Thermally activated escape over time-modulated fluctuating barriers

William Schneller,[1,2] Leon Gunther,[1] and David L. Weaver[1]
[1]Department of Physics, Tufts University, Medford, Massachusetts 02155
[2]The MathWorks, Inc., 24 Prime Park Way, Natick, Massachusetts 01760
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Exact numerical and approximation analytical solutions are obtained for the escape of diffusing particles from a one-dimensional, finite box in which the absorbing boundary has time-modulated gating properties; that is, it has a time-dependent reactivity proportional to a square wave, a saw-toothed wave, or a sine-squared wave. The results may have applications to intramolecular fluorescence quenching, movement of electrons in semiconductors through a time-varying insulating layer, and localization of components on a membrane surface.

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Systems which are overdamped due to the frictional drag of solvent have the motion of their constituents described by the diffusion equation. An important aspect of this general physical process is the problem of diffusion from one side of a potential barrier to the other side (the escape-over-the-barrier problem), as discussed originally by Kramers [1]. Study of this problem is important because of its occurrence as an approximation to the true physical situation in many cases involving interfaces and surfaces. It may also be related to quantum-mechanical barrier penetration using stochastic quantization methods [2].

There has recently been renewed interest in the escape-over-the-barrier problem when the barrier height (and possibly shape) is varying in time [3–6]. A fluctuating barrier could be important in intramolecular fluorescence quenching [7], movement of electrons in semiconductors through a time-varying insulating layer [6], localization of components on the membrane surface [8], and other areas of biology, chemistry, and physics.

In this paper the emphasis is on the absorbing barrier having time-modulated gating properties (rather than a changing barrier height) which allow the diffusing particles to pass to the other side, that is, a first-passage-type problem [9] in which the absorbing boundary has a time-dependent reactivity [10]. The physical system to be examined is diffusion in a one-dimensional box of width L at absolute temperature T and with diffusion coefficient D. The diffusion equation is

$$\frac{\partial \rho}{\partial t} = D \frac{\partial^2 \rho}{\partial x^2} \tag{1}$$

for the position probability density $\rho(x,t)$ in the space $0 < x < L$, as shown in Fig. 1. The initial condition is chosen to be

$$\rho(x,0) = \frac{1}{L} , \tag{2}$$

which is a uniform distribution, and the boundary conditions are

$$\left.\frac{\partial \rho}{\partial x}\right|_{x=L} = 0 \tag{3}$$

at the reflecting boundary and

$$\left. D\frac{\partial \rho}{\partial x}\right|_{x=0} = \kappa(t)\rho|_{x=0} \tag{4}$$

at the boundary which is fluctuating in time (see Fig. 1).

Since $D(\partial \rho/\partial x)$ is the flux at the boundary, Eq. (3) corresponds to complete reflection at the boundary $x = L$. Equation (4) is the "radiation" boundary condition [10–14] at the $x = 0$ interface (e.g., a semiconductor-insulator interface). This boundary has a time-dependent reactivity $\kappa(t)$, which determines the extent to which the boundary is completely absorbing ($\kappa = \kappa_{\max}$, open gate) versus completely reflecting ($\kappa = 0$, closed gate). The gate variability could be due to a potential barrier that changes between high and low states.

To study the properties of the gating boundary at $x = 0$, we calculate the fraction of particles $N(t)$ that have not passed through this boundary at time t, given by

$$N(t) = \int_0^L dx\, \rho(x,t) . \tag{5}$$

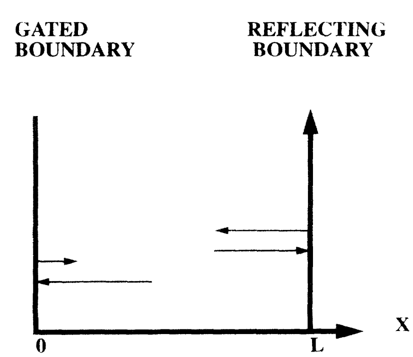


FIG. 1. Schematic view of the diffusion space of length L with the reflecting boundary (infinite potential barrier) and the gated boundary at which the diffusing particles ability to escape is time dependent.

It is the time dependence of $N(t)$ as a function of the gate reactivity $\kappa(t)$ that is of interest.

To find $N(t)$, an approximate analytical form is derived for three cases in which $\kappa(t)$ is a periodic function of time. The analytical approximation is verified by exact numerical solution of Eqs. (1)–(5) for three examples. Because the gate reactivity $\kappa(t)$ is time dependent, there is no first-passage time, but an average over a period of the reactivity $\kappa(t)$ for a periodic gating can be carried out and results are presented for the three examples studied. Finally a brief discussion of the results is given and some future studies are suggested.

To obtain an approximate analytical form for $N(t)$, we use the differential equation that it has been shown [15] previously to satisfy, namely,

$$\frac{L}{\kappa(t)}\frac{dN}{dt}+\frac{1}{D}\frac{d}{dt}[g(t)N(t)]+N(t)=0\ , \tag{6}$$

where $g(t)$ is defined by the integral (see Ref. [15])

$$\int_0^L dx\,\rho(x,t)x\left(L-\tfrac{1}{2}x\right)=g(t)N(t) \tag{7}$$

and is a parameter with units of squared length whose value determines the approximation to $N(t)$. If $g(t)$ were known for all t, then $N(t)$ could be calculated exactly from Eq. (6). Conversely, approximating $g(t)$ leads to an approximate solution for $N(t)$. Knowing $\rho(x,t)$ for a particular value $t=t'$ allows the integrals in Eqs. (5) and (7) to be carried out to determine $g(t')$. For example, if κ were time independent, replacing $g(t)$ by the constant value $g(0)=L^2/3$, which is determined from the initial condition on $\rho(x,t)$ [Eq. (2)] gives the first-passage time approximation [9] to $N(t)$.

As a first approximation to an analytical form for $N(t)$ in the general case with g a function of time, we approximate $g(t)$ by its first-passage time value $g(0)$. Exact numerical calculations of $N(t)$ establish the validity of this approximation. Substituting $g(0)$ into Eq. (6) and integrating gives the approximate analytical value of $N(t)$, namely,

$$N(t)\cong\exp\left[-\int_0^t dt'/\tau(t')\right]\ , \tag{8}$$

where $\tau(t)$ is the first-passage time result for this physical situation with the usual time-independent reactivity replaced by $\kappa(t)$, that is, $\tau(t)=L/\kappa(t)+L^2/3D$. This result may be understood as the mean time to diffuse a distance $L(L^2/3D)$ plus the mean time to pass over the barrier once the particle is at the barrier edge $[L/\kappa(t)]$.

To find exact numerical solutions for $N(t)$, Eqs. (1)–(4) were integrated numerically using the finite-difference method [16]. The resulting values for $\rho(x,t)$ were then used in Eq. (5) to find $N(t)$ with Simpson's rule [17]. All calculations were performed using the Matlab numerical analysis software [18].

In order to calculate $N(t)$ analytically or numerically, $\kappa(t)$ in the boundary condition at $x=0$, given in Eq. (4), must be specified. We used the form of $\kappa(t)$ from kinetic theory [10,13,14] to write the boundary condition at $x=0$ as

$$\left.\frac{\partial\rho}{\partial x}\right|_{x=0}=\frac{\beta(t)}{2-\beta(t)}\frac{\langle v\rangle}{D}\rho\Big|_{x=0}\ , \tag{9}$$

that is,

$$\kappa(t)\equiv\frac{\beta(t)}{2-\beta(t)}\langle v\rangle \tag{10}$$

(see Appendix B of Ref. [10] for a derivation). Here $\langle v\rangle$ is the root-mean-square velocity from kinetic theory, and $\beta(t)$ is the probability that the diffusing particles will pass over the barrier, i.e., $0\le\beta(t)\le 1$. For example, if the barrier at $x=0$ is due to a narrow, time-varying potential-energy function in which the height changes with time, that is, $\beta(t)\approx e^{-V(t)/k_BT}$, then when $V=0$, $\beta=1$, when $V=0.693k_BT$, $\beta=\frac{1}{2}$, and when $V\to\infty$, $\beta\to 0$.

Introducing the parameters $T_D\equiv L^2/D$ and $\gamma\equiv L\langle v\rangle/3D$, the approximate, analytical solution for $N(t)$, Eq. (8), becomes

$$N(t)\cong\exp\left[-\frac{3\gamma}{2T_D}\int_0^t dt'\frac{\beta(t')}{1+\frac{(\gamma-1)}{2}\beta(t')}\right]\ . \tag{11}$$

The parameter γ is the ratio of the size of the diffusion space L to the mean free path between collisions l for the medium, $\gamma=L/l$. This follows from the definition of the diffusion coefficient as $D=l\langle v\rangle/3$. For physically correct results (validity of the diffusion equation), γ should be greater than 1. However, mathematical solu-

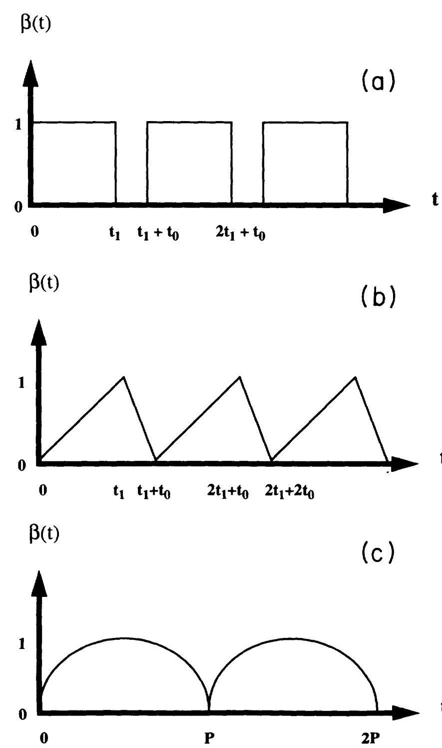


FIG. 2. The three periodic gating probabilities $[\beta(t)]$. The square-wave gating probability is shown in (a) with on-time t_1 and off-time t_0. The saw-toothed gating probability is shown in (b) with rise time t_1 and fall time t_0. The sine-squared gating probability is shown in (c) with periodicity P.

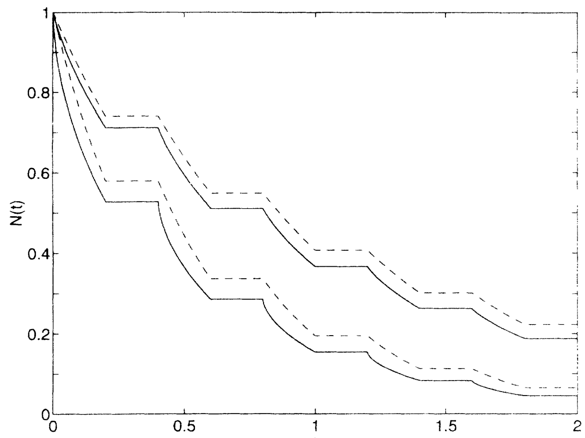


FIG. 3. Results for the remaining fraction $N(t)$ as a function of time for the exact numerical solution (solid lines) and for the approximation of Eq. (7) (dashed lines) for the square-wave probability $\beta(t)$ shown in Fig. 2(a). The parameter $\gamma = L\langle v \rangle / 3D$. The parameters used were $T_D = 1$, $L = 1$, $t_0 = 0.2T_D$, $t_1 = 0.2T_D$, $\gamma = 1$ for the upper two curves and $T_D = 1$, $L = 1$, $t_0 = 0.2T_D$, $t_1 = 0.2T_D$, $\gamma = 10$ for the lower two curves.

tions may also be found for $\gamma \leq 1$ (see below).

Below, we investigate three periodic examples for the time dependence of $\beta(t)$, namely, a square wave [see Fig. 2(a)] with on-time t_1 [$\beta(t) \rightarrow 1$] and down-time t_0 [$\beta(t) \rightarrow 0$], and a sine-squared wave [see Fig. 2(b)] with $\beta(t) = [\sin(\pi t / P)]^2$ and P the period.

Results for particular choices of the parameters for the time-dependent barrier models are shown in Figs. 3–6. As the figures demonstrate, the approximate analytical results for $N(t)$ given by Eq. (7) are in good agreement with the exact numerical solutions, particularly when the

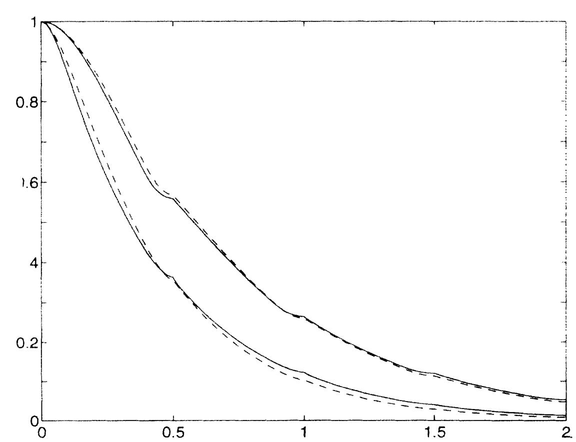


FIG. 4. Results for the remaining fraction $N(t)$ as a function of time for the exact numerical solution (solid lines) and for the approximation of Eq. (7) (dashed lines) for the saw-toothed probability $\beta(t)$ shown in Fig. 2(b). The parameter $\gamma = L\langle v \rangle / 3D$. The parameters used were $T_D = 1$, $L = 1$, $t_0 = 0.1T_D$, $t_1 = 0.4T_D$, $\gamma = 2$ for the upper two curves and $T_D = 1$, $L = 1$, $t_0 = 0.1T_D$, $t_1 = 0.4T_D$, $\gamma = 10$ for the lower two curves.

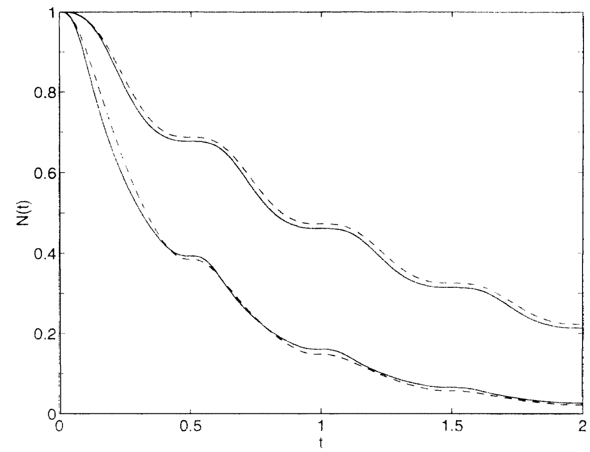


FIG. 5. Results for the remaining fraction $N(t)$ as a function of time for the exact numerical solution and for the approximation of Eq. (7) for the sine-squared probability $\beta(t)$ shown in Fig. 2(c). The parameter $\gamma = L\langle v \rangle / 3D$. The solid lines are the exact, numerical solutions and the dashed lines are the analytical approximation. The parameters used were $T_D = 1$, $L = 1$, $P = T_D/2$, $\gamma = 1$ for the upper pair of curves and $T_D = 1$, $L = 1$, $P = T_D/2$, $\gamma = 10$ for the lower pair of curves.

time modulation of the barrier is smoother. Note also that the error in approximating $N(t)$ with Eq. (8) does not accumulate over time.

Figure 3 shows the behavior of $N(t)$ for a square-wave gating, in which the on time (t_1) and off time (t_0) are the same. Other combinations are, of course, possible. The approximation works least well in this case. Figure 4 shows a second possible periodic gating, that of a saw-toothed reactivity. The approximation is clearly much better in this case in which the reactivity increases and decreases linearly. Figure 5 illustrates the results for a barrier with a sine-squared gating (see also Ref. [10]). The agreement between the exact numerical solution and

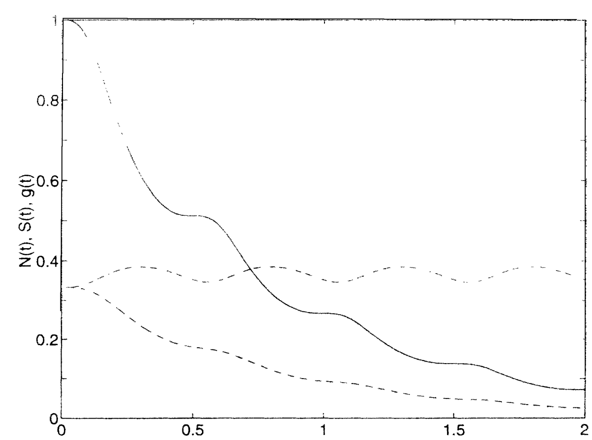
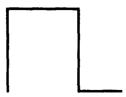
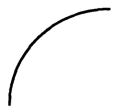


FIG. 6. Plots of the exact numerical solutions for $N(t)$, $S(t)$ [defined as the left-hand side of Eq. (7)], and $g(t) = S(t)/N(t)$ versus time for the sine-squared probability $\beta(t)$ shown in Fig. 2(c). The solid line is $N(t)$, the dash-dot line $g(t)$, and the dashed line $S(t)$. The parameters used were $T_D = 1$, $L = 1$, $P = T_D/2$, and $\gamma = 3$.

TABLE I. The time-averaged first-passage times, averaged over one period for the three periodic reactivity functions $\beta(t)$. The characteristic time $T_D = L^2/D$, the diffusional relaxation time, and the dimensionless parameter $\gamma = L\langle v \rangle / 3D$.

$\beta(t)$	$\langle \tau \rangle$	$\lim_{\gamma\to\infty}$	$\lim_{\gamma\to 0}$
	$\frac{T_D}{3}\left[1+\frac{1}{\gamma}\right]\left[1+\frac{t_0}{t_1}\right]$	$\frac{T_D}{3}\left[1+\frac{t_0}{t_1}\right]$	∞
	$\frac{T_D}{3}\left[\frac{1}{\left[1-\frac{\ln(1+\gamma)}{\gamma}\right]}\right]$	$\frac{T_D}{3}$	∞
	$\frac{T_D}{3}\frac{1}{\left[1-\frac{1}{2\sqrt{1+\gamma}}\right]}$	$\frac{T_D}{3}$	$2\frac{T_D}{3}$

the approximate analytical solution [Eq. (7)] is particularly good for this case in which the barrier reactivity parameter $\beta(t)$ is a smoothly varying function of time.

With a time-dependent reactivity at the absorbing barrier, a mean first-passage time does not strictly exist. However, when the reactivity is periodic in time, it is possible to calculate a first-passage time averaged over an integer number of periods. From Eq. (11), we have

$$\int_0^{\Delta t}\frac{dt'}{\tau(t')} = \frac{3\gamma}{2T_D}\int_0^{\Delta t}dt'\frac{\beta(t')}{1+\frac{(\gamma-1)}{2}\beta(t')} \equiv \frac{\Delta t}{\langle \tau \rangle}, \quad (12)$$

where Δt is an integer number of time periods of the gating function $\beta(t)$ and $\langle \tau \rangle$ is the average mean first-passing time. The results for the three $\beta(t)$ examples are given in Table I.

There are three time scales of relevance to diffusion with a time-modulated barrier: (i) the periodicity of the barrier (e.g., t_0+t_1 for the saw-toothed or square-wave barriers); (ii) the diffusion time scale $T_D = L^2/D$ which is the approximate time to cross the diffusion space via a diffusion mechanism; and (iii) the ballistic time scale $2L/\langle v \rangle = 2T_D(k_BT)/L\mu\langle v \rangle$, where $L\mu\langle v \rangle$ is the work done against the viscous force in traveling a distance L by an object of friction coefficient μ and speed $\langle v \rangle$.

Using the exact numerical results for $\rho(x,t)$, the numerical value of $g(t)$ may be calculated from Eq. (7). This has been done for the sine-squared probability $\beta(t)$ and the result is plotted in Fig. 6 along with $N(t)$ and $S(t)$ [the left-hand side of Eq. (7)]. The exact $g(t)$ is seen to begin at its $t=0$ value of $L^2/3$ and to have the same periodicity as $\beta(t)$, phase shifted to slightly later times. It is also seen to retain its value even though both $N(t)$ and $S(t)$ are decaying to zero. In fact, this behavior of $g(t)$ persists to much longer times.

Recent prior work on surmounting fluctuation barriers has concentrated on the limiting case of a stochastically switching barrier. In this work, we have examined a different physical situation, that of surmounting a well-defined and periodically fluctuating carrier. This could have relevance, for example, for the movement of electrons between two semiconducting layers separated by a periodically biased insulating layer.

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