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First-passage times in phase space for the strong collision model

D. J. Bicout,[1,*] A. M. Berezhkovskii,[1,2,†] Attila Szabo,[1] and G. H. Weiss[2]
[1]*Laboratory of Chemical Physics, National Institute of Diabetes and Digestive and Kidney Diseases, National Institutes of Health, Building 5, Room 136, Bethesda, Maryland 20892*
[2]*Mathematical and Statistical Computing Laboratory, Center for Information Technology, National Institutes of Health, Bethesda, Maryland 20892*
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We consider the dynamics in phase space in which particles follow Newtonian trajectories that are randomly interrupted by collisions which equilibrate both the velocity and position of the particles. Collisions are assumed to be statistically independent events of zero duration and the intercollision time is a random variable with a negative exponential distribution. For this model, we derive an analytical expression for the Laplace transform of the survival probability and quadrature expressions for mean first-passage times.
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I. INTRODUCTION

The first-passage time is the time required for a particle to reach a boundary for the first time. If the particle is destroyed at this boundary, the first-passage time is just the lifetime of the particle. When the dynamics is stochastic, the first-passage time is a random variable, and its average over all realizations of the particle trajectories yields the mean lifetime of the particle in the system. It is well known that for ordinary diffusive dynamics in an arbitrary one-dimensional potential, the calculation of the mean first-passage time can be reduced to quadratures [1,2]. However, when the dynamics of the particle is diffusive in phase space (as described by the Kramers-Klein equation [3]), the problem of calculating the mean first-passage time is as yet unsolved.

The purpose of this paper is to show that the first-passage time problem can be solved analytically for a strong collision model [4,5], which is an alternative to the model described by the Kramers-Klein equation for dynamics in phase space. Different collisional models and their application to reaction rate theory were recently discussed by Berne [6]. In this model, particles follow Newtonian trajectories which are interrupted by collisions of zero duration. These collisions serve to equilibrate both the velocity and position of the particles. The time interval between successive collisions is a random variable described by the probability density $\gamma e^{-\gamma t}$, where γ is the collision frequency. For this model, we derive analytical expressions for both the Laplace transform of the survival probability and quadratures for mean first-passage times.

This model was previously used by Skinner and Wolynes [7] in their analysis of escape of particles from a metastable potential well over a high potential barrier. They found that for moderate values of γ, the escape rate predicted by this model is close to the one obtained from the Bhatnagar-Gross-Krook model [8], in which only the velocity of particles is equilibrated after a collision.

Consider a particle of mass m moving in the region $-\infty < x \leqslant a$. We are interested in the first-passage time to $x=a$ given an initial position x_0 and velocity v_0. We assume that the potential $U(x)$ increases sufficiently fast as $x \to -\infty$ so that a normalized phase-space equilibrium distribution corresponding to a reflecting wall at $x=a$ can be defined as

$$p_{\rm eq}(x,v)=\frac{H(a-x)e^{-\beta[(1/2)mv^2+U(x)]}}{\int_{-\infty}^{a}dx\int_{-\infty}^{+\infty}dv\, e^{-\beta[(1/2)mv^2+U(x)]}}, \quad (1.1)$$

where $\beta^{-1}=k_{\rm B}T$ is the thermal energy and $H(x)$ is the step function defined as $H(x)=0$ for $x<0$ and $H(x)=1$ for $x \geqslant 0$. For the strong collision model, the propagator $P(x,v,t|x_0,v_0)$, which is the probability density of finding the particle at the phase point (x,v) at time *t*, given that it was initially at phase point (x_0,v_0), is described by the equation:

*FAX: (301) 496 0825. Electronic address: bicout@speck.niddk.nih.gov
†Permanent address: Karpov Institute of Physical Chemistry, Ul. Vorontsovo Pole 10, 103064, Moscow K-64, Russia.

$$\frac{\partial P(x,v,t|x_0,v_0)}{\partial t}=\left[-v\frac{\partial}{\partial x}+\frac{1}{m}\frac{dU}{dx}\frac{\partial}{\partial v}\right]P(x,v,t|x_0,v_0)-\gamma\left[P(x,v,t|x_0,v_0)-p_{\mathrm{eq}}(x,v)\int_{-\infty}^{a}dx'\times\int_{-\infty}^{+\infty}dv'\,P(x',v',t|x_0,v_0)\right], \quad (1.2)$$

subject to the initial condition, $P(x,v,t=0|x_0,v_0)=\delta(x-x_0)\delta(v-v_0)$. Since one is interested in the mean lifetime of a particle in the region $-\infty<x\leqslant a$, we treat $x=a$ as an absorbing boundary, and require that $P(x,v,t)$ satisfies the absorbing boundary conditions

$$P(x=a,v<0,t|x_0,v_0)=0 \quad \text{for} \quad x_0<a, \quad (1.3)$$

expressing the fact that no particles enter (or reenter) the system from $x>a$.

II. SURVIVAL PROBABILITY AND LIFETIME IN THE ABSENCE OF COLLISIONS

In the absence of collisions the motion is deterministic and the total energy E of a particle is a constant of motion, i.e.,

$$E=\frac{mv_0^2}{2}+U(x_0)=\frac{mv^2(t)}{2}+U(x(t)), \quad (2.1)$$

where $x_0=x(0)$ and $v_0=v(0)$ are the initial position and velocity of the particle, respectively. For a deterministic motion, one can calculate the time needed for a particle to cover a certain distance as

$$t=\int\frac{dx}{v(x|E)}=\int dx\left\{\frac{m}{2[E-U(x)]}\right\}^{1/2}, \quad (2.2)$$

in which $v(x|E)$ is the velocity of the particle obtained from Eq. (2.1). The particle is able to reach the absorbing boundary at $x=a$ if simultaneously (i) its energy is greater than $U(a)$, i.e., $E\geqslant U(a)$; and (ii) there is no potential barrier greater than E between x_0 and $x=a$, i.e., $U(x)<E$ for $x_0<x<a$. When these conditions are not satisfied the particle never reaches the absorbing boundary at $x=a$. This can be formulated in terms of the time $t(x_0,v_0)$ taken by a particle initially at (x_0,v_0) to reach the absorbing boundary $x=a$,

$$t(x_0,v_0)=\begin{cases}\infty, & E<U_{\max}(x_0)\\ \tau_0(x_0,v_0), & E\geqslant U_{\max}(x_0),\end{cases} \quad (2.3)$$

where $U_{\max}(x_0)=\{\max[U(x)];x_0\leqslant x\leqslant a\}$, and

$$\tau_0(x_0,v_0)=2\int_{x_{\min}(E)}^{x_0}dx\left\{\frac{m}{2[E-U(x)]}\right\}^{1/2}H(-v_0)+\int_{x_0}^{a}dx\left\{\frac{m}{2[E-U(x)]}\right\}^{1/2}, \quad E=\frac{mv_0^2}{2}+U(x_0). \quad (2.4)$$

in which $x_{\min}(E)$ is the largest root of equation $E=U(x)$ in the region $-\infty<x\leqslant x_0$. The first term of Eq. (2.4) is the time for a particle starting at x_0 with negative velocity $-v_0$ to reach $x_{\min}(E)$, bounce back, and return to x_0 with positive velocity v_0, and the second term is the time to travel directly from x_0 to $x=a$ with positive velocity v_0.

The survival probability $S_0(t|x_0,v_0)$ is the probability that a particle initially at the phase point (x_0,v_0) is still in the system at time *t*. This probability is just equal to 1 up to the time $t(x_0,v_0)$, and zero thereafter, which allows us to write

$$S_0(t|x_0,v_0)=H(t(x_0,v_0)-t). \quad (2.5)$$

If we denote the Laplace transform of an arbitrary function $g(t)$ as $\hat{g}(s)=\int_0^\infty e^{-st}g(t)\,dt$, the Laplace transform of the survival probability can be written as

$$\hat{S}_0(s|x_0,v_0)=\frac{1}{s}-\frac{e^{-st(x_0,v_0)}}{s}. \quad (2.6)$$

The lifetime of a particle initially at (x_0,v_0) is the time integral of the survival probability,

$$\int_0^\infty S_0(t|x_0,v_0)\,dt=\hat{S}_0(0|x_0,v_0)=t(x_0,v_0), \quad (2.7)$$

as it should be.

One is often interested in the situation where the system is prepared with an initial distribution that coincides with the equilibrium distribution, $p_{\mathrm{eq}}(x_0,v_0)$. In this case, the equilibrium averaged survival probability $S_0(t)$ is given by

$$S_0(t)=\int_{-\infty}^{a}dx_0\int_{-\infty}^{+\infty}dv_0 S_0(t|x_0,v_0)p_{\mathrm{eq}}(x_0,v_0). \quad (2.8)$$

Instead of using Eq. (2.5) in Eq. (2.8) to obtain $S_0(t)$, the following analysis turns out to be simpler. Using the definition of the survival probability, $S_0(t|x_0,v_0)=\int_{-\infty}^{a}dx\int_{-\infty}^{+\infty}dv\;G_0(x,v,t|x_0,v_0)$, where $G_0(x,v,t|x_0,v_0)$ is the Green's function of Eq. (1.2) with $\gamma=0$, we write the time derivative of Eq. (2.8) as

$$\frac{dS_0(t)}{dt}=\int_{-\infty}^{a}dx_0\int_{-\infty}^{+\infty}dv_0\int_{-\infty}^{a}dx\int_{-\infty}^{+\infty}dv\,\frac{\partial G_0(x,v,t|x_0,v_0)}{\partial t}\times p_{\mathrm{eq}}(x_0,v_0)=-\int_0^\infty dv\,v\int_{-\infty}^{a}dx_0\int_{-\infty}^{+\infty}dv_0 G_0(a,v,t|x_0,v_0)\times p_{\mathrm{eq}}(x_0,v_0). \quad (2.9)$$

The second equality of this expression, which represents the flux escaping the system, is obtained in replacing $\partial G_0/\partial t$ by the expression in the right hand side of Eq. (1.2) with $\gamma=0$, integrating the resulting expression over x and v and using the boundary conditions, $G_0(x,v\to\pm\infty,t|x_0,v_0)=0$ and $G_0(a,v<0,t|x_0,v_0)=0$, as stated in Eq. (1.3).

Next, we use the detailed balance relation

$$G_0(a,v,t|x_0,v_0)p_{\rm eq}(x_0,v_0)=G_0(x_0,-v_0,t|a,-v)\times p_{\rm eq}(a,-v) \qquad (2.10)$$

to transform Eq. (2.9) into

$$\frac{dS_0(t)}{dt}=-\int_0^\infty dv\, v p_{\rm eq}(a,v)\int_{-\infty}^a dx_0 \times\int_{-\infty}^{+\infty}dv_0 G_0(x_0,v_0,t|a,-v) =-\int_0^\infty dv\, v p_{\rm eq}(a,v)S_0(t|a,-v), \qquad (2.11)$$

which relates the time derivative of the equilibrium-averaged survival probability to the survival probability of particles starting at $x=a$ with negative velocity. We introduce the transition state rate $k_{\rm TST}$ as the escape rate $-(dS_0/dt)$ at $t=0$, i.e.,

$$k_{\rm TST}=\int_0^\infty v p_{\rm eq}(a,v)dv=\left(\frac{k_{\rm B}T}{2\pi m}\right)^{1/2}\frac{e^{-\beta U(a)}}{\int_{-\infty}^a e^{-\beta U(x)}dx}. \qquad (2.12)$$

Using this, we rewrite Eq. (2.11) as

$$\frac{dS_0(t)}{dt}=-k_{\rm TST}\int_0^\infty \beta m v e^{-\beta m v^2/2}S_0(t|a,-v)dv. \qquad (2.13)$$

Taking the Laplace transform of this relation with the initial condition $S_0(0)=1$, and making use of the expression for $\hat{S}_0(t|a,-v)$ from Eq. (2.6), we find

$$\hat{S}_0(s)=\frac{1}{s}-\frac{k_{\rm TST}}{s^2}\int_0^\infty \beta m v e^{-\beta m v^2/2}[1-e^{-sT(v)}]dv. \qquad (2.14)$$

In this equation, $T(v)=\tau_0(a,-v)$, as given in Eq. (2.4), is the time period required by a particle starting at $x=a$ with negative velocity $-v$ to reach the turning point $x_{min}(E)$, bounce back, and return to $x=a$. Now, by making the transformation $\epsilon=mv^2/2$, we obtain

$$\hat{S}_0(s)=\frac{1}{s}-\frac{k_{\rm TST}\beta}{s^2}\int_0^\infty e^{-\beta\epsilon}[1-e^{-sT(\epsilon)}]d\epsilon, \qquad (2.15)$$

where the period $T(\epsilon)$ is now given by

$$T(\epsilon)=2\int_{x_{\rm min}(\epsilon)}^a dx\left\{\frac{m}{2[\epsilon+U(a)-U(x)]}\right\}^{1/2}, \qquad (2.16)$$

in which $x_{\rm min}(\epsilon)$ is the largest root of equation $\epsilon=U(x)-U(a)$ in the region $-\infty<x\leqslant a$.

III. SURVIVAL PROBABILITY AND MEAN LIFETIME IN THE PRESENCE OF COLLISIONS

We are now in position to deal with the case of propagation in the presence of collisions as described by Eq. (1.2). The Green's function $P(x,v,t|x_0,v_0)$ is related to the collision-free Green's function $G_0(x,v,t|x_0,v_0)$ by the Dyson-type equation

$$P(x,v,t|x_0,v_0)=e^{-\gamma t}G_0(x,v,t|x_0,v_0)+\gamma\int_0^t dt'\int_{-\infty}^a dx' \times\int_{-\infty}^{+\infty}dv'\, e^{-\gamma(t-t')}G_0(x,v,t-t'|x',v') \times p_{\rm eq}(x',v')\int_{-\infty}^a dx'' \times\int_{-\infty}^{+\infty}dv''\, P(x'',v'',t'|x_0,v_0). \qquad (3.1)$$

The survival probability $S(t|x_0,v_0)$ describing the fate of the particle initially at (x_0,v_0) is given by

$$S(t|x_0,v_0)=\int_{-\infty}^a dx\int_{-\infty}^{+\infty}dv\, P(x,v,t|x_0,v_0). \qquad (3.2)$$

The integration of Eq. (3.1), with respect to x and v leads to

$$S(t|x_0,v_0)=e^{-\gamma t}S_0(t|x_0,v_0)+\gamma\int_0^t e^{-\gamma(t-t')}S_0(t-t') \times S(t'|x_0,v_0)dt', \qquad (3.3)$$

in which $S_0(t|x_0,v_0)$ is the survival probability in the absence of collisions as defined in Sec. II. Taking the Laplace transform of Eq. (3.3), and solving the resulting equation for $\hat{S}$, we find

$$\hat{S}(s|x_0,v_0)=\frac{\hat{S}_0(s+\gamma|x_0,v_0)}{1-\gamma\hat{S}_0(s+\gamma)}, \qquad (3.4)$$

in which $\hat{S}_0(s|x_0,v_0)$ and $\hat{S}_0(s)$ are given in Eqs. (2.6) and (2.15), respectively.

Since the mean first passage time is $\tau(x_0,v_0)=\hat{S}(0|x_0,v_0)$, making use of Eqs. (2.3), (2.4), and (2.6) yields

$$\tau(x_0,v_0)=\begin{cases} k^{-1}, & \frac{1}{2}mv_0^2+U(x_0)<U_{\rm max}(x_0)\\ k^{-1}[1-e^{-\gamma\tau_0(x_0,v_0)}], & \frac{1}{2}mv_0^2+U(x_0)\geqslant U_{\rm max}(x_0),\end{cases} \qquad (3.5)$$

where $\tau_0(x_0,v_0)$ is given by Eq. (2.4) and we have defined the rate k as

$$k=\gamma[1-\gamma\hat{S}_0(\gamma)]=k_{\rm TST}\beta\int_0^\infty e^{-\beta\epsilon}[1-e^{-\gamma T(\epsilon)}]d\epsilon, \qquad (3.6)$$

where $T(\epsilon)$ is given by Eq. (2.16). It is clear from this relation that $k<\gamma$. When $\gamma \to 0$, k is proportional to γ, as one would expect, whereas $k \to k_{\mathrm{TST}}$ when $\gamma \to \infty$. This is the consequence of the fact that the strong collision model does not describe diffusive dynamics in the high collision frequency limit.

When the initial condition is taken to be the equilibrium distribution restricted by additional condition that the initial energy of particles is smaller than $U(a)$, i.e.,

$$p_{\mathrm{eq}}^{-}(x_0,v_0) = \frac{p_{\mathrm{eq}}(x_0,v_0) H[\frac{1}{2}mv_0^2 + U(x_0) - U(a)]}{\int_{-\infty}^{a} dx \int_{-\infty}^{+\infty} dv\, p_{\mathrm{eq}}(x_0,v_0) H[\frac{1}{2}mv_0^2 + U(x_0) - U(a)]}, \tag{3.7}$$

the survival probability $\hat{S}_{-}(s)$, obtained by averaging Eq. (3.4) over this initial distribution is

$$\hat{S}_{-}(s) = \frac{1}{(s+\gamma)[1-\gamma \hat{S}_0(s+\gamma)]}. \tag{3.8}$$

The corresponding mean lifetime is

$$\tau_{-} = \hat{S}_{-}(0) = \frac{1}{k}, \tag{3.9}$$

where k is given by Eq. (3.6).

On the other hand, when the initial preparation is taken to be the equilibrium distribution, $p_{\mathrm{eq}}(x_0,v_0)$, given in Eq. (1.1), the survival probability $\hat{S}(s)$ becomes

$$\hat{S}(s) = \frac{\hat{S}_0(s+\gamma)}{1-\gamma \hat{S}_0(s+\gamma)}. \tag{3.10}$$

In this case the equilibrium-averaged mean lifetime τ is given by,

$$\tau = \frac{1}{k} - \frac{1}{\gamma}. \tag{3.11}$$

Comparison of Eqs. (3.9) and (3.11) shows that τ_{-} is larger than τ by exactly γ^{-1}, which is the expectation time for the occurrence of a collision. This stems from the fact that when the system is initially prepared according to $p_{\mathrm{eq}}^{-}(x_0,v_0)$ no particles can escape from the system prior to the first collision. To summarize, we have shown that for the strong collision model the calculation of the mean first passage time can be reduced to quadrature for an arbitrary one-dimensional potential $U(x)$.

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