

Single-molecule chemical reactions: Reexamination of the Kramers approach

G. Margolin¹ and E. Barkai^{1,2}

¹*Department of Chemistry and Biochemistry, Notre Dame University, Notre Dame, Indiana 46556, USA*

²*Department of Physics, Bar Ilan University, Ramat Gan, Israel 52900*

(Received 15 April 2005; published 2 August 2005)

Single-molecule chemical reactions yield insight into fluctuation phenomena that are obscured in the measurement of the ensemble of molecules. Kramers escape problem is investigated here in a framework suitable for single-molecule reactions. In particular we obtain distributions of escape times in simple limiting cases, rather than their mean, and investigate their sensitivity on initial conditions. Rich physical behaviors are observed: sub-Poissonian statistics when the dynamics is only slightly deviating from the Newtonian, super-Poissonian behavior when diffusion is dominating, and Poissonian behavior when Kramers original conditions hold. By varying initial conditions escape time distributions can follow a (usual) exponential or a $\tau^{-3/2}$ decay, due to regular diffusion. We briefly address experimental results that yield the $\tau^{-3/2}$ behavior (with cutoffs) and propose that this behavior is universal.

DOI: [10.1103/PhysRevE.72.025101](https://doi.org/10.1103/PhysRevE.72.025101)

Chemical reaction of a single molecule evolving between two states $A \rightleftharpoons B$ or of two species $A + B \rightleftharpoons AB$ is now followed in many laboratories using single-molecule spectroscopy techniques [1–7]. Such experiments yield detailed statistical information on chemical conformational changes, and simple chemical processes in condensed phase environments, for example the distribution of occupation times of states A and B in the process $A \rightleftharpoons B$. Such information is impossible to obtain when measurements are made on many molecules, since the ensemble averaging wipes out the detailed information found on the single-molecule level. For ensemble of molecules, usually simple reactions are assumed to follow a rate process.

For ensemble of molecules undergoing a chemical reaction, classical concepts like reaction coordinate, and rate equations, work well in many cases. In particular, Kramers model [8,9] for activation over a barrier is a fundamental tool for modeling chemical reactions in condensed phase environments. In this paper we analyze Kramers problem, in a framework of single molecules. We first discuss Kramers original approach, and its limitations in the single-molecule domain.

Kramers describes a chemical reaction in terms of a reaction coordinate $x(t)$. The complicated interaction of the chemical species with their environment is replaced with a stochastic one-dimensional approach. The coordinate $x(t)$ evolves in a deterministic force field $V(x)$, and is also coupled to a thermal heat bath. The reaction coordinate is supposed to escape a metastable state. The inverse of the average time of escape $\langle \tau \rangle$, from the bottom of the well, serves as an estimate on the ensemble averaged reaction rate. Two important regimes of Kramers problem are the underdamped and overdamped limits. Many refinements, non-trivial results and generalizations of Kramers problem are known, e.g., Kramers turn-over behavior, quantum effects, and non-Markovian generalizations (e.g., [10–12]; see [9] for a review). Experimental validation of the theory is also obtained [13].

At least three aspects of Kramers problem must be revised in the context of the single-molecule chemical reaction. The

PACS number(s): 02.50.-r, 82.37.Np, 05.40.-a

most obvious one is that now we must consider the distribution of occupation times in a chemical state, and not limit the theory to averaged escape rates. Previous work considered temporal dependence of the rate [14,15] until it reaches an equilibrium value in a single escape (transition) event, or the transient behavior after the particle injection close to the bottom of the well [16]. The idea of fluctuating rates in multiple transitions, in the context of single-molecule experiments has been scrutinized and used in, e.g., [1,17–19]. A second issue is the sensitivity of single-molecule chemical reactions to initial conditions. Consider the ongoing chemical reaction $A \rightleftharpoons B$. For example, using fluorescence resonance energy transfer (FRET) methods, one may follow the closing (state A) and opening (state B) of a large molecule [4–6,20,21]. The experimental data then yields the string of occupation times $\{\tau_A^1, \tau_B^2, \tau_A^3, \dots\}$. Following Kramers, assume that such events are described by a reaction coordinate, which goes over a single barrier, to cross from state $A \rightarrow B$ and vice versa. Also we assume that a measurement may distinguish between state A and state B , as is shown in many experiments. In terms of the reaction coordinate this means that when $x(t) < x_b$ the system is in the state A ; otherwise it is in the state B and x_b is the boundary (usually and conveniently assumed to be at the top of the potential barrier). Then, immediately after the transition event from say $A \rightarrow B$, the reaction coordinate is in close vicinity to x_b . Thus a short time after the transition from state $A \rightarrow B$ there is an increased likelihood for a back transition $B \rightarrow A$. This possibility is expected to yield bunching of chemical activity on the time axis, i.e., to intermittency where strong activity is observed for some period of time followed by periods of lesser activity. Of course to observe such effects the resolution time in the experiments must be short compared to relaxation times of the dynamics. A third important point is that in single-molecule experiments, an additional length scale λ is introduced into the problem. For example, the radius of the laser illumination field, or the Förster length scale in FRET experiments [4,21]. Roughly, in the reaction $A \rightleftharpoons B$, a fluorescence signal is recorded if an acceptor and donor are within a range of Förster radius from each other (state A) while otherwise the signal is zero (state B). In terms of the reaction coordi-

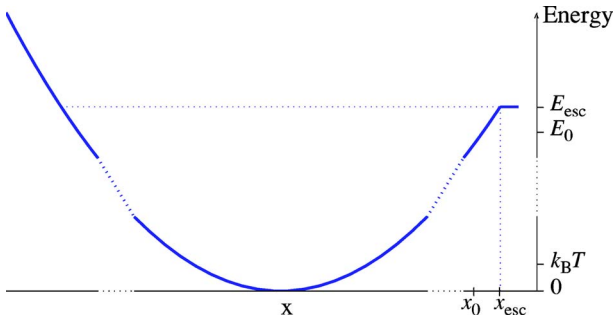


FIG. 1. (Color online) Escape from a metastable well. In the underdamped case, the relevant coordinate is the action I , which is related to the energy E of the particle by $I=2\pi E/\omega$. In the overdamped case, the relevant coordinate is position x in real space.

nate, this implies that when $x(t) < \lambda$, the system is in the state A ; otherwise it is in the state B . The point to notice is that in principle, λ can be anywhere along the reaction coordinate. In particular the classical approach of an escape from a bottom of the well over a maximum in the potential field is not expected to be general.

Hence we investigate Kramers escape problem, obtaining distribution of escape times. With initial conditions both in vicinity of the escape point and far from it. We classify the deviations from exponential behaviors, and show that in many cases rate concept is not valid. In particular we classify a turnover behavior from power-law behavior to exponential, and show that the power-law behavior is general.

Model 1. We consider a classical particle undergoing underdamped diffusion in a harmonic potential well. As well known, the relevant coordinate for underdamped motion is the action I . The probability density function (PDF) P of finding the particle with action I obeys the Fokker-Planck equation

$$\frac{\partial P}{\partial t} = \gamma \frac{\partial}{\partial I} \left(IP + \frac{2\pi k_B T}{\omega} I \frac{\partial P}{\partial I} \right), \quad (1)$$

where ω is the harmonic frequency, E is the particle energy, $k_B T$ is the thermal energy, and γ is the damping coefficient; $\gamma \ll \omega$ (see Fig. 1; $I=2\pi E/\omega$ for constant ω). In what follows we use dimensionless time $\tau = \gamma t$ and action $\mathcal{I} = I\omega/2\pi k_B T$. Let $\phi(\tau)$ be the PDF of escape times from \mathcal{I}_0 to $\mathcal{I}_{esc} > \mathcal{I}_0$. Mathematically we use absorbing boundary conditions at \mathcal{I}_{esc} , so that $\phi(\tau)$ is the first passage time distribution (FPTD) from \mathcal{I}_0 to \mathcal{I}_{esc} . We obtained the Laplace $\tau \rightarrow u$ transform of $\phi(\tau)$, using known solution to Kummer's equation [22,23]. We find

$$\hat{\phi}(u) = \frac{{}_1F_1(u; 1; \mathcal{I}_0)}{{}_1F_1(u; 1; \mathcal{I}_{esc})}, \quad (2)$$

where ${}_1F_1(a; b; c)$ is the regular confluent hypergeometric function. Since ${}_1F_1(0; b; c) = 1$ the function $\phi(\tau)$ is normalized to 1. We note that a second presentation of the solution in terms of an infinite sum of exponentially decaying modes is possible, in time domain. However, as we shall show now for an important parameter regime, one cannot replace such standard eigenfunction solutions with a summation over a finite number of modes consisting of a few exponential func-

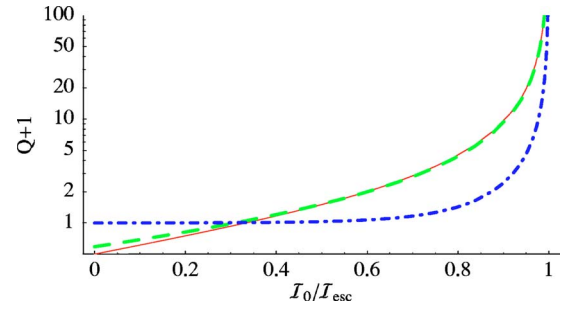


FIG. 2. (Color online) $Q+1$ as a function of $r = \mathcal{I}_0/\mathcal{I}_{esc}$. The full line is the asymptotic line for small \mathcal{I}_{esc} , given by $(1+r)/[2(1-r)]$. The dashed line is for $\mathcal{I}_{esc}=1$ and the dot-dashed line is for $\mathcal{I}_{esc}=10$. Notice the logarithmic scale. Two generic behaviors are observed: (i) if $\mathcal{I}_{esc} \leq 1$, a smooth transition from sub-Poissonian to super-Poissonian behavior is observed; (ii) if $\mathcal{I}_{esc} > 1$, a Poissonian behavior is found until $\mathcal{I}_0 \approx \mathcal{I}_{esc}$ and then a sharp transition from Poissonian to super-Poissonian behavior is observed.

tions; rather, the solution exhibits a power-law behavior.

To quantify deviations from exponential statistics, we use the parameter

$$Q = \frac{\sigma^2}{\langle \tau \rangle^2} - 1,$$

where $\langle \tau \rangle$ is the average escape time and $\sigma^2 = \langle \tau^2 \rangle - \langle \tau \rangle^2$ is its variance. If we have Poissonian behavior consistent with a rate equation approach, then $Q=0$. When the dynamics is Newtonian (i.e., diffusion is weak) the PDF of escape time is narrow, leading to $Q < 0$, a sub-Poissonian behavior. On the contrary, if the PDF of escape times is widespread, there is a super-Poissonian behavior and $Q > 0$. Using the small u expansion of the exact solution, we find

$$\langle \tau \rangle = A(\mathcal{I}_{esc}) - A(\mathcal{I}_0), \quad (3)$$

and

$$\sigma^2 = A^2(\mathcal{I}_{esc}) - A^2(\mathcal{I}_0) - 2[B(\mathcal{I}_{esc}) - B(\mathcal{I}_0)], \quad (4)$$

with

$$A(z) = \sum_{n=1}^{\infty} \frac{z^n}{nn!} \quad \text{and} \quad B(z) = \sum_{n=2}^{\infty} \frac{z^n \sum_{j=1}^{n-1} 1/j}{nn!}. \quad (5)$$

In Fig. 2 we plot $Q+1$ vs \mathcal{I}_0 for three cases where $\mathcal{I}_{esc} < 1$ (escape over a shallow barrier), $\mathcal{I}_{esc} = 1$ and $\mathcal{I}_{esc} > 1$ (escape over a large barrier). As $\mathcal{I}_0 \rightarrow \mathcal{I}_{esc}$, namely the case when the chemical reaction starts close to the escaping zone, we observe $Q \rightarrow \infty$, i.e., strong super-Poissonian behavior. For $\mathcal{I}_{esc} \leq 1$ we do not expect, and indeed do not find, an exponential behavior, since the barrier is not high. Here, depending on initial position, either sub- or super-Poissonian behavior is generally observed. As \mathcal{I}_0 becomes closer to \mathcal{I}_{esc} , diffusion in Eq. (1) becomes more dominant than the deterministic drift, and hence Q grows. Conversely, when $\mathcal{I}_0 \ll \mathcal{I}_{esc}$ and $\mathcal{I}_{esc} \leq 1$ drift becomes more important, leading to negative Q . However, diffusion can never be neglected as it is the only mechanism leading to an eventual escape from the well. Note that always $Q \geq -1/2$ and the absolute minimum of $Q = -1$ is unachievable in this model. For $\mathcal{I}_{esc} > 1$

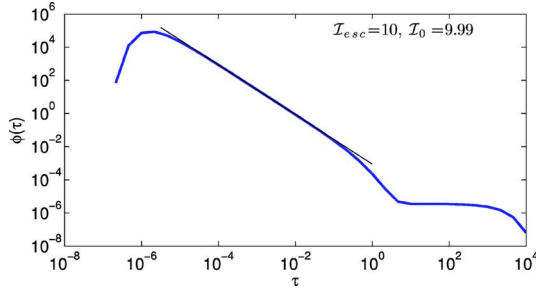


FIG. 3. (Color online) Distribution of escape times $\phi(\tau)$ in the underdamped case. At early and intermediate times $\phi(\tau)$ is governed by Eq. (8), which exhibits a power-law decay $\tau^{-3/2}$ at intermediate times (thin line), if the initial condition \mathcal{I}_0 is close to the escape condition \mathcal{I}_{esc} . At later times, there is an exponential decay with rate given by Kramers rate.

and \mathcal{I}_0 sufficiently below \mathcal{I}_{esc} , we have exponential behavior and $Q \approx 0$. The latter case corresponds to Kramers's original treatment of escape from a deep metastable state.

We now consider $\phi(\tau)$. In Laplace space and in the limit $u \gg \max\{1, 1/\mathcal{I}_0\}$ we use [22] to reduce Eq. (2) to

$$\hat{\phi}(u) \sim \left(\frac{\mathcal{I}_{esc}}{\mathcal{I}_0}\right)^{1/4} e^{(\mathcal{I}_0 - \mathcal{I}_{esc})/2} e^{-2\sqrt{u}(\sqrt{\mathcal{I}_{esc}} - \sqrt{\mathcal{I}_0})}. \quad (6)$$

The important thing to notice is the nonanalytical behavior of this asymptotic solution, namely the term of the form $e^{-\sqrt{u}}$. This term is an indication for power-law behavior (with some cutoffs) since if $\hat{\phi}(u) = e^{-\sqrt{u}}$ for all u then $\phi(\tau) \sim \tau^{-3/2}$ for large τ (e.g., [24]). To find τ for which $\phi(\tau) \sim \tau^{-3/2}$, we have to demand the validity of Eq. (6) for small $\sqrt{u}(\sqrt{\mathcal{I}_{esc}} - \sqrt{\mathcal{I}_0})$, while u is large. This yields

$$(\sqrt{\mathcal{I}_{esc}} - \sqrt{\mathcal{I}_0})^2 \ll \tau \ll \min\{1, \mathcal{I}_0\}, \quad (7)$$

so that the reaction should start in the vicinity of the escaping point. This behavior is demonstrated in Fig. 3.

When $\tau \rightarrow 0$ we find $\phi(\tau) \rightarrow 0$, a nonexponential behavior. This behavior is due to the fact that it takes the particle a certain amount of time to reach the boundary. More quantitatively, for short times Eq. (6) is always a good approximation for $\hat{\phi}(u)$, leading to

$$\phi(\tau) \sim \left(\frac{\mathcal{I}_{esc}}{\mathcal{I}_0}\right)^{1/4} e^{(\mathcal{I}_0 - \mathcal{I}_{esc})/2} (\sqrt{\mathcal{I}_{esc}} - \sqrt{\mathcal{I}_0}) \times \frac{\exp[-(\sqrt{\mathcal{I}_{esc}} - \sqrt{\mathcal{I}_0})^2/\tau]}{\sqrt{\pi\tau^{3/2}}}. \quad (8)$$

Model 2. We turn now to the other limit of particle diffusion—namely to the overdamped limit—and demonstrate the deviation from Poissonian behavior. The relevant coordinate here is the spatial coordinate x . Restricting ourselves to one spatial dimension, the following Fokker-Planck equation is then obtained:

$$\frac{\partial P(x,t)}{\partial t} = (m\gamma)^{-1} \left[\frac{\partial}{\partial x} U'(x) + k_B T \frac{\partial^2}{\partial x^2} \right] P(x,t), \quad (9)$$

where m is the particle mass and $F(x) = -U'(x)$ is the deterministic part of the force, due to potential field. We consider

two cases, when $U(x) = \pm m\omega^2 x^2/2$ near the escape point, i.e., parabolic and inverted parabolic potential, with $\omega \ll \gamma$. We define dimensionless time $\tau = t/\theta$ and position $y = x/l$, where $\theta = \gamma\omega^{-2}$ and $l = \sqrt{k_B T/(m\omega^2)}$.

Parabolic potential. We are interested in the FPTD from initial position y_0 to y_{esc} . This function is known in Laplace space and is given by (e.g., [23])

$$\hat{\phi}(u) = \frac{D_{-u}(-y_0 s) e^{y_0^2/4}}{D_{-u}(-y_{esc} s) e^{y_{esc}^2/4}} = \frac{H_{-u}(-y_0 s/\sqrt{2})}{H_{-u}(-y_{esc} s/\sqrt{2})}, \quad (10)$$

where $D_\lambda(z)$ is the parabolic cylinder, or Weber function, $H_{-u}(z)$ is the generalization of Hermite polynomials used in MATHEMATICA, and $s = \text{sgn}(y_{esc} - y_0)$. The PDF $\phi(\tau)$ is normalized to 1. Using various formulas from [22] we can simplify Eq. (10) for large $u \gg \max\{y_{esc}^2, y_0^2\}$,

$$\hat{\phi}(u) \sim \exp\left[\frac{y_0^2 - y_{esc}^2}{4}\right] e^{-\sqrt{u}|y_{esc} - y_0|},$$

exhibiting a nonanalytical behavior of the $e^{-\sqrt{u}}$ type similar to the previous example. In order to have the $\phi(\tau) \propto \tau^{-3/2}$ scaling we thus have to demand the validity of this approximation for small $\sqrt{u}|y_{esc} - y_0| < 1$. Together with the condition $u \gg \max\{y_{esc}^2, y_0^2\}$ it leads to

$$(y_{esc} - y_0)^2 \ll \tau \ll \frac{1}{\max\{y_{esc}^2, y_0^2\}}. \quad (11)$$

As we are interested in the escape over the barrier, we have either $y_0 < y_{esc}$ if $y_{esc} > 0$, or $y_0 > y_{esc}$ if $y_{esc} < 0$. In a deep well (low T), if $|y_0| \ll |y_{esc}|$, then $\phi(\tau)$ will be nearly exponential, similar to Model 1. If the well is not deep, or y_0 and y_{esc} are close, Q shows a super-Poissonian behavior. Noticeably negative Q is only possible if the initial position of the particle is on the other side of the well from the escape point, and high above it in energy (when y_0/y_{esc} becomes very negative).

Inverted parabolic potential. The FPTD is now given by

$$\hat{\phi}(u) = \frac{D_{-1-u}(-y_0 s)}{D_{-1-u}(-y_{esc} s)} \exp\left[\frac{y_{esc}^2 - y_0^2}{4}\right]. \quad (12)$$

The normalization is

$$\hat{\phi}(0) = \frac{1 + \text{erf}(y_0 s/\sqrt{2})}{1 + \text{erf}(y_{esc} s/\sqrt{2})} < 1.$$

The normalization is less than 1 in this case because some particles will escape in the direction of $-\infty$, where the potential drops unbounded. Of course, if the particles are not allowed to escape to infinity, so that the only exit is through y_{esc} then the normalization should be 1. However, the above formulas serve as a good approximation for a deep well, if we consider the behavior around the parabolically shaped escape barrier at sufficiently short times. Similar to the previous section, for $u \gg \max\{1, y_{esc}^2, y_0^2\}$,

$$\hat{\phi}(u) \sim \exp\left[\frac{y_{esc}^2 - y_0^2}{4}\right] e^{-\sqrt{u}|y_{esc} - y_0|},$$

and the condition for observing $\tau^{-3/2}$ scaling is

$$(y_{esc} - y_0)^2 \ll \tau \ll \frac{1}{\max\{1, y_{esc}^2, y_0^2\}}.$$

In this paper, we demonstrated non-Poisson statistics of escape from a potential well, which contradicts reaction rate approach used for ensemble (bulk) dynamics. Both sub- and super-Poisson statistics were observed, indicated by the sign of the Q parameter. For small travel distances, and for a shallow well in the overdamped case, scaling $\phi \propto \tau^{-3/2}$ is dominant and gives rise to a strong super-Poissonian statistics. The $\tau^{-3/2}$ behavior is a result of diffusion processes [25]. The occurrence of such a behavior is easily understood if one realizes that in many cases a Fokker-Planck equation with variable coefficients [e.g., Eq. (1)] can locally be approximated by an equation with constant coefficients, i.e., by an advection-diffusion equation. As travel distance increases, characteristic time grows and drift term can compete with diffusion, allowing for Poissonian and sub-Poissonian behavior. In the underdamped case, sub-Poissonian behavior is found in many cases (see Fig. 2), in the overdamped case, we may observe sub-Poissonian behavior only under special conditions. As is well known, near-exponential $\phi(\tau)$ is obtained for a deep well if initial energy is sufficiently below the escape energy.

Finally let us compare our model results to experiments on single molecules and to other models. Blinking nanocrystals exhibit a behavior of occupation times of on and off

times close to $\tau^{-3/2}$ with cutoffs [26–28]. The blinking is believed to describe charging of a single nanocrystal (the charged nanocrystal can be off). Shimizu *et al.* [28] briefly suggested a diffusion in energy space to describe such behavior; however, they did not consider the effect of dissipation and temperature, which are always present in case of diffusion in energy space. Recent experiments on diffusing beads that come in and out of focus of a laser field also exhibit the $\tau^{-3/2}$ behavior [29]. Occupation times in single-molecule Raman experiments are described also by $\tau^{-3/2}$ behavior [30]. The dynamics of single ion channels sometimes exhibit the $\tau^{-3/2}$ [31,32]. Goychuk and Hänggi [32] suggested a model based on a reaction where space is divided into two: a zone with free diffusion (which yields the 3/2 law) and a zone where the reaction coordinate is climbing over a potential field. While all these systems and models are very different, they all exhibit a universal tendency for a $\tau^{-3/2}$ and in several cases an exponential cutoff is observed. Thus the turnover behavior we found, from a power-law behavior, to an exponential behavior, will be a useful concept for the single molecule domain. Further we do not expect this behavior to be limited to Kramers problem, since diffusion is expected to control short time dynamics of many reactions.

This work was supported by National Science Foundation Grant No. CHE-0344930. E.B. also thanks Center for Complexity Science, Israel.

-
- [1] X. S. Xie, *J. Chem. Phys.* **117**, 11024 (2002).
 [2] E. Barkai, Y. Jung, and R. Silbey, *Annu. Rev. Phys. Chem.* **55**, 457 (2004).
 [3] H. P. Lu, L. Xun, and X. S. Xie, *Science* **282**, 1877 (1998).
 [4] A. A. Deniz, T. A. Laurence, G. S. Beligere, M. Dahan, A. B. Martin, D. S. Chemla, P. E. Dawson, P. G. Schultz, and S. Weiss, *Proc. Natl. Acad. Sci. U.S.A.* **97**, 5179 (2000).
 [5] E. Rhoades, E. Gussakovskiy, and G. Haran, *Proc. Natl. Acad. Sci. U.S.A.* **100**, 3197 (2003).
 [6] E. Rhoades, M. Cohen, B. Schuler, and G. Haran, *J. Am. Chem. Soc.* **126**, 14686 (2004).
 [7] O. Flomenbom, K. Velonia, D. Loos, S. Masuo, M. Cotlet, Y. Engelborghs, J. Hofkens, A. E. Rowan, R. J. M. Nolte, M. Van der Auweraer, F. C. Schryver, and J. Klafter, *Proc. Natl. Acad. Sci. U.S.A.* **102**, 2368 (2005).
 [8] H. A. Kramers, *Physica (Amsterdam)* **7**, 284 (1940).
 [9] P. H. Hänggi, P. Talkner, and M. Borkovec, *Rev. Mod. Phys.* **62**, 251 (1990).
 [10] M. Büttiker, E. P. Harris, and R. Landauer, *Phys. Rev. B* **28**, 1268 (1983).
 [11] V. I. Mel'nikov and S. V. Meshkov, *J. Chem. Phys.* **85**, 1018 (1986).
 [12] A. N. Drozdov and J. J. Brey, *J. Chem. Phys.* **110**, 2159 (1999).
 [13] L. I. McCann, M. Dykman, and B. Golding, *Nature (London)* **402**, 785 (1999).
 [14] L. Y. Chen and P. L. Nash, *J. Chem. Phys.* **120**, 3348 (2004).
 [15] J.-D. Bao and Y. Jia, *Phys. Rev. C* **69**, 027602 (2004).
 [16] V. A. Shneidman, *Phys. Rev. E* **56**, 5257 (1997).
 [17] J. Wang and P. Wolynes, *Phys. Rev. Lett.* **74**, 4317 (1995).
 [18] V. Chernyak, M. Schulz, and S. Mukamel, *J. Chem. Phys.* **111**, 7416 (1999).
 [19] F. L. H. Brown, *Phys. Rev. Lett.* **90**, 028302 (2003).
 [20] S. Weiss, *Science* **283**, 1676 (1999).
 [21] P. R. Selvin, *Nat. Struct. Biol.* **7**, 730 (2000).
 [22] M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1972).
 [23] A. J. F. Siegert, *Phys. Rev.* **81**, 617 (1951).
 [24] W. Feller, *An Introduction to Probability Theory and its Applications* (Wiley, New York, 1966), Vol. 2.
 [25] S. Redner, *A Guide to First-Passage Processes* (Cambridge University Press, New York, 2001).
 [26] X. Brokmann, J. P. Hermier, G. Messin, P. Desbailles, J.-P. Bouchaud, and M. Dahan, *Phys. Rev. Lett.* **90**, 120601 (2003).
 [27] M. Kuno, D. P. Fromm, S. T. Johnson, A. Gallagher, and D. J. Nesbitt, *Phys. Rev. B* **67**, 125304 (2003).
 [28] K. T. Shimizu, R. G. Neuhauser, C. A. Leatherdale, S. A. Empedocles, W. K. Woo, and M. G. Bawendi, *Phys. Rev. B* **63**, 205316 (2001).
 [29] G. Zumofen, J. Hohlbein, and C. G. Hübner, *Phys. Rev. Lett.* **93**, 260601 (2004).
 [30] A. R. Bizzarri and S. Cannistraro, *Phys. Rev. Lett.* **94**, 068303 (2005).
 [31] W. Nadler and D. L. Stein, *Proc. Natl. Acad. Sci. U.S.A.* **88**, 6750 (1991).
 [32] I. Goychuk and P. Hänggi, *Proc. Natl. Acad. Sci. U.S.A.* **99**, 3552 (2002).