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On mean residence and first passage times in finite one-dimensional systems

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We present a simple derivation of mean residence times (MRTs) and mean first passage times (MFPTs) for random walks in finite one-dimensional systems. The derivation is based on the analysis of the inverse matrix of transition rates which represents the random walk rate equations. The dependence of the MRT and of the MFPT on the initial condition, on the system size, and on the elementary rates is studied and a relationship to stationary solutions is established. Applications to models of light harvesting by supermolecules, and of random barriers, and to relaxation in the Ehrenfest model are discussed in detail. We propose a way to control the MFPT in supermolecules, such as dendrimers, via molecular architecture. © *1998 American Institute of Physics.* [S0021-9606(98)01337-3]

I. INTRODUCTION

Much attention has been devoted recently to potential applications of molecular-scale systems in charge transport,[1] in photochemical reactions,[2] and in mimicking biological functions.[3] Examples of such nanoscale molecular systems are supermolecules,[4] stacked molecular systems,[5] and molecular size cavities.[6] In particular, dendrimer structures have been designed,[7] which among other properties, can be utilized as artificial antenna systems for light harvesting.[8,9] Light harvesting by dendrimers, as well as some other dynamical processes in nanoscale systems, can be described as a trapping process. One wishes, of course, to be able to control the trapping process, a control that depends on the local kinetic rates and on the structure of the system. A deeper understanding of the relationship between kinetics and structure could help in improving the design of such systems.[10] An interplay between structure and a superimposed energy funnel has been recently demonstrated in the case of extended versus compact dendrimers.[9]

In this paper we investigate mean first passage times and mean residence times in finite one-dimensional systems. These give some insight into trapping processes and their dependence on the details of the underlying system. The mean first passage time (MFPT) provides a useful measure for the efficiency of the trapping, and has been investigated in a broad range of problems in chemistry and biology.[11–13] In particular, MFPTs have been recently studied in connection with light harvesting by antenna systems,[10] and in models of protein folding.[14] The MFPT is the mean time it takes a random walker which starts at site n, to get trapped, and it is directly related to $\Phi(t,n)$, the survival probability of the system at time t when starting at site n,

$$\tau(n)=\int_0^\infty \Phi(t,n)dt. \tag{1}$$

The survival probability in a system which is discrete in space is given by

$$\Phi(t,n)=\sum_{m\neq \mathrm{trap}} P(m,t|n), \tag{2}$$

where $P(m,t|n)$ is the probability to be at site m at time t, starting from site n. The summation in Eq. (2) does not include the trap. While $\Phi(t,n)$ contains the detailed time evolution of the trapping process, the calculation of the corresponding MFPT is simpler, and yet provides relevant characteristic information such as dependence on the system size and rates.

Another quantity of interest is the mean residence time (MRT), which is the average time spent in a given region prior to trapping.[15] In the spatially discrete case the MRT is the mean time that a random walker spends at a given site prior to being trapped, and can be calculated from the time integral of the survival probability for the corresponding site.[15,16] The MRT of site m, starting from n, is

$$\tau(m,n)=\int_0^\infty P(m,t|n)dt. \tag{3}$$

From Eqs. (1) to (3) it follows that the MFPT for starting at site n, $\tau(n)$, is the sum of the MRTs,

$$\tau(n)=\sum_{m\neq \mathrm{trap}} \tau(m,n). \tag{4}$$

Finding the MRT at site m, starting from site n, is equivalent to finding the (m,n) element of the inverse matrix of the transition rates.[15] The discrete time analog of the MRT is the mean number of visitations of a given site by the walker before trapping occurs.[17]

Here we present general expressions for the MRT in terms of the local transition rates, and discuss properties of the MRT which are relevant to various dynamical problems. Using the solution of the MRT we derive the expression for the MFPT when starting from any lattice point. This derivation of the MFPT is simpler than in some previous ap-

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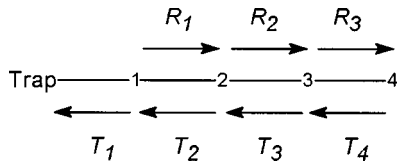

FIG. 1. Schematic representation of the one-dimensional rate equations, Eq. (5), with rates T_i, R_i.

proaches. Applications of MRT and MFPT are exemplified in models of light harvesting, random barriers, and a harmonically bound particle (the Ehrenfest model). We show that the MFPT can be controlled by modifying transition rates along the system. This introduces the possibility for tailoring structures with specific trapping properties.

II. THEORY

We consider a random walker which moves by nearest-neighbor jumps on a one-dimensional system of $N+1$ sites with a reflecting point and an absorbing point (a trap) at the two opposite ends of the system, as shown in Fig. 1. The random walker jumps to nearest sites toward the reflecting point with rates R_i, and toward the trap with rates T_i, where i denotes a site in the one-dimensional system. The coupled rate equations which describe the system in Fig. 1 are

$$\begin{aligned}
&\dot{p}_0(t)=T_1p_1(t) \quad \text{(absorbing boundary)},\\
&\dot{p}_1(t)=T_2p_2(t)-(T_1+R_1)p_1(t),\\
&\dot{p}_i(t)=T_{i+1}p_{i+1}(t)+R_{i-1}p_{i-1}(t)-(T_i+R_i)p_i(t)\\
&\qquad (1<i<N),\\
&\dot{p}_N(t)=R_{N-1}p_{N-1}(t)-T_Np_N(t) \quad \text{(reflecting boundary)},
\end{aligned} \tag{5}$$

where $p_i(t)$ is the probability that the random walker is at the ith site at time t. The above set of differential equations has a matrix $(N\times N)$ representation (note that we do not include the trap site, $n=0$, in the matrix):

$$\frac{d\vec{P}(t)}{dt}=\mathbf{A}\vec{P}(t), \tag{6}$$

where,

$$\mathbf{A}=\begin{bmatrix}
-T_1-R_1 & T_2 & 0 & 0 & 0... & 0\\
R_1 & -T_2-R_2 & T_3 & 0 & 0... & 0\\
0 & R_2 & -T_3-R_3 & T_4 & 0... & 0\\
0 & 0 & R_3 & -T_4-R_4 & \cdots & 0\\
\cdots & \cdots & \cdots & \cdots & \cdots & T_N\\
0 & 0 & 0 & 0 & R_{N-1} & -T_N
\end{bmatrix}. \tag{7}$$

The general solution for the survival probability at the mth site at time t, starting from the nth site, is

$$P(m,t|n)=\vec{Q}\,\exp(\mathbf{A}t)\vec{P}(0). \tag{8}$$

Here $\vec{P}(0)$ is the initial condition, $\vec{P}(0)=[0,0,...1,0...0]^T$, where only the nth element of $\vec{P}(0)$ is occupied, and $\vec{Q}$ is the final state; namely, only the mth element of $\vec{Q}$ is 1. The MRT of the mth site, starting at site n, $\tau(m,n)$, is the time integral of Eq. (8):[15,16]

$$\begin{aligned}
\tau(m,n)&=\int_{t=0}^{\infty}\vec{Q}\,\exp(\mathbf{A}t)\vec{P}(0)dt\\
&=-\vec{Q}\,\mathbf{A}^{-1}\vec{P}(0)=-\mathbf{A}^{-1}(m,n),
\end{aligned} \tag{9}$$

where $\mathbf{A}^{-1}(m,n)$ is the (m,n) element of the inverse matrix $\mathbf{A}^{-1}$. In this notation m corresponds to a row and n to a column in the matrix $\mathbf{A}^{-1}$. The existence of $\mathbf{A}^{-1}$ is guaranteed since there is no stationary solution in the case of a trap, and so the matrix $\mathbf{A}$ does not have zero as an eigenvalue. Having calculated the MRT, $\tau(m,n)$, we can readily obtain the general expression for the MFPT,[11] $\tau(n)$, according to Eq. (4),

$$\tau(n)=-\sum_{m=1}^{N}\mathbf{A}^{-1}(m,n). \tag{10}$$

In what follows we present some properties of the MRT, $\tau(m,n)$, and a general expression for the MFPT, $\tau(n)$, in terms of transition rates in a finite one-dimensional system.

III. PROPERTIES OF MRT

The expressions for the MRT are given in terms of the transition rates R_i and T_i in Eq. (5), and in the matrix $\mathbf{A}$, Eq. (7). The MRTs of site m, when originating at a chosen site n, are obtained from the properties of the inverse matrix $\mathbf{A}^{-1}$:

$$\tau(1,n)=\frac{1}{T_1}, \quad m=1, \tag{11a}$$

$$\tau(m,n)=\tau(m-1,n)\,\frac{R_{m-1}}{T_m}+\frac{1}{T_m}, \quad 1<m\leqslant n, \tag{11b}$$

$$\tau(m,n)=\tau(m-1,n)\,\frac{R_{m-1}}{T_m}, \quad m>n. \tag{11c}$$

Equation 11(a) gives the MRT of site $m=1$ when starting from any site. This MRT does not depend on where the random walker is initiated, namely on n. Equation 11(b) corresponds to the MRT of site m, where $1<m\leqslant n$, and the last recursion, Eq. (11c), describes the MRT of site m for $m>n$. In order to calculate the MRT of a random walker that starts at the reflecting point, $n=N$, only Eq. (11b) is needed,

with m satisfying $1<m\leqslant N$. Further inspection of Eq. (11) leads to the following properties of the MRT.

(1) The MRT of site 1, $\tau(1,n)$, is independent of the starting site, n, and independent of the other rates and of the size of the system, Eq. (11a).

(2) The MRT of site m is independent of the rates from site $m+1$ to the reflecting point N of the system, Eqs. (11b) and (11c).

(3) The MRT of site m, when starting at site n, $m\leqslant n$, Eq. (11b), is the same as starting at site $n+1$; namely, $\tau(m,n)=\tau(m,n+1)$. In other words, suppose that we perform two calculations so that in the first one the random walker starts at site i and in the second one it starts at site j where $j>i$, then the MRTs of sites 1,2,3...i in both calculations are the same. Note that from $\tau(m,n)=\tau(m,n+1)$ ones obtains that $\tau(1,n)=\tau(1,n+1)$ which results also from property (1).

(4) Property (3) yields that $\tau(m,m)=\tau(m,N)$, where N is the reflecting point, and so

$$\sum_{m=1}^{N}\tau(m,m)=\sum_{m=1}^{N}\tau(m,N).$$

This leads to the MFPT for starting at the reflecting point,[18]

$$\tau(N)=\sum_{m=1}^{N}\tau(m,N)=-\mathrm{trace}(A^{-1}). \tag{12}$$

(5) Consider two systems, where one is described by the matrix **A**, Eq. (7), and the other one by matrix **B**, which is similar to **A** except that $T_1=0$. This means that the second system **B** has two reflecting points. The vector solution of the MRTs for a walker which starts at site $n=1$ in system **A**, $\vec{X}=[\tau(1,1),\tau(2,1),\ldots\tau(N,1)]^T$, is also the stationary solution of the system described by **B**.[19] Matrix **B** satisfies $\mathbf{B}\vec{X}=\vec{0}$ (see the Appendix), which leads to

$$\exp(\mathbf{B}t)\vec{X}=\sum_{n=0}^{\infty}\frac{\mathbf{B}^n}{n!}\vec{X}=\vec{X}. \tag{13}$$

Therefore, the stationary distribution of site m of system **B** is given in terms of the MRT and MFPT of system **A**,

$$P_m(\mathrm{eq})=\frac{\tau(m,1)}{\Sigma_{m=1}^{N}\tau(m,1)}=\frac{\tau(m,1)}{\tau(1)}. \tag{14}$$

Equation (14) relates between the two systems which have different boundary conditions. If we assign energies to the sites in system **B** then,

$$P_1(\mathrm{eq})=\frac{\tau(1,1)}{\tau(1)}=\frac{e^{-\beta E_1}}{Q}, \tag{15}$$

where Q is the partition function, $Q=\Sigma_m e^{-\beta E_m}$, E_1 is the corresponding energy of site 1, and β^{-1} is the Boltzmann factor multiplied by the temperature. The partition function of system **B** can be expressed in terms of the kinetics of system **A**,

$$Q=\tau(1)T_1e^{-\beta E_1}. \tag{16}$$

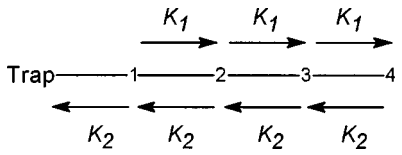

FIG. 2. Same as Fig. 1 for the asymmetric case, $T_i=K_2$, $R_i=K_1$.

Using Eqs. (14) and (16) we can relate between the MRT of site m, starting at site 1, and the corresponding energy E_m of the site

$$\tau(m,1)=\frac{1}{T_1}e^{-\beta(E_m-E_1)}. \tag{17}$$

In the above considerations we did not include possible degeneracy in the site energies.[10] One can define the free energy of the nth site,

$$F_n=E_n-\beta^{-1}\ln f_n, \tag{18}$$

where f_n is the degeneracy in the energy of the nth site. The degeneracy has been shown to play an important role in the case of trapping in model dendrimers.[10,20] In this case E_n should be replaced by F_n in Eqs. (15)–(17).

(6) Summing the MRTs over the system sites, using Eq. (11), we obtain the MFPT for starting from any lattice point n,

$$\tau(n)=\sum_{i=1}^{N}\rho_i+\sum_{r=1}^{n-1}\frac{1}{\rho_r R_r}\sum_{s=r+1}^{N}\rho_s, \tag{19}$$

where

$$\rho_i=\frac{R_1R_2\ldots R_{i-1}}{T_1T_2\ldots T_{i-1}T_i},\quad \rho_1=\frac{1}{T_1}. \tag{20}$$

The first term in Eq. (19) is the MFPT for starting at site $n=1$,[11] $\Sigma_{i=1}^{N}\rho_i=\tau(1)$. $\rho_i=\tau(i,1)$ is the MRT of site i of a walker that starts at $n=1$, as obtained from Eq. (11c). Substituting $N\to\infty$ in Eq. (19) we recover the MFPT for an infinite system.[21]

IV. APPLICATIONS

A. Asymmetric random walk

We consider an asymmetric random walk, as shown in Fig. 2, which is given by identifying T_i and R_i in the transition matrix, Eq. (7), as

$$T_i=K_2,\quad R_i=K_1. \tag{21}$$

Substituting Eq. (21) into Eq. (11c) yields the recursion relation for the MRT starting at site $n=1$,

$$\tau(m,1)=\tau(m-1,1)\frac{K_1}{K_2},\quad 1<m\leqslant N,$$
$$\tau(1,1)=\frac{1}{K_2},\quad m=1. \tag{22}$$

Solving Eq. (22) we obtain the MRT for starting at site $n=1$,

TABLE I. Dependence of the MFPT on system size; $K=K_1/K_2$.

$K>1$ bias to the reflecting point	$K=1$ no bias	$K<1$ bias to the trap
$\tau(1)=\frac{1}{K_2}\frac{1}{(K-1)}e^{N\ln K}$	$\tau(1)=\frac{1}{K_2}N$	$\tau(1)=\frac{1}{K_2(1-K)}$
$\tau(N)=\frac{1}{K_2}\frac{K}{(K-1)^2}e^{N\ln K}$	$\tau(N)=\frac{1}{2K_2}N^2$	$\tau(N)=\frac{1}{K_2(1-K)}N$

$$\tau(m,1)=\frac{1}{K_1}(K_1/K_2)^m. \tag{23}$$

Equation (23) also presents the stationary solution (without normalization) for the same system with $T_1=0$. Substituting Eq. (21) into Eq. (19) we recover the expression for the MFPT of a random walker which starts at any lattice point,

$$\begin{aligned}\tau(n)&=\frac{n}{K_2-K_1}-\frac{K_1}{(K_2-K_1)^2}\left[\left(\frac{K_1}{K_2}\right)^{N-n}-\left(\frac{K_1}{K_2}\right)^N\right],\\ &\quad K_1\neq K_2,\\ \tau(n)&=\frac{n(2N-n+1)}{2K_1},\quad K_1=K_2,\end{aligned} \tag{24}$$

where N is the reflecting site.

For a finite but large system the dependence of the MFPT on the size of the system is summarized in Table I,[20] where $K=K_1/K_2$.

We can use this model to describe a linearly descending energy funnel. For example, we assume that the energy of site n is $E_n=nU$ where U is positive. Due to detailed balance $K=z\exp^{-\beta U}$, where z is a positive constant which depends on the system. For $z\leqslant 1$, K always satisfies $K<1$, while for $z>1$ all values $K>0$ are possible, and the actual behavior is dictated by the value of βU, namely the ratio of the characteristic funnel energy U to the temperature. We have recently applied this model, which is known also in queueing theory,[22] to calculate the MFPT in the case of the treelike structures of dendrimers. Based on the MFPT calculations we have shown that dendrimers can serve as efficient antenna systems for light harvesting.[10,20]

B. Random barrier model

Another example is the random barrier model,[23] shown in Fig. 3, in which the rate to jump from site $i\rightarrow i+1$ is equal to the rate back from $i+1\rightarrow i$. The transition matrix elements are

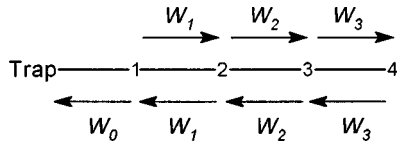

FIG. 3. Same as Fig. 1 for random barriers with rates, $R_i=T_{i+1}=W_i$.

$$\begin{aligned}&R_i=T_{i+1}=W_i,\quad 1\leqslant i\leqslant N-1,\\ &T_1=W_0.\end{aligned} \tag{25}$$

This corresponds to a symmetric matrix in Eq. (7), which therefore has a symmetric inverse transition matrix. From Eq. (11a) we obtain

$$\tau(1,m)=1/W_0 \tag{26}$$

and from the symmetry of the inverse transition matrix,

$$\tau(1,m)=\tau(m,1)=1/W_0. \tag{27}$$

The MRT at each site, starting from site 1, is the same and is equal to $1/W_0$. Summing $\tau(m,1)$ leads to the MFPT

$$\tau(1)=\sum_{m=1}^{N}\tau(m,1)=N/W_0, \tag{28}$$

and so the stationary distribution (for the system without a trap, $T_1=0$) is independent of the transition rates, as expected,[23]

$$P_m(\mathrm{eq})=\frac{\tau(m,1)}{\tau(1)}=\frac{1/W_0}{N/W_0}=1/N. \tag{29}$$

Substituting Eq. (25) into Eq. (19) leads to

$$\tau(n)=\sum_{i=1}^{n}\frac{N+1-i}{T_i}. \tag{30}$$

The MFPT, starting at the n site, depends only on the transition rates T_i, $i=1,2,...,n$, and not on the other rates of the system. In the special case $T_i=K_1$ we recover Eq. (24) of the previous model for $K_1=K_2$. When averaging the MFPT over all realizations we obtain

$$\langle\tau(n)\rangle=\frac{n(2N+1-n)}{2}\left\langle\frac{1}{T}\right\rangle, \tag{31}$$

where $\langle 1/T\rangle$ is the inverse average rate toward the trap. The average over all realizations gives the results of Eq. (24) again. Substituting $n=N$ in Eq. (31) we recover the results of Ref. 24.

C. Continuous time version of the Ehrenfest model

An interesting case is the continuous time version of the Ehrenfest model in which a trap and a reflecting point are located at the two opposite ends of a line shown in Fig. 4. The Ehrenfest model, in the appropriate limit, leads to Smoluchowski's equation with a harmonic potential.[25] The finite matrix which represents the model is characterized in terms of T_i and R_i in the transition matrix, Eq. (7),

$$T_i=\frac{k}{N}i,\quad R_i=\frac{k}{N}(N-i). \tag{32}$$

We should point out that this choice of rates guarantees that for large systems the rates are bounded: $0<T_i\leqslant k$, $0<R_i<k$.

Substituting Eq. (32) into Eq. (20) we arrive at

$$\rho_i=\frac{R_1R_2\ldots R_{i-1}}{T_1T_2\ldots T_{i-1}T_i}=\frac{1}{k}\binom{N}{i}, \tag{33}$$

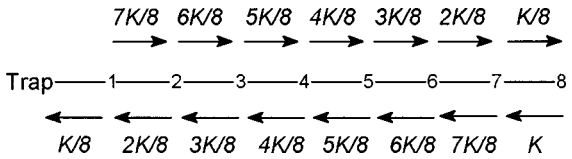

FIG. 4. Schematic representation of the one-dimensional continuous time version of the Ehrenfest model, Eq. (32), with rates $T_i=(k/N)i$ and $R_i=(k/N)(N-i)$.

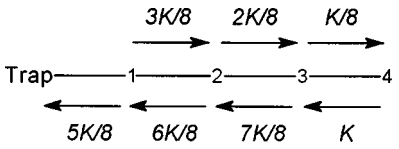

FIG. 5. The model in Fig. 4, but now with the trap situated in the center (site 4 in Fig. 4).

which leads to the MFPT, starting from the nth site,

$$\tau(n)=\frac{1}{k}\sum_{r=0}^{n-1}\binom{N-1}{r}^{-1}\sum_{j=r+1}^{N}\binom{N}{j}. \tag{34}$$

In particular,

$$\tau(1)=\frac{(2^N-1)}{k}. \tag{35}$$

For an even N one can write the MFPT, starting at the reflecting point, as

$$\tau(N)=\frac{1}{k}2^N\sum_{r=0}^{N/2-1}\binom{N-1}{r}^{-1}. \tag{36}$$

For large N the sum in Eq. (36) can be estimated by lower and upper bounds,[26]

$$\frac{1}{k}2^N\left(1+\frac{1}{N}\right)\leqslant\tau(N)\leqslant\frac{1}{k}2^N\left(1+\frac{2}{N}\right), \tag{37}$$

so that

$$\tau(N)\cong\frac{1}{k}2^N\left(1+\frac{c}{N}\right),\quad 1\leqslant c\leqslant 2.$$

For a large system the MFPT starting at the reflecting point, and the MFPT starting at site 1, are almost the same, which indicates independence of the initial condition. Using Eqs. (33) and Eq. (35) we derive the stationary solution which behaves as the binomial distribution. For large systems, using the DeMoivre–Laplace approximation, $P_m(\mathrm{eq})$ tends to the normal distribution,

$$p_m(\mathrm{eq})=\frac{\tau(m,1)}{\tau(1)}=\frac{\rho_m}{\tau(1)}=\binom{N}{m}\frac{1}{2^N-1}$$

$$\cong\frac{1}{\sqrt{\pi N/2}}e^{-(m-N/2)^2/(N/2)}. \tag{38}$$

The stationary distribution is for a system with N sites while the system with a trap has $N+1$ sites. This model is a special case of a model discussed by Zwanzig,[14] which was introduced to exemplify the effect of a bias on protein folding. In this model the calculation of the MFPT to reach the native configuration demonstrates a change from an inefficient random search to an efficient biased search as a function of temperature. We now modify the model by placing the trap in the center of Fig. 4, for an even N, as shown in Fig. 5. It is clear from Eq. (38) that the center is the most probable site for the equilibrium occupation. The $L\times L$ matrix ($L=N/2$) which represents this case is given by the rates

$$T_i=\frac{k}{2L}(L+i),\quad R_i=\frac{k}{2L}(L-i). \tag{39}$$

Here the MRT, Eq. (20), is

$$\rho_i=\frac{R_1R_2\ldots R_{i-1}}{T_1T_2\ldots T_{i-1}T_i}=\frac{2}{k}\binom{2L}{L}^{-1}\binom{2L}{L-i}. \tag{40}$$

Using Eq. (19) we derive the MFPT,

$$\tau(n)=\frac{2L}{k}\sum_{r=0}^{n-1}\frac{1}{L-r}\binom{2L}{L-r}^{-1}\sum_{s=r+1}^{L}\binom{2L}{L-s}. \tag{41}$$

When starting at $n=1$,

$$\tau(1)=\sum_{i=1}^{L}\rho_i=\frac{2^{2L}}{k\binom{2L}{L}}-\frac{1}{k}, \tag{42}$$

which for $L\gg 1$ follows

$$\tau(1)\approx\frac{1}{k}\sqrt{\pi L}. \tag{43}$$

Substituting $n=L$ into Eq. (41) we obtain

$$\tau(L)=\frac{2L}{k}\sum_{n=0}^{L-1}\frac{1}{2+4n}, \tag{44}$$

which for a large system, $L\gg 1$, behaves according to $\tau(L)\approx(1/k)L\log(L)$. If one assumes the rates $T_i=k(L+i)$ and $R_i=k(L-i)$, then $\tau(1)\approx(1/k)\sqrt{\pi/L}$ and $\tau(L)\approx(1/k)\times\log(L)$, which correspond to a very rapid capture by the trap.

V. CONTROLLING THE MFPT

The trapping efficiency, as measured by the MFPT, depends on the local transition rates according to Eq. (19). These local rates should depend on the architecture of the molecular-scale systems, as demonstrated by two types of dendrimers, compact and extended.[9,27] The ability to synthesize molecular systems with desired properties raises the possibility of designing structures with different local transition rates. This introduces a possible way to control the MFPT. As an example we modify the asymmetric random walk, Fig. 2, by changing one of the rates, K_2, toward the trap,

$$\begin{aligned}&T_i=K_2,\quad R_i=K_1,\\&T_x=K_3,\quad R_x=K_1,\end{aligned} \tag{45}$$

where x can be any site $1\leqslant x\leqslant N$.

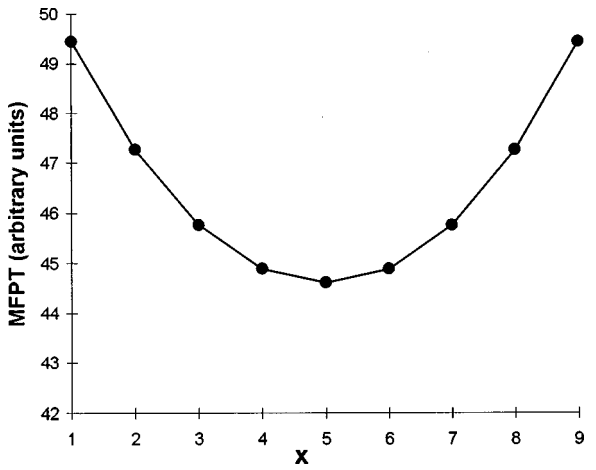

FIG. 6. The dependence of the MFPT when starting at N, $\tau(N)$, on the location x of the rate K_3 ($K_3>K_2$).

The MFPT changes as we change the ''location'' of the rate K_3 in the chain. For starting at the reflecting point, $n=N$, the MFPT as a function of the position x of the rate K_3, along the one-dimensional system is

$$\tau_x(N)=\frac{N+K_2/K_3-1}{K_2-K_1}+\frac{K_1}{(K_1-K_2)^2}\left[\left(1-\frac{K_2}{K_3}\right)\left(\left(\frac{K_1}{K_2}\right)^{N-x}+\left(\frac{K_1}{K_2}\right)^{x-1}\right)+\frac{K_2}{K_3}\left(\frac{K_1}{K_2}\right)^{N}+\frac{K_2}{K_3}-2\right],\quad K_1\neq K_2. \tag{46}$$

For an odd N Eq. (46) is characterized by an extremum when $x=(N+1)/2$. This corresponds to $T_{(N+1)/2}=K_3$. We obtain a minimum in the value of $\tau_{(N+1)/2}(N)$ for $K_3>K_2$ and a maximum in $\tau_{(N+1)/2}(N)$ for $K_3<K_2$. In Fig. 6 we plot the MFPT as a function of the position of K_3 for the case $K_3>K_2$. For a given system one can control the MFPT by choosing the location of K_3 and its value. This allows, at least in our example, for minimizing $\tau(N)$. The same considerations hold for an even N.

A similar calculation for a random barrier model, Fig. 3, with $W_i=K_2$ and $W_x=K_3$ shows that the preferred ''location'' of the rate $K_3(K_3>K_2)$ so that $\tau(N)$ is minimal at site $n=1$. This follows directly from Eq. (30) for $\tau(N)$ where the weight of site 1 in the sum is higher than of other sites.

Combining recent developments in tailoring molecular systems to carry out specific functions with theoretical considerations of the kinetics on molecular scale can therefore help control properties such as the MFPT.

VI. CONCLUSIONS

We have presented a simple framework for calculating MRTs and MFPTs in finite one-dimensional systems under different assumptions which represent different possible realizations. We have investigated the dependence of the MFPT on the system size and on the local kinetic rates for asymmetric random walks, which can be related to symmetric dendrimer structures, for random barriers, and for the Ehrenfest model. Modifying the rates in some of the systems allows for minimizing the MFPT to arrive from the reflecting point to the trap.

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APPENDIX

Here we show that $\mathbf{B}\vec{X}=\vec{0}$. This leads to Eq. (13) in the main text. We calculate the different contributions to the matrix multiplication $\mathbf{B}\vec{X}$.

(a) When multiplying the first row of matrix $\mathbf{B}$ by the vector $\vec{X}=[\tau(1,1),\tau(2,1),\ldots\tau(N,1)]^T$, and by considering Eq. (11c) we obtain

$$-R_1\tau(1,1)+T_2\tau(2,1)=-R_1\tau(1,1)+T_2\tau(1,1)R_1/T_2=0. \tag{A1}$$

(b) Row m of matrix $\mathbf{B}$, where $1<m<N$, when multiplied by the vector $\vec{X}$ is

$$R_{m-1}\tau(m-1,1)-(T_m+R_m)\tau(m,1)+T_{m+1}\tau(m+1,1)=R_{m-1}\frac{\tau(m,1)T_m}{R_{m-1}}-(T_m+R_m)\tau(m,1)+T_{m+1}\frac{\tau(m,1)R_m}{T_{m+1}}=0. \tag{A2}$$

(c) The last row of matrix $\mathbf{B}$, $m=N$, when multiplied by the vector $\vec{X}$ is

$$R_{N-1}\tau(N-1,1)-T_N\tau(N,1)=R_{N-1}\tau(N-1,1)-T_N\frac{\tau(N-1,1)R_{N-1}}{T_N}=0. \tag{A3}$$

Therefore the vector $\vec{X}$ satisfies $\mathbf{B}\vec{X}=\vec{0}$, and it is a stationary solution (without normalization) of system $\mathbf{B}$.

[1] J. Jortner and M. Ratner, Molecular Electronics (IUPAC, 1997).
[2] (a) D. L. Jiang and T. Aida, Nature (London) **388**, 454 (1997); (b) D. M. Junge and D. V. McGrath, Chem. Commun. (Cambridge), 857 (1997).
[3] (a) S. Mattei, P. Wallimann, B. Kenda, W. Amrein, and F. Diederich, Helv. Chim Acta **80**, 2391 (1997); (b) D. K. Smith and F. Diederich, Chem. Eur. J. (in press).
[4] J. M. Lehn, *Supramolecular Chemistry* (VCH, 1995).
[5] I. Yamazaki, M. Yamaguchi, N. Okada, S. Akimoto, T. Yamazaki, and N. Ohta, J. Lumin. **72**, 71 (1997).
[6] L. Jullien, J. Canceill, B. Valeur, E. Bardez, and J. M. Lehn, Angew. Chem. Int. Ed. Engl. **33**, 2438 (1994).
[7] Z. F. Xu, M. Kahr, K. L. Walker, C. L. Wilkins, and J. S. Moore, J. Am. Chem. Soc. **116**, 4537 (1994).
[8] V. Balzani, S. Campagne, G. Denti, J. Alberto, S. Serroni, and M. Venturi, Sol. Energy Mater. Sol. Cells **38**, 159 (1995).
[9] R. Kopelman, M. Shortreed, Z. Y. Shi, W. Tan, Z. Xu, J. S. Moore, A. Bar-Haim, and J. Klafter, Phys. Rev. Lett. **78**, 1239 (1997).
[10] A. Bar-Haim, J. Klafter, and R. Kopelman, J. Am. Chem. Soc. **119**, 6197 (1997).
[11] (a) G. H. Weiss, Adv. Chem. Phys. **13**, 1 (1966); (b) N. G. Van Kampen, *Stochastic Processes in Physics and Chemistry* (North-Holland, Amsterdam, 1981).
[12] I. Procaccia, S. Mukamel, and J. Ross, J. Chem. Phys. **68**, 3244 (1978).

[13] V. Seshadri, B. J. West, and K. Lindenberg, J. Chem. Phys. **72**, 1145 (1980).
[14] (a) R. Zwanzig, A. Szabo, and B. Bagchi, Proc. Natl. Acad. Sci. USA **89**, 20 (1992); (b) R. Zwanzig, *ibid.* **92**, 9801 (1995).
[15] A. Blumen and Z. Zumofen, J. Chem. Phys. **75**, 892 (1981).
[16] N. Agmon, J. Chem. Phys. **81**, 3644 (1984); A. M. Berezhkovskii, V. Zaloj, and N. Agmon, Phys. Rev. E **57**, 3937 (1998).
[17] J. G. Kemeny and J. L. Snell, *Finite Markov Chains* (Van Nostrand, Princeton, NJ, 1967), p. 59.
[18] E. W. Montroll and K. E. Shuler, Adv. Chem. Phys. **1**, 361 (1958).
[19] W. Zwerger and K. W. Kehr, Z. Phys. B **40**, 157 (1980).
[20] (a) A. Bar-Haim and J. Klafter, J. Phys. Chem. B **102**, 1662 (1998); (b) J. Lumin. **76**, 197 (1998).
[21] S. Karlin, *A First Course in Stochastic Processes* (Academic, New York, 1966), p. 205.
[22] N. T. J. Bailey, *The Elements of Stochastic Processes* (Wiley, New York, 1964), pp. 157–160.
[23] P. J. H. Denteneer and M. H. Ernst, Phys. Rev. B **29**, 1755 (1984).
[24] K. P. N. Murthy and K. W. Kehr, Phys. Rev. A **40**, 2082 (1989).
[25] M. Kac, Am. Math. Monthly **54**, 369 (1947).
[26] J. G. Kemeny and J. L. Snell, in Ref. 17, p. 175.
[27] S. Tretiak, V. Chernyak, and S. Mukamel, J. Phys. Chem. B **102**, 3310 (1998).