Propagators and related descriptors for non-Markovian asymmetric random walks with and without boundaries

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There are many current applications of the continuous-time random walk (CTRW), particularly in describing kinetic and transport processes in different chemical and biophysical phenomena. We derive exact solutions for the Laplace transforms of the propagators for non-Markovian asymmetric one-dimensional CTRW's in an infinite space and in the presence of an absorbing boundary. The former is used to produce exact results for the Laplace transforms of the first two moments of the displacement of the random walker, the asymptotic behavior of the moments as $t\to\infty$, and the effective diffusion constant. We show that in the infinite space, the propagator satisfies a relation that can be interpreted as a generalized fluctuation theorem since it reduces to the conventional fluctuation theorem at large times. Based on the Laplace transform of the propagator in the presence of an absorbing boundary, we derive the Laplace transform of the survival probability of the random walker, which is then used to find the mean lifetime for terminated trajectories of the random walk. [DOI: 10.1063/1.2830254]

I. INTRODUCTION

The continuous-time random walk[1,2] (CTRW) is frequently used as a model for kinetics and transport in chemical and biophysical processes. Several instances, in which its utility has been demonstrated, include (1) single-molecule enzyme kinetics, i.e., the rate of transformation of reactants into products by single enzyme molecules; (2) the transport of molecular motors in biological systems; (3) the transport of large solutes, exemplified by metabolites, different macromolecules, etc., through singly occupied channels in biological membranes. Further references are to be found in Refs. 3–10.

The most commonly met kinetic scheme of the one-dimensional nearest-neighbor CTRW has the generic form

$$\cdots \rightleftarrows -2 \rightleftarrows -1 \rightleftarrows 0 \rightleftarrows 1 \rightleftarrows 2 \rightleftarrows \cdots . \tag{1.1}$$

The state of the system at time t will be denoted by n and three independent quantities are needed to specify the subsequent kinetic development of the system. The first of these is W_+, the probability that the following step will be $n\to n+1$. Then, $W_-=1-W_+$ is the probability that the step will be $n\to n-1$. Since we are dealing with a CTRW, we define two pausing time densities $\varphi_\pm(t)$, normalized to unity, where, for example, $\varphi_+(t)$ is the probability density for the random time between a step taken between sites n and $n+1$. Further, we will assume that all the moments derived from $\varphi_\pm(t)$ are finite.

In the present paper, we derive an exact expression for the Laplace transform of the propagator $P_n(t)$, the probability that the difference in the number of steps in positive and negative directions in time t is equal to n, assuming that the system arrives at the initial site at $t=0$. Although there are many publications on random walks, to our knowledge, this result has not been published. The propagator will be used to derive the mean displacement of the random walker as a function of time as $t\to\infty$ and the effective diffusion constant. The transform will be denoted by $\hat{P}_n(s)=\int_0^\infty e^{-st}P_n(t)dt$, and because the system in Eq. (1.1) is non-Markovian, in general, it will only be possible to find general results in terms of Laplace transforms. We use the result for $\hat{P}_n(s)$ to show that the propagator obeys a generalized fluctuation theorem which reduces to the conventional one,[11–25] when $\varphi_+(t)=\varphi_-(t)$. In our case, the latter establishes a relation between $P_n(t)$ and $P_{-n}(t)$ of the form

$$\frac{P_n(t)}{P_{-n}(t)}=\left(\frac{W_+}{W_-}\right)^n. \tag{1.2}$$

The CTRW in Eq. (1.1) has been defined without boundaries. Later, we generalize the solution for the Laplace transform of the propagator still further to allow for the presence of a single absorbing boundary, say at $n=0$. That is to say, the random walk terminates when site 0 is reached. This possibility suggests further parameters of interest to be discussed in the course of the paper. Specifically, we find an exact solution for the Laplace transform of the survival probability. This can either be finite or zero as $t\to\infty$, depending on the relation between W_+ and W_-.[1,2] We find the mean lifetime for trapped realizations of the random walk, which is a conditional lifetime when the system survives as $t\to\infty$.

The main results of our analysis are summarized in the next section and derived in the remainder of the paper.

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II. FORMULATION OF RESULTS

A. The propagator and generalized fluctuation theorem

Having defined the pausing-time densities $\varphi_+(t)$ and $\varphi_-(t)$, it is convenient to also define $w_+(t)=W_+\varphi_+(t)$ and $w_-(t)=W_-\varphi_-(t)$ so that, for example, $w_+(t)$ is the probability density for a transition $n\to n+1$ to follow a sojourn of time t at site n, which is normalized to W_+. As before, $\hat{w}_\pm(s)$ will denote the Laplace transform of $w_\pm(t)$. A second useful function is

$$\hat{K}(s) = 1 + \sqrt{1-4\hat{w}_+(s)\hat{w}_-(s)}. \tag{2.1}$$

We will show that the Laplace transform of the propagator is

$$\hat{P}_n(s) = \left[\frac{\hat{w}_+(s)}{\hat{w}_-(s)}\right]^{n/2}\left[\frac{2\sqrt{\hat{w}_+(s)\hat{w}_-(s)}}{\hat{K}(s)}\right]^{|n|}\hat{P}_0(s), \tag{2.2}$$

in which

$$\hat{P}_0(s) = \frac{1-\hat{w}_+(s)-\hat{w}_-(s)}{s\sqrt{1-4\hat{w}_+(s)\hat{w}_-(s)}}. \tag{2.3}$$

The transform of the propagator in Eq. (2.2) satisfies the normalization condition $\Sigma_{n=-\infty}^{\infty}\hat{P}_n(s)=1/s$.

An explicit expression for $P_n(t)$ can be found only for the case of the Markovian system in which $w_\pm(t)=k_\pm\exp(-kt)$, where $k=k_++k_-$, so that the transforms can be inverted explicitly. The results are found to be

$$P_n(t) = \left(\frac{k_+}{k_-}\right)^{n/2} e^{-kt} I_n(2t\sqrt{k_+k_-}), \tag{2.4}$$

where $I_n(z)$ is a modified Bessel function of the first kind, which is a symmetric function of n, $I_n(z)=I_{-n}(z)$.[25]

The transform in Eq. (2.2) satisfies the relation

$$\frac{\hat{P}_n(s)}{\hat{P}_{-n}(s)} = \left[\frac{\hat{w}_+(s)}{\hat{w}_-(s)}\right]^n = \left[\frac{W_+\hat{\varphi}_+(s)}{W_-\hat{\varphi}_-(s)}\right]^n. \tag{2.5}$$

This leads us to the fluctuation theorem in Eq. (1.2) when $\varphi_+(t)=\varphi_-(t)$. Therefore, we will call the relation in Eq. (2.5) a generalized fluctuation theorem.

B. Moments of displacement and the diffusion constant

When the pausing-time densities have at least two finite moments, the moments of displacement $n(t)$ will likewise also have two finite moments. We will see that at long times, the first moment is asymptotically proportional to t and that it is possible to define an effective diffusion constant in terms of the large-t behavior of the first two moments of the displacement. The Laplace transforms of the moments can be generated from the transforms of the propagators. Let $w(t)=w_+(t)+w_-(t)$. This is the probability density for a single sojourn time spent by the random walk on a site. The transforms of the first two moments can be written in terms of the transforms of $w(t)$ and $w_\pm(t)$ as

$$\langle\hat{n}(s)\rangle = \sum_{n=-\infty}^{\infty} n\hat{P}_n(s) = \frac{\hat{w}_+(s)-\hat{w}_-(s)}{s[1-\hat{w}(s)]} \tag{2.6}$$

and

$$\langle\hat{n}^2(s)\rangle = \sum_{n=-\infty}^{\infty} n^2\hat{P}_n(s) = \frac{\hat{w}(s)[1+\hat{w}(s)]-8\hat{w}_+(s)\hat{w}_-(s)}{s[1-w(s)]^2}. \tag{2.7}$$

The long-time behavior of these moments can be found using small-s expansions of their Laplace transforms in Eqs. (2.6) and (2.7).[26] The results can be expressed in terms of the first two moments of the sojourn times on a site, $\langle\tau_\pm^m\rangle$ and $\langle\tau^m\rangle$, where

$$\langle\tau_\pm^m\rangle = \int_0^\infty t^m\varphi_\pm(t)dt \tag{2.8}$$

and

$$\langle\tau^m\rangle = \int_0^\infty t^m w(t)dt = W_+\langle\tau_+^m\rangle + W_-\langle\tau_-^m\rangle. \tag{2.9}$$

The long-time limit of the average displacement is up to the constant term,

$$\langle n(t)\rangle \approx \frac{W_+-W_-}{\langle\tau\rangle}t - \frac{W_+\langle\tau_+\rangle - W_-\langle\tau_-\rangle}{\langle\tau\rangle} + (W_+-W_-)\frac{\langle\tau^2\rangle}{2\langle\tau\rangle^2}, \tag{2.10}$$

so that $(W_+-W_-)/\langle\tau\rangle$ is a measure of bias induced by the asymmetry of the transition probabilities. When $\varphi_+(t)=\varphi_-(t)=w(t)$ so that $\langle\tau_+\rangle=\langle\tau_-\rangle=\langle\tau\rangle$, Eq. (2.10) takes the form

$$\langle n(t)\rangle \approx \frac{W_+-W_-}{\langle\tau\rangle}t + (W_+-W_-)\left(\frac{\langle\tau^2\rangle}{2\langle\tau\rangle^2}-1\right). \tag{2.11}$$

When the random walk is Markovian, the second term vanishes since $\langle\tau^2\rangle=2\langle\tau\rangle^2$.

A second parameter of physical interest is the effective diffusion constant D_{eff}, which is defined in terms of the moments of displacement as

$$D_{\text{eff}} = \frac{1}{2}\lim_{t\to\infty}\frac{1}{t}[\langle n^2(t)\rangle - \langle n(t)^2\rangle]. \tag{2.12}$$

A straightforward calculation based on the transforms leads to the expression

$$D_{\text{eff}} = \frac{1}{2\langle\tau\rangle^2}\left[4W_+W_-(\langle\tau_-\rangle+\langle\tau_-\rangle) + (W_+-W_-)^2\frac{\langle\tau^2\rangle}{\langle\tau\rangle} - \langle\tau\rangle\right]. \tag{2.13}$$

When $\varphi_+(t)=\varphi_-(t)=\varphi(t)$ so that $\langle\tau_+\rangle=\langle\tau_-\rangle=\langle\tau\rangle$, the expression for D_{eff} reduces to

$$D_{\text{eff}} = \frac{1}{2\langle\tau\rangle}\left[1 + (W_+ - W_-)^2\left(\frac{\langle\tau\rangle^2}{\langle\tau\rangle^2} - 2\right)\right]. \tag{2.14}$$

In the special case of the Markovian random walk $\langle\tau^2\rangle = 2\langle\tau\rangle^2$, from which it follows that $D_{\text{eff}} = 1/(2\langle\tau\rangle)$ is independent of the asymmetry of the transition probabilities.

It can be shown in a number of different ways that at sufficiently long times the propagator approaches a Gaussian form

$$P_n(t) \approx \frac{1}{\sqrt{4\pi D_{\text{eff}} t}} \exp\left[-\frac{(n - \langle n(t)\rangle)^2}{4D_{\text{eff}} t}\right]. \tag{2.15}$$

This is known in the mathematical literature as the central limit theorem.[1,2]

C. Effect of the absorbing boundary

A different set of questions arises when a random walker moves in the presence of a perfectly absorbing site. Suppose that the absorbing site is located at $n=0$ and the random walk begins its sojourn at site $n_0 > 0$ at $t=0$. The propagator for this walk will be denoted by $P_{\text{abs}}(n,t|n_0)$, which must satisfy the absorbing boundary condition, $P_{\text{abs}}(0,t|n_0)=0$. The solution for the Laplace transform of the propagator can be found in terms of the transforms of the propagators in the infinite space

$$\hat{P}_{\text{abs}}(n,s|n_0) = P_{n-n_0}(s) - \left[\frac{\hat{w}_-(s)}{w_+(s)}\right]^{n_0} \hat{P}_{n+n_0}(s). \tag{2.16}$$

Setting $n=0$ in $\hat{P}_{\text{abs}}(n,s|n_0)$ and using the generalized fluctuation theorem in Eq. (2.5), one can see that $\hat{P}_{\text{abs}}(n,s|n_0)$ satisfies the absorbing boundary condition. A further generalization can be made to the case in which the system consists of a finite number of states terminated by two absorbing/reflecting ones, in which case the method of images produces a solution in terms of an infinite series of terms in place of the two-term expression in Eq. (2.16).

Having an expression for $\hat{P}_{\text{abs}}(n,s|n_0)$ in hand we can calculate the transform of the probability that the random walk has not been absorbed by time t, $S(t|n_0)$. It will be shown that its Laplace transform has the form

$$\hat{S}(s|n_0) = \sum_{n=1}^{\infty} \hat{P}_{\text{abs}}(n,s|n_0) = \frac{1}{s}\left\{1 - \left[\frac{2\hat{w}_-(s)}{\hat{K}(s)}\right]^{n_0}\right\}, \tag{2.17}$$

where $\hat{K}(s)$ is defined in Eq. (2.1).

More specific information is available in terms of $\hat{S}(s|n_0)$ related to the moment at which a random walk is absorbed. First, we observe that not all of the random walks will be eventually absorbed. A well-known result in probability theory is that the probability that the random walk will survive indefinitely is equal to $1-(W_-/W_+)^{n_0}$ when $W_+ > W_-$ and 0 otherwise.[1,2] If $f(t|n_0)dt$ is the probability that the random walk is absorbed at the origin at a time between t and $t+dt$, then it is related to $S(t|n_0)$ by $-dS(t|n_0) = f(t|n_0)dt$. It then follows that the conditional probability density for the absorption time is

$$\chi(t|n_0) = \frac{f(t|n_0)}{1 - S(\infty|n_0)}. \tag{2.18}$$

The transform of this relation can be used to generate expressions for the moments, i.e., the conditional first moment of the time to absorption is

$$\langle\tau_{\text{abs}}(n_0)\rangle = -\left.\frac{d\hat{\chi}(s|n_0)}{ds}\right|_{s=0} = n_0\begin{cases}\dfrac{W_-\langle\tau_+\rangle + W_+\langle\tau_-\rangle}{W_+ - W_-}, & W_+ > W_- \\[2ex] \dfrac{\langle\tau\rangle}{W_+ - W_-}, & W_- > W_+.\end{cases} \tag{2.19}$$

Both the probability density in Eq. (2.18) and $\langle\tau_{\text{abs}}(n_0)\rangle$ are unconditional when $S(\infty|n_0)=0$. When $W_+=W_-$, this result indicates that the mean time to absorption is infinite while $S(\infty|n_0)=0$, a result first derived by Polya in 1924.[1,2]

III. DERIVATIONS

A. The propagator and the generalized fluctuation theorem

Since all sites are identical, the initial state will be taken to be $n_0=0$ without loss of generality. Let $\Psi(t)$ be the survival probability on a site for time t, i.e., the probability that a random walk remains at any site for a time greater than t,

$$\Psi(t) = 1 - \int_0^t w(t')dt' = 1 - \int_0^t [w_+(t') + w_-(t')]dt' \tag{3.1}$$

and let $\omega_n(t)$ be the probability flux entering site n at time t. The propagator $P_n(t) = P(n,t|0,0)$ can be expressed in terms of $\omega_n(t)$ and $\Psi(t)$ as

$$P_n(t) = \int_0^t \omega_n(t')\Psi(t-t')dt', \tag{3.2}$$

since the random walker enters site n at time t' and remains there for the time $t-t'$. Transforming Eqs. (3.1) and (3.2), we obtain the relation

$$\hat{P}_n(s) = \frac{1}{s}[1 - \hat{w}_+(s) - \hat{w}_-(s)]\hat{\omega}_n(s). \tag{3.3}$$

A final step in the derivation of $\hat{P}_n(s)$ is that of finding $\hat{\omega}_n(s)$, which will be done by formulating and solving a recursion relationship for it. The function $\omega_n(t)$ satisfies

$$\omega_n(t) = \delta(t)\delta_{n,0} + \int_0^t [w_+(t-t')\omega_{n-1}(t') + w_-(t-t')\omega_{n+1}(t')]dt', \tag{3.4}$$

where the first term on the right-hand side accounts for the initial condition, and the remaining terms account for all remaining interchanges in the random walk. Since Eq. (3.4) has the form of a convolution, it can be simplified through the application of a Laplace transform, becoming

$$\hat{\omega}_n(s) = \delta_{n,0} + \hat{w}_+(s)\hat{\omega}_{n-1}(s) + \hat{w}_-(s)\hat{\omega}_{n+1}(s). \tag{3.5}$$

This can be simplified still further by defining a new function which has the effect of setting the coefficients of the unknowns equal on the right-hand side of the transformed equation. The required transformation is

$$\hat{\omega}_n(s) = \left[\frac{\hat{w}_+(s)}{\hat{w}_-(s)}\right]^{n/2} \hat{v}_n(s), \tag{3.6}$$

so that the $\hat{v}_n(s)$ now satisfy

$$\hat{v}_n(s) = \delta_{n,0} + \sqrt{\hat{w}_+(s)\hat{w}_-(s)}[\hat{v}_{n-1}(s) + \hat{v}_{n+1}(s)]. \tag{3.7}$$

This can be solved by introducing the generating function

$$\hat{V}(\theta,s) = \sum_{n=-\infty}^{\infty} \hat{v}_n(s)e^{in\theta}. \tag{3.8}$$

By multiplying both sides of Eq. (3.7) by $\exp(in\theta)$ and summing we see that $\hat{V}(\theta,s)$ satisfies

$$\hat{V}(\theta,s) = 1 + 2\sqrt{\hat{w}_+(s)\hat{w}_-(s)} \cos\theta\hat{V}(\theta,s), \tag{3.9}$$

whose solution is

$$\hat{V}(\theta,s) = \frac{1}{1 - 2\sqrt{\hat{w}_+(s)\hat{w}_-(s)}\cos\theta}. \tag{3.10}$$

We use this solution to find $\hat{v}_n(s)$

$$\hat{v}_n(s) = \frac{1}{2\pi}\int_{-\pi}^{\pi} \hat{V}(\theta,s)e^{-in\theta}d\theta = \frac{1}{\sqrt{1-4\hat{w}_+(s)\hat{w}_-(s)}}\left[\frac{2\sqrt{\hat{w}_+(s)\hat{w}_-(s)}}{\hat{K}(s)}\right]^{|n|}. \tag{3.11}$$

The combination of Eqs. (3.3) and (3.6), and this last equation leads to the final result for $\hat{P}_n(s)$ cited in Eq. (2.2).

Note that the generalized fluctuation theorem in Eq. (2.5) is an immediate consequence of the transformation in Eq. (3.6). By substituting $\hat{\omega}_n(s)$ in this equation into Eq. (3.3), we obtain

$$\hat{P}_n(s) = \frac{1}{s}\left[\frac{\hat{w}_+(s)}{\hat{w}_-(s)}\right]^{n/2}[1 - \hat{w}_+(s) - \hat{w}_-(s)]\hat{v}_n(s). \tag{3.12}$$

The generalized fluctuation theorem is a consequence of this expression and the fact that $\hat{v}_n(s)=\hat{v}_{-n}(s)$.

B. Laplace transform of the first two moments of displacement

The definitions of Laplace transforms of the moments of displacements are given in Eqs. (2.6) and (2.7). Performance of the necessary calculations is straightforward since the n-dependence of $\hat{P}_n(s)$ in Eq. (2.2) is relatively simple. To evaluate the sums, we define the two functions

$$\hat{C}_\pm(s) = 2\hat{w}_\pm(s)/\hat{K}(s). \tag{3.13}$$

In terms of these, we find

$$\langle\hat{n}(s)\rangle = \left\{\sum_{n=1}^{\infty} n[\hat{C}_+^n(s) - \hat{C}_-^n(s)]\right\}\hat{P}_0(s). \tag{3.14}$$

The sums are elementary and lead to the intermediate result

$$\langle\hat{n}(s)\rangle = \frac{[\hat{C}_+(s) - \hat{C}_-(s)][1 - \hat{C}_+(s)\hat{C}_-(s)]}{\{[1-\hat{C}_+(s)][1-\hat{C}_-(s)]\}^2}\hat{P}_0(s). \tag{3.15}$$

The final result given in Eq. (2.6) is obtained by substituting the detailed expressions for the functions appearing on the right-hand side of this equation.

The long-time behavior of $\langle n(t)\rangle$ is found by expanding $\langle\hat{n}(s)\rangle$ in Eq. (2.6) in a power series in s assuming that $s \to 0$. This can be done using the expansion of $\hat{w}_\pm(s)$ to the second order in s

$$\hat{w}_\pm(s) = W_\pm\hat{\varphi}_\pm(s) \approx W_\pm\left(1 - \langle\tau_\perp\rangle s + \langle\tau_\pm^2\rangle\frac{s^2}{2}\right). \tag{3.16}$$

The singular behavior of $\langle\hat{n}(s)\rangle$ at $s=0$ can be used to determine the long-time behavior of $\langle n(t)\rangle$.[26] Eventually, we arrive at the expansion

$$\langle\hat{n}(s)\rangle \approx \frac{W_+ - W_-}{s^2\langle\tau\rangle} - \frac{1}{s\langle\tau\rangle}\left[W_+\langle\tau_+\rangle - W_-\langle\tau_-\rangle + (W_+ - W_-)\frac{\langle\tau^2\rangle}{2\langle\tau\rangle}\right]. \tag{3.17}$$

An inversion of this leads us to $\langle n(t)\rangle$ in Eq. (2.10).

The Laplace transform of $\langle n^2(t)\rangle$ given in Eq. (2.7) can be obtained by a technique similar to that used to derive $\langle\hat{n}(s)\rangle$. After expanding $\langle\hat{n}^2(s)\rangle$ in a power series in s and inverting the result one can derive the large-t behavior of $\langle n^2(t)\rangle$, from which the expression for D_{eff} given in Eq. (2.13) is a consequence.

C. Effects of an absorbing site: Survival probability and mean lifetime

The result for $\hat{S}(s|n_0)$ in Eq. (2.17) is based on the expression in Eq. (2.16), which gives $\hat{P}_{\text{abs}}(n,s|n_0)$ in terms of the transform of the propagator for an infinite space in Eq. (2.2),

$$\hat{S}(s|n_0) = \sum_{n=1}^{\infty}\hat{P}_{n-n_0}(s) - \left[\frac{\hat{w}_-(s)}{\hat{w}_+(s)}\right]^{n_0}\sum_{n=1}^{\infty}\hat{P}_{n+n_0}(s). \tag{3.18}$$

By making use of the Laplace transform of the normalization condition for $P_n(t)$ in this expression, we obtain

$$\hat{S}(s|n_0) = \frac{1}{s} - \sum_{n=n_0}^{\infty}\hat{P}_{-n}(s) - \left[\frac{\hat{w}_-(s)}{\hat{w}_+(s)}\right]^{n_0}\sum_{n=n_0+1}^{\infty}\hat{P}_n(s). \tag{3.19}$$

The sums in this equation have an easily summable form as seen from Eq. (2.2) and lead to the result in Eq. (2.17).

Our final results are those given in Eq. (2.19). We use the fact that $f(t|n_0)=-dS(t|n_0)/dt$ so that the Laplace transform of $f(t|n_0)$ is

$$\hat{f}(s|n_0) = 1 - s\hat{S}(s|n_0) = \left[\frac{2\hat{w}_-(s)}{\hat{K}(s)}\right]^{n_0}, \tag{3.20}$$

which may be substituted into the Laplace transform of Eq. (2.18) to find the result in Eq. (2.19).

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[1] G. H. Weiss, *Aspects and Applications of the Random Walk* (North-Holland, Amsterdam, 1994).
[2] B. D. Hughes, *Random Walks and Random Environments*, Random Walks, Vol. 1 (Clarendon Press, Oxford, 1995).
[3] W. Min, L. Jiang, J. Yu, S. C. Kou, H. Qian, and X. S. Xie, Nano Lett. **5**, 2573 (2005).
[4] H. Qian and X. S. Xie, Phys. Rev. E **74**, 010902(R) (2006).
[5] A. Yu. Morozov, E. Pronina, A. B. Kolomeisky, and M. N. Artyomov, Phys. Rev. E **75**, 031910 (2007).
[6] D. Tsygankov, M. Lindén, M. E. Fisher, Phys. Rev. E **75**, 021909 (2007).
[7] A. B. Kolomeisky and M. E. Fisher, Annu. Rev. Phys. Chem. **58**, 675 (2007).
[8] M. Linden and M. Wallin, Biophys. J. **92**, 3804 (2007).
[9] O. Flomenbom and J. Klafter, Phys. Rev. E **68**, 041910 (2003).
[10] A. M. Berezhkovskii and S. M. Bezrukov, Phys. Rev. Lett. **100**, 038104 (2008); J. Phys. Chem. B (in press).
[11] D. J. Evans, E. G. D. Cohen, and G. Morriss, Phys. Rev. Lett. **71**, 2401 (1993).
[12] D. J. Evans and D. J. Searles, Phys. Rev. E **50**, 1645 (1994).
[13] D. J. Evans and D. J. Searles, Adv. Phys. **51**, 1529 (2002).
[14] G. Gallavotti and E. G. D. Cohen, Phys. Rev. Lett. **74**, 2694 (1995).
[15] G. Gallavotti and E. G. D. Cohen, J. Stat. Phys. **80**, 931 (1995).
[16] J. J. Kurchan, J. Phys. A **31**, 3719 (1999).
[17] J. L. Lebowitz and H. Spohn, J. Stat. Phys. **95**, 333 (1999).
[18] C. Maes, J. Stat. Phys. **95**, 367 (1999).
[19] P. Gaspard, J. Chem. Phys. **120**, 8898 (2004).
[20] D. Andrieux and D. P. Gaspard, J. Chem. Phys. **121**, 6167 (2004).
[21] D. Andrieux and D. P. Gaspard, J. Stat. Mech.: Theory Exp. **2006**, P01011.
[22] C. Jarzynski and D. K. Wojcik, Phys. Rev. Lett. **92**, 230602 (2004).
[23] U. Seifert, J. Phys. A **37**, L517 (2004).
[24] U. Seifert, Europhys. Lett. **70**, 36 (2005).
[25] M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1972).
[26] H. G. ter Morsche, J. C. van den Berg, E. M. van de Vrie, and R. J. Beerends, *Fourier and Laplace Transforms* (Cambridge University Press, Cambridge, 2003).