upper limit of integration can be replaced by ∞, but fails to be valid near the boundary. For x near B it is necessary to construct a boundary layer correction to $u_0(x)$.

We introduce the stretched variable

$$\eta = \frac{B-x}{\varepsilon} \tag{2.8}$$

and the scaled boundary layer function

$$U(\eta) = u(B - \varepsilon\eta) \tag{2.9}$$

into (2.1) to obtain

$$\int_{-\infty}^{\eta} U(\eta - z)\, w(z, B - \varepsilon\eta)\, dz - U(\eta) \sim 0 \tag{2.10}$$

We assume that $U \sim U_0 + \varepsilon U_1 + \cdots$ and that $w(z, x)$ has a power series expansion in x near $x = B$, so that

$$w(z, B - \varepsilon\eta) \sim w(z, B) - \varepsilon w_x(z, B)\eta + \cdots \tag{2.11}$$

Using (2.11) and the change of variables, $\eta - z \to \hat{z}$, the boundary layer equation (2.10) then becomes, to leading order, the Wiener–Hopf equation

$$U_0(\eta) = \int_0^\infty w(\eta - \hat{z}, B)\, U_0(\hat{z})\, d\hat{z}, \qquad \eta > 0 \tag{2.12}$$

subject to

$$U_0(\eta) = 0, \qquad \eta \leqslant 0 \tag{2.13}$$

In addition, $U_0(\eta)$ must match with the outer $u_0(x)$, so that the matching condition is

$$\lim_{\eta \to \infty} U_0(\eta) = 1 \tag{2.14}$$

Problem (2.12)–(2.14) is solvable by the Wiener–Hopf technique,[38] but the solution cannot be expressed in terms of elementary functions for an arbitrary density $w(z, x)$. However, since $m_1(B) < 0$, the Fourier transform of $U_0(\eta)$ has a simple pole at the origin so that $U_0(\eta)$ approaches a constant for $\eta \gg 1$ and satisfies the matching condition (2.14). For the specific example we consider in Section 3, the boundary layer function will be constructed explicitly.

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

$$n(x) \sim C(\varepsilon)\, U_0\left(\frac{B - x}{\varepsilon}\right) \tag{2.15}$$

In general, $U_0(0^+) \neq 0 = U_0(0^-)$ so that $n(B^-) \neq 0 = n(B^+)$ and $n(x)$ is discontinuous at $x = B$ (cf. Fig. 2). In fact, $n(B^-) = O(C(\varepsilon))$ when $m_1(B) < 0$.

To determine the as yet unknown constant $C(\varepsilon)$ we multiply equation (2.1) by the solution $p(x)$ of the stationary forward equation

$$L^* p(x) = \int_{-\infty}^{\infty} p(x - \varepsilon z)\, w(z, x - \varepsilon z)\, dz - p(x) = 0 \tag{2.16}$$

and integrate over $(-\infty, B)$, to obtain

$$- \int_{-\infty}^{B} p(x)\, dx = - \int_{-\infty}^{B} n(x)\, p(x)\, dx + \int_{-\infty}^{B} \int_{-\infty}^{(B - x)/\varepsilon} n(x + \varepsilon z)\, w(z, x)\, p(x)\, dz\, dx \tag{2.17}$$

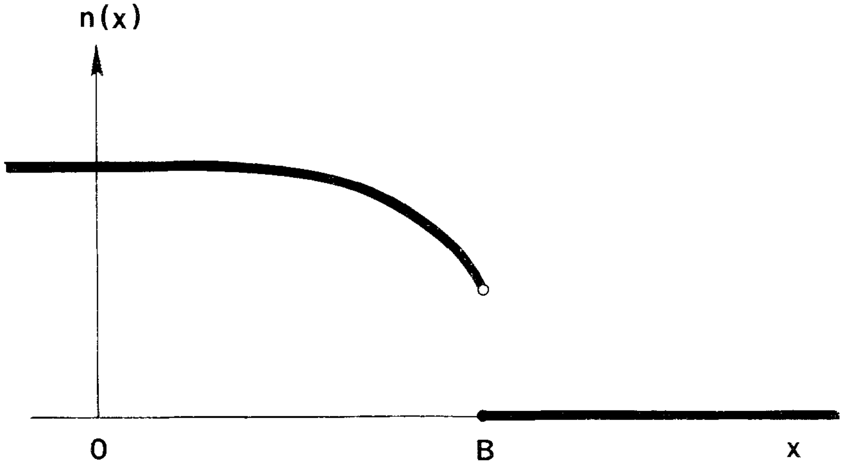

Fig. 2. A sketch of the mean exit time $n(x)$ versus x illustrating the existence of a discontinuity at $x = B$.

Now we interchange the order of integration in the double integral on the right side of (2.17) to obtain

$$-\int_{-\infty}^{B} p(x)\,dx = \int_{-\infty}^{B} n(x)\,L^*p(x)\,dx - \int_{-\infty}^{0}\int_{B}^{B-\varepsilon z} p(x)\,w(z,x)\,n(x+\varepsilon z)\,dx\,dz \qquad (2.18)$$

where the operator L^* is defined in (2.16). Finally, using $L^*p = 0$ we obtain the identity

$$\int_{-\infty}^{B} p(x)\,dx = \int_{B}^{\infty} p(x) \int_{-\infty}^{(B-x)/\varepsilon} w(z,x)\,n(x+\varepsilon z)\,dz\,dx \qquad (2.19)$$

Next we replace $p(x)$ by its WKB approximation (cf. Appendix)

$$p(x) \sim K(x)\,e^{-\psi(x)/\varepsilon}, \qquad \psi(0) = 0, \qquad \psi'(0) = 0 \qquad (2.20)$$

and $n(x)$ by its uniform approximation (2.15). Then, noting that the major contribution to the integral with respect to x comes from the point $x = B$, where $p(x)$ is maximal in (B, ∞), we again introduce the stretched variable $\eta = (B - x)/\varepsilon$ and expand both $p(x)$ and $w(z, x)$ near $\eta = 0$. Finally, using Laplace's expansion of the integral on the left-hand side of equation (2.19) about the stable rest point $x = 0$ and solving for $C(\varepsilon)$, we obtain

$$C(\varepsilon) \sim \left[\frac{2\pi}{\psi''(0)\varepsilon}\right]^{1/2} \frac{K(0)\,e^{(1/\varepsilon)\psi(B)}}{K(B)\int_{-\infty}^{0} e^{\eta\psi'(B)} \int_{-\infty}^{\eta} w(z,B)\,U_0(\eta - z)\,dz\,d\eta} \qquad (2.21)$$

For processes X_n that must hit the boundary point $x = B$ to exit the interval $(-\infty, B)$ (i.e., processes that do not jump over the boundary), the Kramers–Moyal expansion (2.2) is valid up to the boundary. The solution $n(x)$ of (2.1) is then continuous at the boundary, hence it is determined by the simpler absorbing boundary condition $n(B) = 0$. This case, with applications in physics and chemistry, was considered in Refs. 24–26. This boundary condition is also used in diffusion processes for an exit point.

Next, we consider a characteristic boundary, where $m_1(B) = 0$. Again a boundary layer analysis is required. As in the noncharacteristic case, we introduce the stretched variable $\eta = (B - x)/\varepsilon$ and the boundary layer function $U(\eta) = u(B - \varepsilon\eta)$ into (2.1) to obtain the boundary layer equation (2.12) subject to the condition (2.13). The solution can be constructed using the Wiener–Hopf technique. However, if $m_1(B) = 0$, the Fourier transform of $U_0(\eta)$ how has a double pole at the origin and hence $U_0(\eta)$ grows linearly for $\eta \gg 1$, i.e.,

$$U_0(\eta) \sim \hat{c}\eta \tag{2.22}$$

Thus the matching condition (2.14) is not satisfied and another boundary layer correction is needed. This boundary layer, sometimes referred to as an intermediate layer, connects the original boundary layer expansion and the outer (regular) expansion (2.5). We now introduce the new scaling and intermediate layer function by

$$\begin{aligned} n(x) &= C(\varepsilon)\, V(\xi) \\ \xi &= (B - x)/\sqrt{\varepsilon} \end{aligned} \tag{2.23}$$

where $C(\varepsilon) \to \infty$ as $\varepsilon \to 0$. Using (2.33) in (2.1), we obtain

$$V(\xi) = \int_{-\infty}^{\xi/\sqrt{\varepsilon}} w(z, B - \sqrt{\varepsilon}\,\xi)\, V(\xi - \sqrt{\varepsilon}\, z)\, dz \tag{2.24}$$

subject to the matching condition

$$\lim_{\xi \to \infty} V(\xi) = 1 \tag{2.25}$$

with the outer expansion and the second matching condition with the boundary layer expansion, which is that $V(\xi)$ for $\xi \ll 1$ match with $U_0(\eta)$ for $\eta \gg 1$, [see (2.22)]. For $\xi = O(1)$, we extend the upper limit of integration in (2.24) to ∞ and expand the integral in powers of $\sqrt{\varepsilon}$. Using $V(\xi) \sim V_0(\xi) + \sqrt{\varepsilon}\, V_1(\xi) + \cdots$, we obtain to leading order,

$$\tfrac{1}{2} m_2(B)\, V_0''(\xi) + \xi m_1'(B)\, V_0'(\xi) = 0 \tag{2.26}$$

The solution of (2.26) with the matching condition (2.25) yields

$$V_0(\xi)=2c\left[\frac{m_1'(B)}{\pi m_2(B)}\right]^{1/2}\int_0^{\xi} e^{-m_1'(B)u^2/m_2(B)}\,du+(1-c) \tag{2.27}$$

We note that (2.27) is uniformly valid for all x satisfying $B-x\gg\varepsilon$. We now apply the second matching condition described above. As $\xi\to 0$, we find that

$$V_0(\xi)\sim(1-c)+2\left[\frac{m_1'(B)}{\pi m_2(B)}\right]^{1/2}\sqrt{\varepsilon}\,\eta c \tag{2.28}$$

so to match (2.22) with (2.28), we choose

$$\begin{aligned} c&=1\\ \hat{c}&=2\sqrt{\varepsilon}\left[\frac{m_1'(B)}{\pi m_2(B)}\right]^{1/2} \end{aligned} \tag{2.29}$$

Thus, the solution of (2.1) is given by

$$n(x)\sim C(\varepsilon)\begin{cases} 2\left[\dfrac{m_1'(B)}{\pi m_2(B)}\right]^{1/2}\displaystyle\int_0^{(B-x)/\sqrt{\varepsilon}} e^{-m_1'(B)u^2/m_2(B)}\,du, & B-x\gg\varepsilon\\ U_0\left(\dfrac{B-x}{\varepsilon}\right), & \dfrac{B-x}{\varepsilon}=O(1) \end{cases} \tag{2.30}$$

where $U_0((B-x)/\varepsilon)$ is the solution of (2.12)–(2.14). We again observe that $n(x)$ will, in general, be discontinuous at $x=B$. However, in contrast to the case when $m_1(B)<0$, we now have $n(B^-)=O(\sqrt{\varepsilon}\,C(\varepsilon))$ when $m_1(B)=0$.

Finally, we compute the constant $C(\varepsilon)$ using the procedure described above. Thus, using (2.20) and (2.30) in (2.19), we find that

$$C(\varepsilon)\sim\frac{\pi}{\varepsilon}\frac{K(0)}{K(B)}e^{(1/\varepsilon)\psi(B)}\left|\frac{m_2(0)\,m_2(B)}{m_1'(0)\,m_1'(B)}\right|^{1/2}\frac{1}{m_2(B)} \tag{2.31}$$

This formula was derived in Ref. 25 for the case when the process X_n hits the boundary as it exits.

The procedure used above applies directly to problems on a finite interval, where the second boundary point can be an exit boundary, a reflecting boundary, or a partially reflecting boundary.[24–27] The analysis of the mean first passage problem for the continuous time Markov jump process $\{X(t)\}$ is similar to that of the discrete case and is given in Ref. 35.

3. EXAMPLE

We now consider a model of unimolecular dissociation that was posed as a Markov jump process in Refs. 36 and 37. The model describes the thermal excitation of large molecules and the quantity of interest is the dissociation rate which is the reciprocal of the mean number of collisions until dissociation.

Let E be the energy of the excited molecule and E_0 be the threshold value, i.e., dissociation occurs if $E \geqslant E_0$. The excited molecule undergoes collisions which cause an increase or decrease in its energy (cf. Refs. 36 and 37 for details).

We define a nondimensional process by letting $x = E/E_0$ and scale the jump size between energies E_1 and E_2 by $z = (E_1 - E_2)/kT$, where T is the absolute temperature and k is Boltzmann's constant. Then the conditional jump density function of $\{Z_n\}$ for this model is given by

$$w(z, x) = K \begin{cases} e^{z/a}, & -\dfrac{x}{\varepsilon} < z < 0 \\ \left[\dfrac{1}{K} - a - b + ae^{-x/a\varepsilon}\right] \delta(z), & z = 0 \\ e^{-z/b}, & z > 0 \end{cases} \tag{3.1}$$

Here the parameter $\varepsilon = kT/E_0$ is assumed to be small. The parameter K is the collision frequency and the parameters a and b are defined by $a = \alpha/kT$ and $b = \beta/kT$ where α and β are the average energy loss and gain, respectively, per collision. We assume that the stationary distribution is the Boltzmann distribution so that

$$p(x) \propto e^{-x/\varepsilon} \tag{3.2}$$

which requires that

$$\frac{1}{b} - \frac{1}{a} = 1 \tag{3.3}$$

In this example, we find that

$$m_1(x) \cong b - a \qquad \text{for} \quad x \gg \varepsilon \tag{3.4}$$

so that for the dissociation to occur the process must move against the flow of the drift equation (1.4).

Let $n(x)$ be the mean number of collisions until dissociation for a molecule with initial energy x. Then $n(x)$ satisfies (1.7), with $w(z, x)$ given by (3.4), and the condition

$$n(x) = 0, \qquad x \notin (0, 1) \tag{3.5}$$

which gives

$$\int_{-x/\varepsilon}^{0} n(x+\varepsilon z)\, e^{z/a}\, dz + [-a-b+ae^{-x/a\varepsilon}]\, n(x) + \int_{0}^{(1-x)/\varepsilon} n(x+\varepsilon z)\, e^{-z/b}\, dz = -\frac{1}{K} \tag{3.6}$$

We note that the process must exit by crossing $x=1$. That is, jumps across $x=0$ are not allowed since they would lead to negative energies [cf. (3.1)].

We now apply the method described in Section 2 for the noncharacteristic boundary case. Away from $x=0$ and $x=1$, we extend the limit $-x/\varepsilon \to -\infty$ and $(1-x)/\varepsilon \to \infty$ in (3.6) and find that the outer solution is given by

$$n(x) \sim C(\varepsilon) \tag{3.7}$$

where $C(\varepsilon) \to \infty$ as $\varepsilon \to 0$. The boundary layer expansion near $x=1$ is constructed by introducing the stretched variable $\eta = (1-x)/\varepsilon$ and the boundary layer function $U(\eta)$ [recall $n(x) = C(\varepsilon)\, u(x)$] to obtain to leading order the Wiener–Hopf problem[38] (2.12), (2.13) with $B=1$ and the matching condition (2.14). Using (3.1) in (2.12) we obtain the Wiener–Hopf equation

$$(a+b)\, U_0(\eta) = \int_{-\infty}^{0} U_0(\eta - z)\, e^{z/a}\, dz + \int_{0}^{\eta} U_0(\eta - z)\, e^{-z/b}\, dz, \qquad \eta > 0 \tag{3.8}$$

with

$$U_0(\eta) = 0, \qquad \eta \leqslant 0 \tag{3.9}$$

We note that for $\eta < 0$ the left side of (3.8) is an unknown function, $\phi(\eta)$ which must be determined along with the solution $U_0(\eta)$ for $\eta > 0$. Applying the Wiener–Hopf technique to (3.8) we find that the solution satisfying the matching condition (2.14) is

$$\begin{aligned} U_0(\eta) &= 1 - \frac{b}{a}\, e^{-\eta}, \qquad && \eta > 0 \\ \phi(\eta) &= (a+b)\, b e^{\eta/a}, \qquad && \eta < 0 \end{aligned} \tag{3.10}$$

Hence, the uniform solution for the mean number of collisions until dissociation is given by

$$n(x) \sim C(\varepsilon) \left[1 - \frac{b}{a}\, e^{-(1-x)/\varepsilon} \right], \qquad a > b \tag{3.11}$$

We note that $n(1) = C(\varepsilon)(1 - b/a) \neq 0$ and hence the mean exit time has a jump at $x = 1$; see Fig. 2. Clearly, the use of an absorbing point condition at $x = 1$ would lead to a serious error.

Finally, we compute the value of $C(\varepsilon)$ using the integral identity (2.19) which in this case is

$$-\frac{1}{K}\int_0^1 p(x)\,dx = \int_1^\infty p(x) \int_{-x/\varepsilon}^{(1-x)/\varepsilon} n(x + \varepsilon z)\, w(z, x)\, dz\, dx \tag{3.12}$$

We now use $p(x)$ given in (3.2) and observe that the major contribution to the integral on the right side of (3.1) comes from a neighborhood of $x = 1$. Thus, we let $\eta = (1 - x)/\varepsilon$ so that (3.12) becomes

$$\frac{\varepsilon}{K} \sim \varepsilon e^{-1/\varepsilon} C(\varepsilon) \int_{-\infty}^0 e^\eta \int_{-\infty}^\eta U_0(\eta - z)\, w(z, 1)\, dz\, d\eta \tag{3.13}$$

Here we have asymptotically evaluated the integral on the left side of (3.12), localized the jump density at $x = 1$, and extended the lower limit $-x/\varepsilon$ to $-\infty$. Hence, we find that

$$\begin{aligned} C(\varepsilon) &\sim \frac{e^{1/\varepsilon}}{K \int_{-\infty}^0 e^\eta \int_{-\infty}^\eta U_0(\eta - z)\, w(z, 1)\, dz\, d\eta} \\ &= \frac{e^{1/\varepsilon}}{K \int_{-\infty}^0 e^\eta \phi(\eta)\, d\eta} \\ &= \frac{e^{1/\varepsilon}}{K(a + b)\, b^2} \end{aligned} \tag{3.14}$$

Thus, the uniform expansion for the mean number of collisions until dissociation is

$$n(x) \sim \frac{e^{1/\varepsilon}}{K(a + b)\, b^2} \left[1 - \frac{b}{a} e^{-(1-x)/\varepsilon} \right] \tag{3.15}$$

We now construct the exact solution to (3.6) and show that the leading term in its asymptotic expansion for small ε is the solution (3.15) which we constructed. To construct the exact solution, we first introduce the new variable $\xi = x + \varepsilon z$ into the integrals in (3.6) to obtain

$$\begin{aligned} \pounds n(x) = {} & \frac{1}{\varepsilon}\int_0^x n(\xi)\, e^{(\xi - x)/a\varepsilon}\, d\xi + [-a - b + a e^{-x/a\varepsilon}]\, n(x) \\ & + \frac{1}{\varepsilon}\int_x^1 n(\xi)\, e^{-(\xi - x)/b\varepsilon}\, d\xi = -\frac{1}{K} \end{aligned} \tag{3.16}$$

We now apply the operator $1+\varepsilon ab(d/dx)-\varepsilon^2 ab(d^2/dx^2)$ to $\pounds n(x)=-1/K$ in (3.16) which leads to the second-order differential equation

$$(a+b-ae^{-x/a\varepsilon})\,n''(x)+\frac{1}{\varepsilon}\,[-a-b+(a+2)\,e^{-x/a\varepsilon}]\,n'(x)=-\frac{1}{\varepsilon^2 abK} \tag{3.17}$$

We obtain a boundary condition at $x=0$ by applying the operator $1-\varepsilon b(d/dx)$ to $\pounds n(x)=-1/K$ and setting $x=0$ to obtain

$$n'(0)=-\frac{1}{\varepsilon b^2 K} \tag{3.18}$$

Similarly we apply the operator $1+\varepsilon a(d/dx)$ to $\pounds n(x)=-1/K$ with $x=1$ to obtain

$$(a+b-ae^{-1/a\varepsilon})\,n'(1)+\frac{a+b}{\varepsilon a}\,n(1)=\frac{1}{\varepsilon aK} \tag{3.19}$$

The solution of (3.17) with the boundary conditions (3.19) and (3.18) is

$$\begin{aligned} n(x)=&\frac{1}{\varepsilon abK}\int_1^x \frac{a+b-abe^{-s/a\varepsilon}}{[a+b-ae^{-s/\varepsilon a}]^2}\,ds+\frac{a+b}{\varepsilon Kab}\int_x^1 \frac{e^{s/\varepsilon}}{[a+b-ae^{-s/\varepsilon a}]^2}\,ds \\ &+\frac{1}{(a+b)K}+\frac{e^{1/\varepsilon}}{bK(a+b-ae^{-1/\varepsilon a})}-\frac{a+b-abe^{-1/a\varepsilon}}{(a+b)\,bK(a+b-ae^{-1/\varepsilon a})} \end{aligned} \tag{3.20}$$

We now expand $n(x)$ given by (3.20) for $\varepsilon\to 0$, with x bounded away from 1. The leading term in the asymptotic expansion has contributions from the second and fourth terms in (3.20) which give

$$n(x)\sim\frac{e^{1/\varepsilon}}{Kb^2(a+b)} \tag{3.21}$$

This agrees with our asymptotic solution (3.15) when x is bounded away from 1, i.e., $(1-x)/\varepsilon$ is large.

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APPENDIX: WKB SOLUTION

We now describe the WKB approximation to the stationary solution of the forward equation. For the process $\{X_n\}$ on $(-\infty, \infty)$ described in Section 1, the stationary forward equation is

$$L^*p(x) = \int_{-\infty}^{\infty} p(x-\varepsilon z)\, w(z, x-\varepsilon z)\, dz - p(x) = 0 \tag{A1}$$

Here L^* is the formal adjoint of the backward operator L defined in (1.7). We seek an asymptotic solution of (A1) for small ε in the WKB form[30,24–27]

$$p(x) \sim [K_0(x) + \varepsilon K_1(x) + \cdots]\, e^{-\psi(x)/\varepsilon}, \qquad 0 < \varepsilon \ll 1 \tag{A2}$$

Substituting (A2) into (A1), expanding for $\varepsilon \gg 1$, and equating the coefficient of each power of ε to zero yields to leading order

$$\int_{-\infty}^{\infty} [e^{z\psi'(x)} - 1]\, w(z, x)\, dz = 0 \tag{A3}$$

At the next order in ε, we find that $K_0(x)$ satisfies

$$\int_{-\infty}^{\infty} \left\{ \frac{\partial}{\partial x} [w(z, x)\, K_0(x)] + \frac{zw(z, x)}{2} \psi''(x)\, K_0(x) \right\} z e^{z\psi'(x)}\, dz = 0 \tag{A4}$$

Equation (A3) has a unique solution $\psi = \psi(x)$ satisfying $\psi(0) = 0$ and $\psi(x) > 0$, $x \neq 0$. Given the solution of (A3), we construct the solution of (A4) as

$$K_0(x) = \frac{\exp\{-\frac{1}{2}\int_0^x [\int_{-\infty}^{\infty} z(\partial w/\partial y)(z, y) e^{z\psi'(y)} dz / \int_{-\infty}^{\infty} z e^{z\psi'(y)} w(z, y) dz]\, dy\}}{[\int_{-\infty}^{\infty} z e^{z\psi'(x)} w(z, x)\, dz]^{1/2}}$$

This solution is used in the integral (2.19) to determine the constant $C(\varepsilon)$ in the expression for the mean exit time $n(x)$.

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