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LETTER

How a finite potential barrier decreases the mean first-passage time

Vladimir V Palyulin[1] **and Ralf Metzler**[2,3]

[1] Physics Department, Technical University of Munich, 85747 Garching, Germany
[2] Institute for Physics and Astronomy, University of Potsdam, 14476 Potsdam-Golm, Germany
[3] Physics Department, Tampere University of Technology, FIN-33101 Tampere, Finland
E-mail: vladimir.palyulin@tum.de and rmetzler@uni-potsdam.de

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Abstract. We consider the mean first-passage time of a random walker moving in a potential landscape on a finite interval, the starting and end points being at different potentials. From analytical calculations and Monte Carlo simulations we demonstrate that the mean first-passage time for a piecewise linear curve between these two points is minimized by the introduction of a potential barrier. Due to thermal fluctuations, this barrier may be crossed. It turns out that the corresponding expense for this activation is less severe than the gain from an increased slope towards the end point. In particular, the resulting mean first-passage time is shorter than for a linear potential drop between the two points.

Keywords: diffusion

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Contents

1. Introduction

In classical mechanics, Bernoulli's 1696 *brachistochrone* problem addresses the curve between two points that is covered by a point particle in the least time, under the influence of gravity. If the particle starts at rest, the brachistochrone curve is a cycloid. More steeply at first, the particle is accelerated, keeping its momentum in the absence of friction. In particular, at no point along this curve is the particle elevation higher than that of the starting point, for reasons of energy conservation. An overdamped, diffusing particle may appear to behave classically: driven by a constant external force the mean first-passage time (MFPT) T from one point to another along the direction of the force equals L/V, the ratio of distance L to the particle velocity V [1]. However, as the diffusing particle is coupled to a heat bath, thermal fluctuations may lift it across a potential barrier. At the same time, the overdamping does not allow the particle to take along its momentum. To minimize the MFPT, one would thus naively expect that the particle should constantly move downhill. As we are going to show here for the case of a piecewise linear potential, it is indeed beneficial for the MFPT if the particle first crosses a potential barrier, that is, the particle initially moves uphill. As a consequence the following downhill slope becomes steeper, leading to a smaller overall MFPT.

Generally, the question of the interplay between the potential landscape and diffusion properties is of great interest, resulting in often surprising behaviour such as giant diffusivity [2]. But which shape of the potential should one choose in order to optimize the escape time on an interval? A large number of previous studies were concerned with problems of the escape from a potential well [3], following Kramers' classical work [4]. Optimization of the escape time may involve phenomena such as resonant activation [5]. One of the simplest models for a potential landscape is a piecewise linear potential (figure 1). Only recently was it realized that an asymmetry in this kind of potential is important for escape properties in resonant activation [6, 7]. The asymmetry of the potential also plays a crucial role in systems with periodic potentials relevant to molecular motor models [8]–[10], or for molecular shuttles in suprachemical compounds [11]. However, to the best of our knowledge the role of asymmetry for the MFPT for a static potential as displayed in figure 1 has not been discussed.

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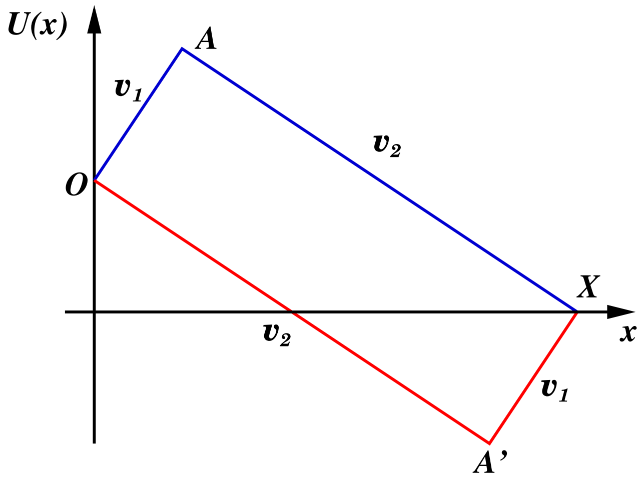

Figure 1. Scheme of the piecewise linear potential (blue line) considered here. The particle is initially placed at point O (at $x = 0$), at which we impose a reflecting boundary condition. The end point is X, and we choose $x_X = 1$. At the turnover point A the slope of the potential changes. v_1 and v_2 are the drift velocities on the two linear slopes ($v_1 < 0$ and $v_2 > 0$). The red line shows the inversely symmetrical potential resulting in the same MFPT (see the text).

2. Mean first-passage time minimization

We consider a particle diffusing from the starting point O at $x = 0$, to point X located at $x_X = 1$, in a piecewise linear potential going through point A at x_A. This situation is sketched in figure 1. The values of the potential at these points are U_O, U_A, and $U_X = 0$, without loss of generality. At the starting point O we impose a reflecting boundary condition while at the end point X we apply an absorbing boundary condition for the calculation of the MFPT. The question that we pursue is: which shape of the piecewise linear potential minimizes the MFPT from O to X?

The MFPT for the piecewise linear potential with bias velocities v_1 (on $0 \leq x \leq x_A$) and v_2 (on $x_A < x < 1$) on the unit interval, shown in figure 1, is readily obtained analytically [1, 12]. A unit current $j(0,t) = \delta(t)$ is injected at $x = 0$, and the output is calculated from the solution of the Fokker–Planck equation,

$$\frac{\partial P(x,t)}{\partial t} = \left(\frac{\partial}{\partial x}\frac{U'(x)}{m\eta} + D\frac{\partial^2}{\partial x^2}\right) P(x,t), \qquad (1)$$

where $U'(x)$ is the derivative of the external potential. Moreover m is the particle mass, η the friction experienced by the particle, and D is its diffusion constant. For the gravitational potential $U(x) = mgh(x)$ for a particle at elevation $h(x)$ at position x and with the gravitational constant g, the drift term in the Fokker–Planck equation becomes $\partial/\partial x(gh'(x)/\eta)P(x,t)$. The ratio g/η has the dimension of a velocity, so the Fokker–Planck equation may be rewritten in the form

$$\frac{\partial P(x,t)}{\partial t} = \left(-v_i\frac{\partial}{\partial x} + D\frac{\partial^2}{\partial x^2}\right) P(x,t), \qquad (2)$$

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with piecewise constant drift velocity v_i, where $i = 1, 2$ denotes the two domains with piecewise linear potential. Note the sign of the drift velocity: an increase of the potential causes a drift to the left, and vice versa. The reflecting and absorbing boundary conditions at $x = 0$ and $x = 1$, respectively, read $\partial P/\partial x|_{x=0}$ and $P(1, t) = 0$. Requiring continuity of the distribution P and the probability flux at point A, the MFPT is yielded in the form [1]

$$T = \frac{D}{v_1 v_2}(1 - \mathrm{e}^{-v_1 x_A/D})(1 - \mathrm{e}^{-v_2(1-x_A)/D}) + \frac{x_A}{v_1} + \frac{1 - x_A}{v_2} + \frac{D(\mathrm{e}^{-v_1 x_A/D} - 1)}{v_1^2} + \frac{D\left(\mathrm{e}^{-v_2(1-x_A)/D} - 1\right)}{v_2^2}, \quad (3)$$

as a function of x_A, v_1, and v_2. We note that all variables occurring in equations (1)–(3) are dimensional. In what follows we measure lengths in units of cm and time in s. Thus when writing $L = 1$ for the distance between the starting and end points, this actually means 1 cm. In the following we use a unit diffusion constant, $D = 1\ \mathrm{cm}^2\ \mathrm{s}^{-1}$.

Let us study the MFPT (3) in detail. We first note that expression (3) is symmetric under the simultaneous exchanges $v_1 \leftrightarrow v_2$ and $x_A \leftrightarrow 1 - x_A$, i.e., inversion through the midpoint of the line connecting O and X. This inverse case corresponds to the red line in figure 1. Secondly, we observe that on increasing the elevation of point A with respect to O and X and shifting the turnover point A towards the starting point O such that $|v_1 x_A| \gg 1$, $|v_2|(1 - x_A) \gg 1$, and $x_A \ll 1$, the MFPT (3) reduces to

$$T \approx \frac{D}{v_1^2}\mathrm{e}^{|v_1 x_A|/D} + \frac{1}{v_2}. \quad (4)$$

This is the sum of the MFPTs on the two subintervals. Indeed, the first term corresponds to the Kramers rate for crossing of a high potential barrier—see below—while the second term represents the MFPT at constant drift v_2 over the unit distance. Result (4) demonstrates that the overall MFPT T and both individual terms are reduced by the increase of A's elevation while keeping the product $v_1 x_A$ constant. This is one of the central results of our study: the introduction of a high but narrow barrier reduces the MFPT.

For the thermally activated crossing of a sufficiently high potential barrier the corresponding barrier crossing time was obtained by Kramers [4, 13]:

$$T_{\mathrm{K}} = \frac{2\pi}{\sqrt{U''(x_{\min})|U''(x_{\max})|}}\mathrm{e}^{[U(x_{\min})-U(x_{\max})]/D}. \quad (5)$$

Here $x_{\min}$ and $x_{\max}$ denote the positions of the potential minimum (where the particle is initially placed) and the saddle of the potential. According to expression (5) this characteristic time depends on both the potential difference $\Delta U = U(x_{\max}) - U(x_{\min})$ and the curvature of the potential at these two points. If we imagine that we smooth the piecewise linear potential around the minimum and maximum points, it becomes clear that for fixed ΔU a decrease of the distance between $x_{\min}$ and $x_{\max}$ implies an increase of the respective curvatures and thus a *decrease* of the barrier crossing time. This observation underlines that our above result for the MFPT in the piecewise linear potential is consistent with the physics of barrier crossing.

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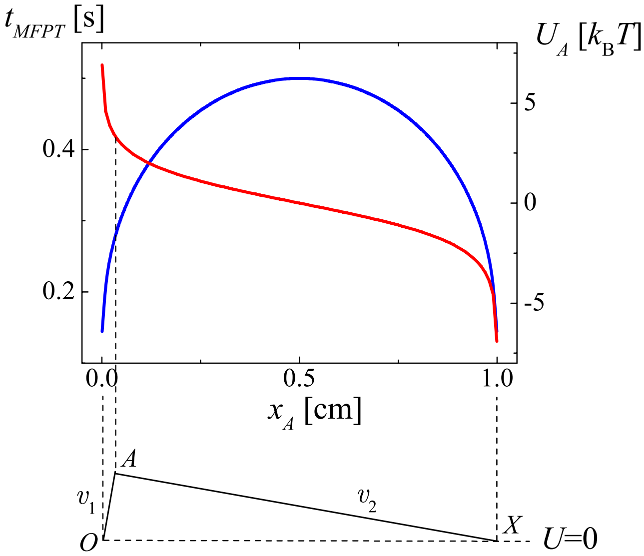

Figure 2. Minimal MFPT in the piecewise linear potential for vanishing potential difference between the starting and end points, as a function of the turnover point position x_A (blue curve). The corresponding optimum value for the value of the potential at the turnover point is shown as the red line. The dashed line emanating from the turnover point in the schematic diagram of the potential profile (bottom of graph) intersects the two curves at the associated values of MFPT and U_A.

What happens in the case opposite to equation (4), when the two drift velocities are small: $|v_1|, |v_2| \ll 1$? Expansion of equation (3) up to first order yields

$$T \approx \frac{1}{2D} - \frac{v_1 x_A^2}{6D^2}(1 + 2(1 - x_A)) - \frac{v_2(1 - x_A)^2}{6D^2}(1 + 2x_A). \tag{6}$$

Here, the first term represents the MFPT of free diffusion on the unit interval. The next two terms are the first-order corrections in v_1 and v_2. Depending on the actual values of v_1 and v_2 these terms may lead either to a decrease or to an increase of the MFPT.

While the MFPT can be arbitrarily reduced by increasing v_1 (and thus also v_2) and simultaneously decreasing the position x_A of the turnover point, a finite potential barrier may still reduce the MFPT. We analyse the three possible, different cases in figures 2–4. Starting with the case where the starting and end points are at the same potential level, in figure 2 we show the minimal value for the MFPT (3) together with the corresponding optimal value for the potential at A, U_A, as a function of the position x_A of the turnover point. This minimization was performed numerically with Mathematica. We see that the largest value of the MFPT is obtained when the turnover point is located in the middle of the interval at $x_A = 0.5$. In this special case the optimum is reached in the absence of a potential barrier ($U_A = 0$), i.e., for unbiased diffusion. Away from the midpoint, the MFPT appears dramatically reduced. For $x_A \to 0$ and $x_A \to 1$, the fastest MFPT is obtained when the potential diverges, $U_A \to \pm\infty$. Notice the symmetries of both the MFPT and the profile of optimal turnover points with respect to the midpoint, $x_A = 0.5$.

For the case of very asymmetric positions of turnover points $x_A \to 0$, the optimal value for the drift v_1 can be computed analytically if the potential difference

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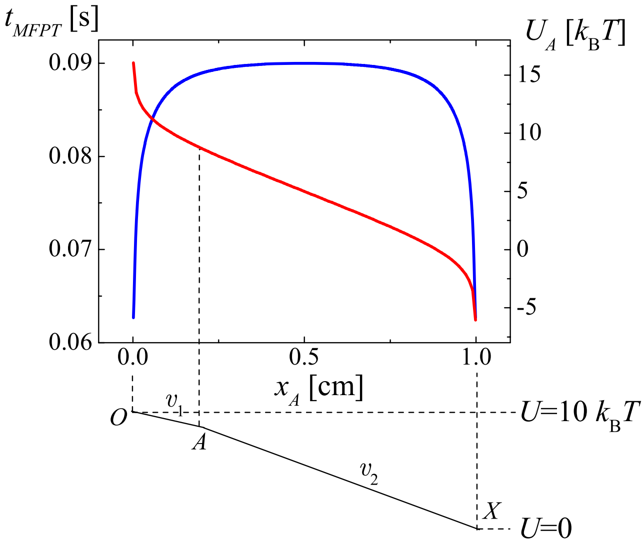

Figure 3. Minimal MFPT and corresponding height of the potential at the turnover point A as a function of the position x_A, in the case where the potential difference between the starting and end points is $10k_BT$.

$\Delta U = v_1 x_A + v_2(1 - x_A)$ and x_A are fixed. Expansion of expression (3) as a series for small x_A leads to the first-order approximation

$$T \approx \frac{1}{\Delta U} + \frac{D\Omega_-}{\Delta U^2} - \frac{D(\Delta U - v_1)\left((\Delta U/D)\Omega_+ + 2\Omega_-\right)}{\Delta U^3} x_A, \qquad (7)$$

where $\Omega_\pm = \exp(-\Delta U/D) \pm 1$. Here the first two terms are the MFPT for a uniform linear bias with potential difference ΔU. The third term is the correction linear in x_A. Analysing its form shows that an increase of the height of the turnover point (i.e., an increase of $|v_1|$) always leads to a decrease of the MFPT if ΔU is positive. For the optimal slope v_1 we obtain the approximate expression

$$v_1 \approx -\frac{\Delta U}{2x_A} \frac{\left((\Delta U/D)\Omega_+ + 2\Omega_-\right)(2 - 4x_A - (\Delta U/D)x_A)}{(6\Omega_- + (\Delta U^2/D^2)\mathrm{e}^{-\Delta U/D} + 2(\Delta U/D)(1 + 2\mathrm{e}^{-\Delta U/D}))}. \qquad (8)$$

In the range of small x_A and $\Delta U > 0$ all terms in the brackets are positive. Hence, expression (8) proves analytically that in this case a barrier does indeed optimize the MFPT. Note that the numerical accuracy of this approximation is actually not too good. In order to reproduce the functional behaviour over a longer range of x_A, higher order terms need to be considered.

For the case where the starting point is higher than the end point, the result for the minimal MFPT is displayed in figure 3. Here the MFPT shows an extended plateau around $x_A = 0.5$. Exactly at this midpoint the minimum MFPT corresponds to the naively expected case of a constant slope from starting to end point. For x_A closer to zero the MFPT again drops down to zero while the value of the potential at the turnover point diverges. Both curves for the MFPT and the potential at the turnover point are again symmetric with respect to the midpoint. In contrast to the case for figure 2, however, the curve for the MFPT is not symmetric around the zero-line of the potential.

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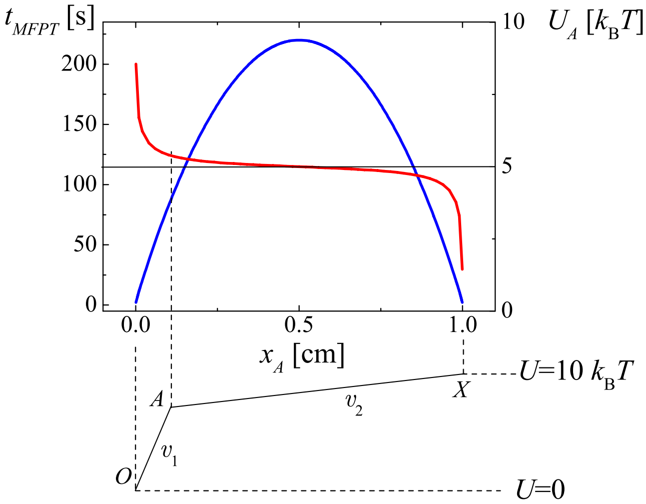

Figure 4. Minimal MFPT and associated turnover potential for the case where the potential difference between the starting and finishing points is $-10k_{\mathrm{B}}T$ (the end point is higher than the starting point).

For completeness we consider the case where the end point is elevated with respect to the starting point. While a classical particle would never reach this end point, a thermally driven particle may gain the necessary energy from the heat bath. The corresponding optimal potential of the turnover point in the piecewise linear potential and the associated MFPT are shown in figure 4. This turns out to be beneficial when an initial barrier exists whose height exceeds the overall potential difference $|\Delta U|$ between the starting and end points, such that the drift velocity v_2 is positive.

Let us compare the minimal MFPTs in the three cases of positive, zero, and negative potential difference between the initial and end points of our set-up, for $x_{A1} = 10^{-3}$ and $x_{A2} = 0.5$ (i.e., the longest MFPT). For $\Delta U = 10k_{\mathrm{B}}T$ (figure 3) the ratio $T(x_{A1})$:$T(x_{A2}) \approx 0.7$, for $\Delta U = 0$ (figure 2) it is $T(x_{A1})$:$T(x_{A2}) \approx 0.29$, and for $\Delta U = -10k_{\mathrm{B}}T$ (figure 4) we find $T(x_{A1})$:$T(x_{A2}) \approx 0.01$. Thus, the introduction of a potential barrier or kink does indeed have the largest effect on the MFPT when the end point has a *higher* energy. That is, when it is harder to reach the end point energetically, the benefit from a potential turnover is larger. This is the second central result of our study.

We simulated the Brownian motion of a particle in a piecewise linear potential with a Monte Carlo approach, based on the Metropolis algorithm: if the potential difference δU between the current position and the potential new position is positive, $\delta U > 0$, then the step is accepted with probability $\exp(-\delta U/[k_{\mathrm{B}}T_{\mathrm{M}}])$, where $k_{\mathrm{B}}T_{\mathrm{M}}$ is a measure of temperature. Otherwise the step is immediately accepted.

Comparison with the analytical results was achieved by consideration of the continuum limit of a discrete biased random walk on a lattice. The probability distribution of jumps of length ℓ, $p(\ell)$, defines the Fokker–Planck equation for the continuum probability density function $p(x, t)$ [14]

$$\frac{\partial p(x,t)}{\partial t} = -\frac{\Delta}{\tau} m_1 \frac{\partial p(x,t)}{\partial x} + \frac{\Delta^2}{2\tau} m_2 \frac{\partial^2 p(x,t)}{\partial x^2} \tag{9}$$

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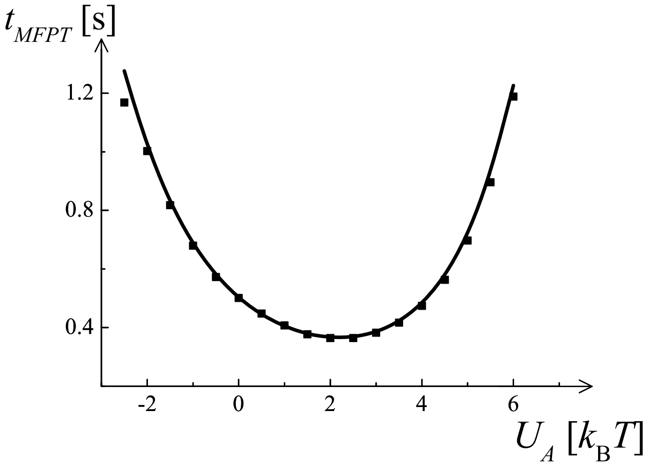

Figure 5. Comparison of Monte Carlo simulations (squares) with the analytical result from equation (3) shown as the full line. The lattice size is $N = 1001$, and the number of runs is 100 000.

where it is assumed that the lattice spacing and time step are infinitely small: $\Delta \to 0$, $\tau \to 0$, and $m_1 = \sum \ell p(\ell)$, $m_2 = \sum \ell^2 p(\ell)$. Hence,

$$D = \lim_{\Delta,\tau\to 0} \frac{m_2 \Delta^2}{2\tau}, \qquad v = \lim_{\Delta,\tau\to 0} \frac{m_1 \Delta}{\tau}. \tag{10}$$

In the case that we considered, the values of diffusion constants and the slopes in the continuum limit are

$$D \approx \frac{1}{2N^2\tau}, \qquad |v_1| \approx \frac{U_A}{2x_A N^2 k_B T_M \tau}, \qquad |v_2| \approx \frac{U_A}{2(1-x_A) N^2 k_B T_M \tau}, \tag{11}$$

where N is the lattice size and x_A the position of the turnover point.

The simulations demonstrate excellent agreement with our analytical results. We show the comparison between the simulations and equation (3) for the case $\Delta U = 0$ for $x_A = 0.1$, $k_B T_M = 1$, and $N = 1001$ in figure 5.

3. Discussion

On a flat potential landscape, significant progress has been achieved in the theory of MFPTs on arbitrary, finite domains [15]. In particular, the role of compact versus non-compact explorations has been revealed in generality [16]. Much less is known about MFPT properties in potential landscapes.

We analysed the value of the MFPT in a finite interval for a piecewise linear potential, finding that the introduction of a barrier reduces the MFPT. In the ideal case where the barrier height is unlimited, the MFPT can be reduced arbitrarily. These *a priori* surprising results were shown to be in line with physical arguments such as Kramers escape theory, and may be of interest in the design of potential energy landscapes, for instance, for functional molecules (molecular shuttles), or for molecular motors. Conversely, our results may shed new light on the role of barriers in known landscapes, for instance, in the folding

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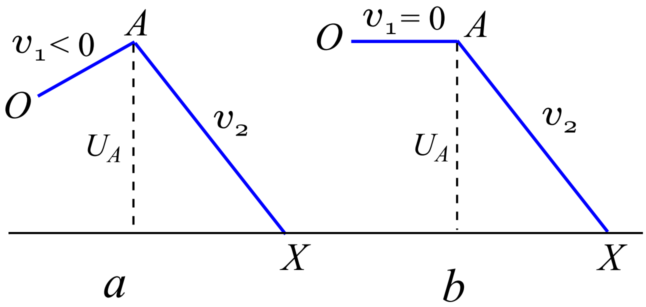

Figure 6. The MFPT in case (a) is larger than that in case (b) as long as U_A is fixed.

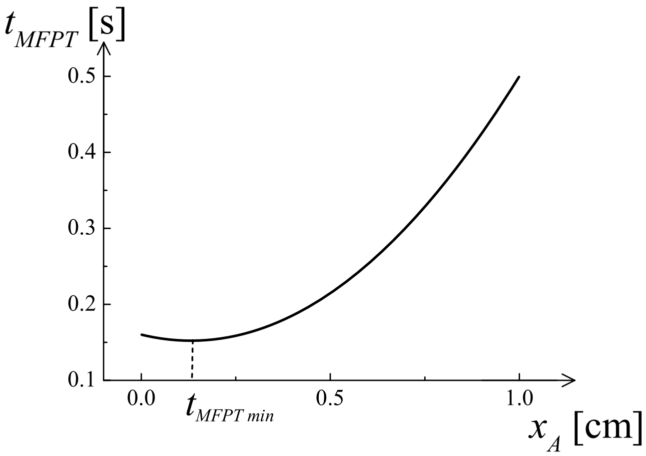

Figure 7. MFPT for the case of fixed potential U_A corresponding to figure 6(b) as a function of the position x_A of the turnover point. Here, $\Delta U = 5k_\mathrm{B}T$.

landscape of proteins. Indeed, it was shown in [17] that intermediate barriers of height $>1k_\mathrm{B}T$ increase the folding rate of proteins.

All results presented above demonstrate the critical importance of the asymmetry of the potential barrier for optimization of the MFPT. This gain rests on the significant facilitation of the passage on the long easy slope which overcompensates losses for crossing of the barrier. The result (3) allows the adjustment of the MFPT to any finite value, including infinitely large and infinitely small times. However, if one wants to decrease the MFPT to some specific, small value, this result also shows that, to compensate an increase in barrier height, a substantial reduction of the position x_A of the turnover point is required.

What happens if the height of the potential barrier is limited? Consider the situation sketched in figure 6. If the values of U at the starting and end points of the interval are fixed and the height of the potential at point A is fixed, it is clear that in case (a) the MFPT is higher than that in case (b). This changes considerably the answer to the MFPT minimization problem. Starting with a horizontal slope we could still imagine that a shift of the turnover point A may optimize the MFPT: if it is shifted to the right we have an increase in the time taken to reach A but a gain from an increased drift velocity v_2. Variation of x_A in this case leads to the dependence shown in figure 7. At the right

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end of the interval between the starting and end points the behaviour tends to the value $T = 0.5$ s, corresponding to unbiased diffusion. The gain at the optimum value for x_A in this case is in fact only a few per cent, compared to the case of a linear potential drop ($x_A = 0$).

In classical mechanics the cycloid is the optimal curve for a point particle in the absence of friction: after an initial steep descent, i.e., high acceleration, the momentum of the particle carries on. For a diffusing, overdamped particle in the case of a piecewise linear potential, the answer is qualitatively the opposite: in order to minimize the MFPT there should be a steep and short ascent.

It will be interesting to consider more complex shapes of the potential, in particular, the case of multiple barriers as mentioned in the context of protein folding [17]. Moreover, numerical analysis of the first-passage distribution associated with the process considered herein will be of interest, as well as the consideration of the full motion including inertial effects. Although it is possible to optimize the potential by trial and error for a fixed set of potential shapes, the question about whether the optimization algorithm exists in generality remains to be investigated. Another interesting question is that of whether similar results could be obtained under anomalous diffusion conditions [18].

Acknowledgments

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