Transition events in one dimension

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The instanton or stationary-phase formula has received much attention recently as a way of determining transition paths in reacting systems. In this paper, we analyze the instanton approach for some one-dimensional problems and compare the results it gives with data from a numerical simulation. We show that a proper comparison of the analytic and numerical results must take into account the boundary conditions used in the numerical simulations and also suggest values for the integration constant in the instanton formula that gives the best agreement with the simulated results.

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I. INTRODUCTION

The concept of a reaction path, although a simplification, is an important one in molecular science. A path provides a mechanistic picture of how molecules move from one region of configuration space to another, and can be used to obtain numerical results, usually related to the kinetics or the thermodynamics of the transition process. There are many approaches for determining reaction paths, but one, which we term the instanton approach, has received much attention recently [1–4].

Consider a system whose dynamics is Brownian and is governed by the overdamped Langevin equation

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{DF(x)}{k_\mathrm{B}T} + R(t). \tag{1}$$

Here x is the position, t is the time, D is the diffusion constant, T is the temperature, and k_B is Boltzmann's constant. $F(x)$ is the force on the particle and is equal to $-\partial U(x)/\partial x$ $(\equiv -U')$, where $U(x)$ is the potential energy. $R(t)$ is a Gaussian random force with zero mean and variance:

$$\langle R(t)R(0)\rangle = 2D\,\delta(t). \tag{2}$$

An expression for the transition probability, P, that a system starting at a will be at position x after a time t can be derived and is a path integral that sums over all paths that start in a and end in x with time t [5,6]:

$$P(x,t|a,0) = \int_{(0,a)}^{(t,x)} \mathcal{D}x(s)\, e^{-S[x]}. \tag{3}$$

Here s is a parameter that defines the degree of advance of a path and $S[x]$ can be considered to be an action that is given by

$$S[x] = \frac{1}{4D}\int_0^t \mathrm{d}s \left[\left(\dot{x}(s) - \frac{DF(x(s))}{k_\mathrm{B}T}\right)^2 + \frac{2D^2F'(x(s))}{k_\mathrm{B}T}\right]. \tag{4}$$

Due to the position of the action in the exponential, the trajectories that contribute most to the transition probability are those that minimize the action. Such a minimization leads to a deterministic equation of motion that in quantum mechanics is called the instanton [5]. The equation of motion is

$$(\dot{x}_c)^2 = \left(\frac{DF(x)}{k_\mathrm{B}T}\right)^2 - \frac{2D^2F'(x)}{k_\mathrm{B}T} + C, \tag{5}$$

where $\dot{x}_c$ is the instanton velocity and C is a constant of integration whose value needs to be determined. Knowing the velocity the total time for a transition can be calculated from

$$t = \int_a^b \frac{\mathrm{d}x}{\dot{x}_c}, \tag{6}$$

where the starting and finishing values of x are taken to be in the range $[a,b]$.

Equations (5) and (6) can, in principle, provide much useful information concerning transitions in reacting systems but there remain a number of unresolved questions (for a fuller discussion of which, see Ref. [7]). Open questions include: (i) the proper choice of the integration constant, C, in Eq. (5) because for certain values and potentials the velocity can become imaginary and because the value of C determines the geometry of the most probable path in multidimensional potentials [3]; (ii) the importance of the force derivative term in Eq. (5) which has been neglected by many workers in the field [1,3]; (iii) comparison of the instanton approach with numerical simulation data. In the next sections we attempt to resolve some of these questions for one-dimensional systems. The extension to many dimensions will be left to future work.

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II. INFLUENCE OF BOUNDARY CONDITIONS

Before proceeding to explicit cases, it is necessary to consider how instanton data can be compared to simulation results. It is straightforward to solve Eq. (1) with a suitable finite-difference algorithm and observe that transitions occur. But how can transitions be picked out? One can start particles at a minimum in the potential ($x=a$) and move them until they cross the boundary at $x=b$ that defines the start of the product state. This corresponds to adding an absorbing boundary at b. The trajectories calculated in this way will stay for a long time around a and eventually get to b. For molecular systems, the time of these trajectories, τ_{rxn}, is of the order of the inverse reaction rate [8,9] and only the last portions of these trajectories will correspond to actual transitions. Therefore, a reasonable approach for picking out transitions, and the one used by previous workers [1,7,10], is to identify the transition time τ_{trn} as the interval between consecutive crossings of a and b. τ_{trn} is, in general, much shorter than τ_{rxn}.

Although reasonable, it is important to emphasize that this way of identifying transitions is equivalent to adding absorbing boundary conditions at $x=a$ and $x=b$. This is to be contrasted with the derivations of Sec. I, which were performed with the assumption of an infinite domain. This difference complicates comparison of the two methods as the boundary conditions will affect the path data. Unfortunately, the inclusion of boundary conditions in the derivation of the instanton formula (using δ functions) is not at all trivial [11,12].

III. FREE DIFFUSION

Motion in the absence of a potential is the simplest case, and admits analytical solutions for both the probability distribution and the flux when there are absorbing boundaries at $x=0$ and at $x=b$ [13]. The τ_{trn} distribution for a particle starting at position $x=0$ to attain $x=b$ is given by the time variation of the particle flux at b. The normalized flux at $x=b$ may be straightforwardly calculated and is

$$J(b,t|a,0)=\frac{-2\pi^2 D}{b^2}\sum_{n=1}^{\infty}\exp\left[-\left(\frac{n\pi}{b}\right)^2 Dt\right]n^2(-1)^n. \tag{7}$$

Figure 1 shows a comparison between the results obtained with Eq. (7) and a numerical simulation. In addition to the full analytic result, the figure also shows an approximation to the flux obtained by taking the first two terms of Eq. (7). The agreement is good at long times, and both the height and the position of the maximum flux are well approximated. In the two-term approximation the maximum flux occurs at a time of

$$\tau_{\mathrm{trn}}=\frac{\log(16)}{3\pi^2}\frac{b^2}{D}, \tag{8}$$

which is about 2% in error. This time defines the most probable (MP) τ_{trn}.

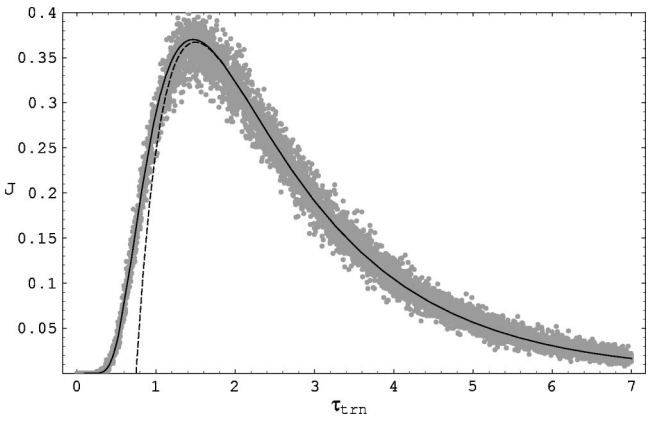

FIG. 1. τ_{trn} distributions for Brownian motion in the absence of a potential. The numerical results (gray) are compared with the analytical result of Eq. (7) using expansions of 15 terms (solid line) and only two terms (dashed line). In all simulations in this paper $k_{\mathrm{B}}T=1$, $D=1$, $b=4$, and the numerical integration time step $\Delta t=10^{-3}$.

The MP τ_{rxn} is obtained if the same calculation is performed for the case of a single absorbing barrier at $x=b$. The result is [14]

$$\tau_{\mathrm{rxn}}=\frac{1}{6}\frac{b^2}{D}. \tag{9}$$

Even though τ_{rxn} is not really the time for a reaction, because the particle is not in any well, we see that the boundary conditions affect the τ_{trn} and that we have $\tau_{\mathrm{trn}}<\tau_{\mathrm{rxn}}$. However, we also see that both times scale as the square of the distance to be covered and the inverse of the diffusion constant. This is a typical behavior for a diffusing particle.

Putting these results into Eq. (6) allows us to estimate a value for the constant C for the free-diffusion process, which is

$$C=\left(\frac{3\pi^2 D}{b\log(16)}\right)^2. \tag{10}$$

This means that C depends upon the size of the domain in contrast, for example, to values of the constant chosen in a similar context by Elber and Shalloway [3]. The same dependence upon distance traveled is also found for the *average* τ_{trn} [10].

Plots of average position for a simulated particle versus time are shown in Fig. 2. All trajectories have total times given by the MP times of Eqs. (8) and (9). When there are two absorbing boundaries, the average position in the center of the trajectory changes linearly with time, in accord with Eq. (5). Towards the boundaries, however, the particle accelerates due to the presence of the boundary conditions [10–12]. This is because simulation steps that cross a boundary are omitted, leading to a bias towards trajectories with a higher velocity at the edge of the simulation domain. This behavior at the boundaries was also noticed by Zuckerman and Woolf [4], but they did not specify its origin. If the absorbing boundary at $x=0$ is removed, the trajectory in the

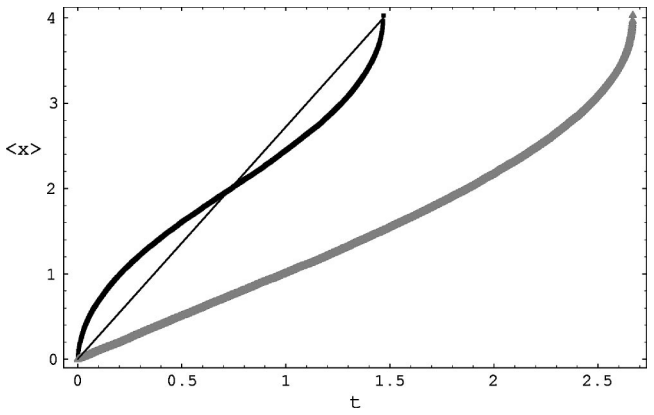

FIG. 2. Plots of $\langle x \rangle$ vs time for a diffusion process with one absorbing barrier at $x=4$ (black boxes) and with two absorbing barriers at $x=0$ and 4 (gray triangle). The solid line is the result predicted by Eq. (5).

region of the boundary becomes linear, in agreement with the instanton approach, and the time for the MP trajectory increases, the difference being given by Eqs. (8) and (9). The solid line in Fig. 2 is the instanton result with the value of C from Eq. (10) and it does not reproduce the accelerations at the boundaries.

IV. EXTERNAL POTENTIALS: INFLUENCE OF THE SECOND DERIVATIVE TERM

In this section we will consider the influence of the force derivative term in Eq. (5) and see if the value of C in Eq. (10) is transferable to cases where a potential is present. We consider a harmonic potential of the form $U=kx^2/2$, where the potential can have positive (well) or negative (barrier) signs. Importance sampling was used to speed up the numerical calculations for positive k [4]. The resulting arrival time distributions were then fitted to a generalized form of the equation used by Zuckerman and Woolf [7],

$$P_{\tau_{\mathrm{trn}}} = \exp(\alpha/t + \beta + \gamma t), \tag{11}$$

and the MP τ_{trn} were deduced from the maxima of the fitted curves.

Plots of the τ_{trn} distributions for potentials with the same absolute value of $|k|$ but with different signs are given in Fig. 3. The distributions are different due to the importance of the second derivative term in Eq. (5). This is not a result of the ascending or descending character of the potential because ascending or descending linear potentials ($U=\pm kx$) give exactly the same distributions (data not shown). The difference between the MP τ_{trn} for the same $|k|$ diminishes as temperature decreases and becomes negligible in the limit of low temperature [1].

Inclusion of the force derivative term for positive potentials leads to a negative term that can cause the velocity to be imaginary. Manipulation of Eq. (5) shows that this will occur when

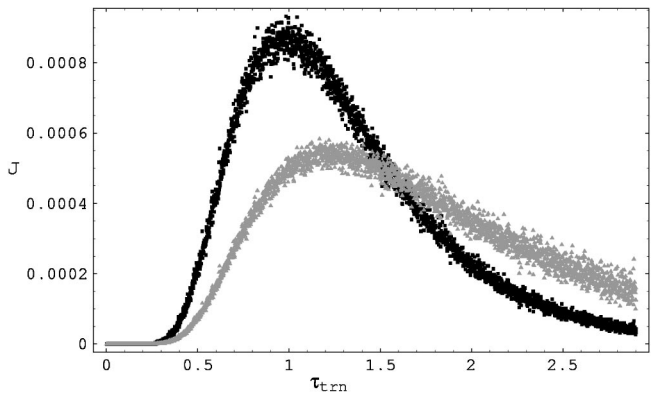

FIG. 3. τ_{trn} distributions for Brownian motion in harmonic potentials with $k=5$ (black boxes) and $k=-5$ (gray triangles).

$$k > \frac{Ck_{\mathrm{B}}T}{2D^2}. \tag{12}$$

Whenever this condition is satisfied, the total time, determined from Eq. (6), is undefined. If one chooses the value $C=0$, then the region with imaginary velocity is given by

$$x \in \sqrt{\frac{2k_{\mathrm{B}}T}{k}}. \tag{13}$$

Interestingly, this is the region where the energy of the particle is below the thermal energy $k_{\mathrm{B}}T$. This is probably the underlying reason that led Astumian *et al.* [1] to say that the instanton approach is not valid close to the minimum. For $k \to 0$, the complete interval $(0,b)$ should have an imaginary velocity. However, in this case, it is clear that the choice of $C=0$ is not valid, as the reaction is diffusion controlled, and a better choice for C is given by Eq. (10).

In order to compare velocities we will use the concept of the local time, that can be defined as [10]

$$L_a = \lim_{\delta \to 0} \frac{1}{2\delta} \int_0^{t_b} \mathcal{I}\{x \in (a-\delta, a+\delta)\} \mathrm{d}s, \tag{14}$$

where $\mathcal{I}\{\Theta\}=1$ if Θ is true, and is zero otherwise. The local time represents the ''density'' of time per unit length and its integration for all the path length gives the total duration of the path. It is a stochastic variable but its average is smooth and can be considered as the inverse of the average velocity. The use of a quantity that is a function of the coordinates and not of time allows for a direct comparison with Eq. (5). The calculation of the velocity via $\mathrm{d}\langle x \rangle / \mathrm{d}t$ is more cumbersome because we have to transform a dependence on time to a dependence on position and this can only be done knowing the time-dependent probability distribution which is not normally available.

Figure 4 shows the results obtained by using the formula for the instanton velocity [Eq. (5)], with $C=0$ and with C given by the free diffusion value of Eq. (10). At lower barriers the free-diffusion value gives a much better agreement with experiment. As the barrier gets larger, the MP τ_{trn} gets smaller and so particles arrive, on average, more quickly.

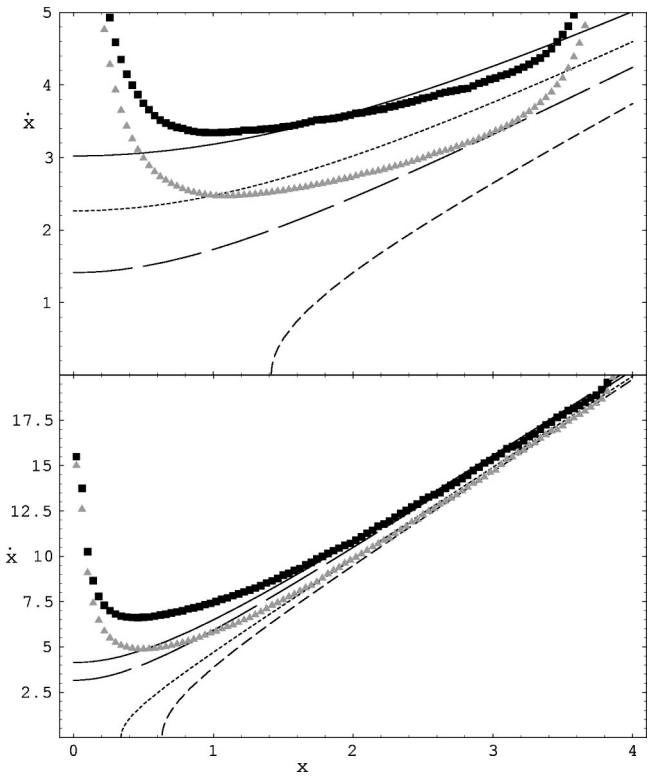

FIG. 4. Inverse of the local time vs position for Brownian motion in harmonic potentials. Top: $|k|=1$ and bottom $|k|=5$. Positive k (gray triangles) and negative k (black boxes) show better fits to the predicted velocities of Eq. (5) with a value for C given by Eq. (10) ($k<0$ solid line, $k>0$ dotted line) than with $C=0$ ($k<0$, short dashed line; $k>0$, long dashed line). $\Delta a=b/100$ and the number of paths is 10^5.

The distributions of arrival times also get more compact, so that there is less dispersion and the instantonic trajectory becomes more representative. Eventually the C defined in Eq. (10) gives an imaginary velocity for $x\sim 0$ and the total τ_{trn} is undefined. A comparison with the simulation is impossible here because the region of imaginary velocity corresponds to the region where the instanton approach fails. Practically, however, the value of C is less relevant in these regimes as the magnitude of the velocity in the region of the barrier [from Eq. (5)] is determined largely by the force term and not by C. Thus, to summarize, choosing C via Eq. (10) gives a smooth transition between the diffusion-controlled and drift-controlled regimes in the description of the velocity.

V. SUMMARY

In this paper we have compared the information given about transition processes using the instanton approach with that from a numerical simulation. We have shown that a proper comparison of results from the two methods requires a consideration of the boundary conditions used to isolate transitions, and that the instanton formulas are not valid close to the boundaries. In addition we estimated a value for the C constant from the free diffusion case, and examined its pertinence for describing transitions with harmonic potentials of various force constants. The value of C is only critical when the transition process is diffusion controlled. When a high potential barrier is present, the value of C is much smaller than the force and is thus less relevant. Finally, we also evaluated the importance of the force derivative term. These results are also valuable for constructing biased importance sampling schemes to find optimum trajectories.

Our future work will be focused in two directions. First, more theoretical work is necessary to elucidate the effect of boundary conditions on the determination of transition times. Second, we want to investigate the forms of the paths that the instanton approach gives in more than a single dimension and how good a representation they are of the most probable or average paths arising from numerical simulation. The current work was a necessary preliminary to work in many dimensions because the distribution of arrival times and the velocity with which a certain path is traveled helps determine the shape of a path on a multidimensional potential energy surface.

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