Exact Dynamics of a Continuous Time Random Walker in the Presence of a Boundary: Beyond the Intuitive Boundary Condition Approach

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We derive the exact dynamics of a random walker with arbitrary non-Markovian transport and reaction rate distribution at a boundary, and present exact solutions in the continuum limit. We find that the ultimate escape probability of the particle is independent of the transport mechanism in contradiction to the long-standing belief based on the conventional approach. We also find a phase transition in the relaxation kinetics associated with the heterogeneity of the transport media.

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Brownian motion is one of the most mature subjects in nonequilibrium statistical mechanics, for which we now have a rigorous description [1]. Examples include the Fokker-Planck equation and diffusion equation [2], generalizations of which have also been made to describe anomalous transport phenomena [3,4]. However, the derivations of these equations have been carried out for a system in the absence of boundaries, while many interesting systems in nature involve a reaction at a boundary of the system. In the conventional approach, the effects of the reaction at the boundary are taken into account merely by imposing either the absorbing boundary condition (ABC) [5,6] or the radiation boundary condition (RBC) on the diffusion equation. Recently, the conventional approach has been further generalized [7–10].

In contrast to the conventional assumptions, transport in the vicinity of the boundary may not be described by the simple diffusion equation because of its coupling to the reaction and a possibly different physical environment at the boundary. In addition, in heterogeneous environments, the transport in bulk can also deviate from diffusion. Furthermore, the validity of the ABC and RBC is a controversial issue. The result of the conventional approach with the ABC has an unphysical singularity at time 0 [11], and Naqvi *et al.* showed that, in the hydrodynamic limit, Brownian motion in the presence of an absorbing sphere reduces to the conventional approach with the RBC instead of the ABC [12]. On the other hand, ABC rather than the RBC gives the correct hydrodynamic description of random walk in the presence of a reaction at a boundary [13]. Little progress has been made beyond the phenomenological boundary condition approaches for lack of the relationship of the microscopic dynamics of the reaction at a boundary to that of the transport in the vicinity of a boundary [14,15].

In this Letter, we first present the exact stochastic dynamics of a particle in the presence of a boundary allowing for arbitrary stochastic transport and reaction properties. We choose the continuous time random walk (CTRW) model [16,17] as the starting point, because it can describe a wide range of transport phenomena [18–22]. We generalize the CTRW to consider a boundary at which a reaction can take place with an arbitrary waiting time distribution, taking into account the effects of an external field. For this model the generalized master equation (GME) is derived [23], and the solution of the GME is obtained that becomes exact in the small lattice constant, ϵ, limit. The exact solution reduces to that of the conventional approach for a model in which the reaction and transport are independent Poisson processes, and the transport at the boundary is the same as that in bulk. For this model, it turns out the correct condition is the RBC if the reaction probability at the boundary is proportional to the size of reaction zone, ϵ, in the small ϵ limit, but it is the ABC when the reaction probability is constant in ϵ [13]. Nevertheless, the result for the general case shows that the ultimate escape probability is independent of the bulk transport property, such as the diffusion constant, in contradiction to the long-standing belief based on the conventional approach.

This approach can deal with the system in which the reaction and the transport are arbitrary non-Poisson processes as well. When the observation time scale is much longer than the average sojourn time at identical hydrodynamic volume elements, the dynamics of any non-Poisson transport model is in qualitative agreement with that of a Poisson transport model, irrespective of the details of the non-Markovian transport model, because the correlation between jump events becomes negligible in a time much longer than the average sojourn time. The average sojourn time increases with environmental heterogeneity and can be comparable to or even longer than the observation time scale in strongly disordered media. In this case, the relaxation dynamics loses its universal character, and is dependent on the details of the correlation between jumps as described by the sojourn time distribution. Especially when the reactant transport is subdiffusive [3,18], or when the average sojourn time is infinite, the exact result never reduces to the conventional Smoluchowski based on the Poisson transport model or its generalizations, even at asymptotically long times.

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We consider a random walk on a one-dimensional lattice with a lattice constant ϵ in the presence of a boundary at the leftmost site labeled 0. The other lattice sites are labeled by $n = 1, 2, \ldots$ from left to right. A random walker located at n initially can move to either left or right nearest neighbor site with a probability L_n or R_n, related by the detailed balance condition: $L_{n+1} p_{n+1}^{\rm eq} = R_n p_n^{\rm eq}$ $(n \geq 0)$, where $p_n^{\rm eq}$ is the equilibrium probability in the absence of reaction. $\psi_n(\tau) d\tau$ denotes the probability that the jump from site n occurs between $\tau \sim \tau + d\tau$, where τ is the time elapsed after the random walker's arrival at the site. The sojourn time distribution ψ_n is assumed to be the same for all sites except for site 0; i.e., $\psi_n = \psi$ $(n \geq 1)$, $\psi_0 \neq \psi$. If ψ_0^0 denotes the transition time distribution at site 0 in the absence of reaction, and $\phi^0(\tau) d\tau$ denotes the probability that the reaction event at the boundary takes place between time $\tau \sim \tau + d\tau$ after the random walker's arrival at site 0, in the absence of the jump process back to site 1, ψ_0 is given by $\psi_0(t) = \phi(t) + \psi_0^{nr}(t)$ with $\phi(t) = \phi^0(t) \int_t^\infty d\tau\, \psi_0^0(\tau)$ and $\psi_0^{nr}(t) = \psi_0^0(t) \int_t^\infty d\tau\, \phi^0(\tau)$, when the microscopic reaction process is independent of the transport process at the boundary. ψ_0 as given here is normalized, once ϕ^0 and ψ_0^0 are normalized. Note, however, if there is a coupling between microscopic reaction and transport processes at the boundary, the relation of $\phi(t)$ and $\psi_0^{nr}(t)$ to ϕ^0 and ψ_0^0 may not hold. In general, $\phi(t)$ and $\psi_0^{nr}(t)$ can be any positive functions satisfying the normalization of ψ_0. For the present model, $f_n(t)dt$, the probability that the random walker arrives at a site n between time $t \sim t + dt$ satisfies (in Laplace domain)

$$\hat{f}_n(u) = \hat{\psi}_{n+1}^L(u) \hat{f}_{n+1}(u) + \hat{\psi}_{n-1}^R(u) \hat{f}_{n-1}(u) + \delta_{nm} \quad (n \geq 0), \tag{1}$$

where $\psi_{-1}^R = 0$, $\psi_0^R = \psi_0^{nr}$, and $\hat{\psi}_n^{L(R)}(u) = L_n(R_n) \hat{\psi}(u)$. Hereafter, $\hat{y}(u)$ denotes the Laplace transform of $y(t)$, with u being the Laplace variable. $f_n(t)$ is related to the probability $p_n(t)$ that the random walker is found at site n at time t by $\hat{p}_n(u) = [1 - \hat{\psi}_n(u)] \hat{f}_n(u)/u$ [24]. From this relation and Eq. (1), we can obtain the generalized master equation (GME) for $\hat{p}_n(u)$:

$$\begin{aligned} \hat{\dot{p}}_n(u) &= \mathrm{D}(u)[L_{n+1} \hat{p}_{n+1}(u) + R_{n-1} \hat{p}_{n-1}(u) + \hat{p}_n(u)] \qquad (n \geq 2), \\ \hat{\dot{p}}_1(u) &= \mathrm{D}(u)[L_2 \hat{p}_2(u) + \mathsf{R}_0(u) \hat{p}_0(u) - p_1(u)], \\ \hat{\dot{p}}_0(u) &= \mathrm{D}(u)[L_1 \hat{p}_1(u) - \mathsf{R}_0(u) \hat{p}_0(u)] - \mathrm{k}(u) \hat{p}_0(u), \end{aligned} \tag{2}$$

with $\hat{\dot{p}}_j(u) = u \hat{p}_j(u) - \delta_{jm}$, $\mathrm{D}(u) = u \hat{\psi}(u)/[1 - \hat{\psi}(u)]$, $\mathrm{k}(u) = u \hat{\phi}(u)/[1 - \hat{\psi}_0(u)]$, and $\mathsf{R}_0(u) = [1 - \hat{\psi}(u)] \hat{\psi}_0^{nr}(u)/[1 - \hat{\psi}_0(u)] \hat{\psi}(u)$. We can see from Eq. (2) that the dynamics at sites 0 and 1 is different from those at the other sites due to the reaction at the impenetrable boundary at site 0. In contrast to R_i, $\mathsf{R}_0(u)$ (appearing in the GME for sites 0 and 1) is not a probability, since the value of $\mathsf{R}_0(u)$ can be much greater than 1 in the small u limit, if the first moment $\lim_{u \to 0} [1 - \hat{\psi}_0(u)]/u$ of ψ_0 is much smaller than that of ψ. By adding up all equations in Eq. (2), one can show that the survival probability $\hat{\dot{S}}(u) [\equiv \sum_{j=0}^\infty \hat{\dot{p}}_j(u)]$ is related to $\hat{p}_0(u)$ and $\hat{f}_0(u)$ as $\hat{\dot{S}}(u) = -u \hat{\phi}(u) \hat{p}_0(u)/[1 - \hat{\psi}_0(u)] = -\hat{\phi}(u) \hat{f}_0(u)$.

At first we will relate the quantities p_n and S of interest to the probability $h_0(t|m)dt$ that a random walker initially located at site m arrives at site 0 for the first time between time t and $t + dt$, and later we will obtain the expression for h_0. Noting $\hat{f}_0(u|m) = \hat{h}_0(u|m) \sum_{k=1}^\infty [\hat{\psi}_0^{nr}(u) \hat{h}_0(u|1)]^{k-1}$, we get the expression for the survival probability $\hat{\dot{S}}(u|m)$ of the random walker in terms of h_0 from the relation between $\hat{\dot{S}}$ and $\hat{f}_0$:

$$\hat{\dot{S}}(u|m) = \frac{-\hat{\phi}(u) \hat{h}_0(u|m)}{1 - \hat{\psi}_0^{nr}(u) \hat{h}_0(u|1)}, \tag{3}$$

where $\hat{\dot{S}}(u) = u \hat{S}(u) - 1$. Now let us turn our focus into the probability density distribution, $\{p_n\}$. Noting the GME for site 1 can be rewritten as $\hat{\dot{p}}_1(u) = \mathrm{D}(u)[L_2 \hat{p}_2(u) - R_1 \hat{p}_1(u)] + \hat{\dot{S}}'(u)$ with $S'(t) = S(t) - p_0(t)$, we can transform Eq. (2) in a simpler form:

$$\hat{\dot{p}}_n(u) = \mathrm{D}(u)[L_{n+1} \hat{p}_{n+1}(u) + R_{n-1} \hat{p}_{n-1}(u) - \hat{p}_n(u)] + \delta_{n1} \hat{\dot{S}}'(u) \qquad (n \geq 1), \tag{4}$$

in which p_0 is defined by $p_0(t) = L_1 p_1(t)/R_0$. Note that p_0 in Eq. (4) (that will not be referred to any further) is a different quantity from p_0 in Eq. (2). However, given that $\hat{\dot{S}}'(u)$ in Eq. (4) is exact, the solution $\{p_j\}$ for $j \geq 1$ of Eq. (4) is the same as that of Eq. (2), which is given by

$$\hat{p}_n(u|m) = \hat{G}_n^1(u|m) - \hat{G}_n^1(u|1) \hat{\dot{S}}'(u) \qquad (n, m \geq 1). \tag{5}$$

Here, $\hat{G}_n^1(u|m)$ is defined by $u \hat{G}_n^1(u) - \delta_{nm} = \mathrm{D}(u)[L_{n+1} \hat{G}_{n+1}^1(u) + R_{n-1} \hat{G}_{n-1}^1(u) - \hat{G}_n^1(u)]$ and $R_0 G_0^1 = L_1 G_1^1$. The exact expression for $\hat{\dot{S}}'(u)$ can be found in terms of $h_0(t|m)$. From Eq. (3) and the relation between $\hat{p}_0(u)$ and $\hat{\dot{S}}(u)$ given below Eq. (2), we have

$$\hat{p}_0(u|m) = \frac{[1 - \hat{\psi}_0(u)] \hat{h}_0(u|m)}{u[1 - \hat{\psi}_0^{nr}(u) \hat{h}_0(u|1)]}. \tag{6}$$

Subtracting Eq. (6) from (3), we get

$$\hat{\dot{S}}'(u) = -\frac{[1 - \hat{\psi}_0^{nr}(u)] \hat{h}_0(u|m)}{1 - \hat{\psi}_0^{nr}(u) \hat{h}_0(u|1)}. \tag{7}$$

We have obtained the expressions for the quantities of interest in terms of $\hat{h}_0(u|m)$. To obtain the expressions for $\hat{h}_0(u|m)$, we consider the survival probability for a special case where $\mathsf{R}_0(u) = R_0$ or $\hat{\psi}_0^{nr}/[1 - \hat{\psi}_0] = R_0 \hat{\psi}/(1 - \hat{\psi})$. From now on, ψ_0, ψ_0^{nr}, and ϕ that satisfy the latter condition will be designated by ψ_0^*, ψ_0^{nr*}, and ϕ^*, respectively. Under this condition, the GME in Eq. (2) reduces to the generalized Smoluchowski equation (GSE) in the small ϵ limit: $\hat{p}(r, u) = \hat{D}(u)L_{FP}\hat{p}(r, u) - \delta(r)\hat{\kappa}^*(u)\hat{p}(0, u)$, $(r \geq 0)$ with the reflecting boundary condition $(\partial/\partial r)[e^{\beta U}\hat{p}(r, u)]_{r=0-} = 0$, where $p(r, t)$ denotes the probability density function having the initial condition $p(r, 0) = \delta(r - r_0)$ with $r = \epsilon n$ and $r_0 = \epsilon m$. Here, $\hat{D}(u) = \epsilon^2 \mathrm{D}(u)/2$, $\hat{\kappa}^*(u) = \epsilon u\hat{\phi}^*(u)/[1 - \hat{\psi}_0^*(u)]$, and $L_{FP}\hat{p}(r, u) = (\partial/\partial r)\{e^{-\beta U}(\partial/\partial r)[e^{\beta U}\hat{p}(r, u)]\}$, where $U(r)$ denotes the external potential related to the equilibrium probability density $p^{\mathrm{eq}}(r)$ in the absence of reaction by $p^{\mathrm{eq}}(r) = e^{-\beta U(r)}/\int dr' e^{-\beta U(r')}$ with β being inverse temperature. The solution of the GSE is given by $\hat{p}(r, u|r_0) = \hat{G}^*(r, u|r_0) + \hat{G}^*(r, u|0)\hat{S}^*(u|r_0)$ and

$$\hat{S}^*(u|r_0) = -\frac{\hat{\kappa}^*(u)\hat{G}^*(0, u|r_0)}{1 + \hat{\kappa}^*(u)\hat{G}^*(0, u|0)}. \tag{8}$$

Here, $\hat{G}^*(r, u|r_0)$ is defined by $[u - \hat{D}(u)L_{FP}]\hat{G}^*(r, u|r_0) = \delta(r - r_0)$ $(r \geq 0)$ and $\partial/\partial r[e^{\beta U}\hat{G}^*(r, u|r_0)]_{r=0-} = 0$. $\hat{G}^*(r, u|r_0)$ can be obtained by the method of solution developed for the Fokker-Planck equation [25], noting that $\hat{G}^*(r, u|r_0) = \sigma\hat{D}(u)^{-1}\mathsf{G}(x, z|x_0)$ with $z = u\sigma^2/\hat{D}(u)$, $x = r/\sigma$, $x_0 = r_0/\sigma$, and $\hat{\mathsf{G}}(x, z|x_0) = [z - L_{FP}]^{-1}\delta(x - x_0)$. Here, σ is a chosen length unit. The expression for $\hat{h}_0(u|m)$ can be obtained in terms of $\hat{G}^*(0, u|r_0)$ by noting that, in the small ϵ limit, $\hat{S}(u|m)$ for the system with $\psi_0 = \psi_0^*$ and $\psi_0^{nr} = \psi_0^{nr*}$ should be the same as $\hat{S}^*(u|r_0)$ and that $\hat{h}_0(u|m)$ is irrelevant to the dynamics at the boundary described by ψ_0^{nr} and ψ_0:

$$\hat{h}_0(u|m) = \frac{u\hat{G}_0^*(u|m)}{1 - \hat{\psi}_0^*(u) + u\hat{\psi}_0^*(u)\hat{G}_0^*(u|1)}, \tag{9}$$

with $\hat{G}_0^*(u|m) = \epsilon\hat{G}^*(0, u|r_0)$ and $\hat{\psi}_0^*(u) = [1 + \epsilon^2 u/\hat{D}(u)]^{-1}$. In addition, $\hat{G}_n^1(u|m)$ defined below Eq. (5) reduces to $\epsilon\hat{G}^*(r, u|r_0)$ in the small ϵ limit. With these relations at hand, Eqs. (3) and (5)–(7) constitute the solution of Eq. (2) for a finite ϵ, which becomes exact in the small ϵ limit.

In the small ϵ and u limits, Eqs. (3) and (5) can be approximated as

$$\hat{S}(u|r_0) = -\frac{\hat{\lambda}(u)\hat{\mathsf{G}}(0, z|x_0)}{1 + \hat{\lambda}(u)\hat{\mathsf{G}}(0, z|0)}, \tag{10}$$

$$\hat{p}(r, u|r_0)dr = [\sigma^2/\hat{D}(u)]\{\hat{\mathsf{G}}(x, z|x_0) - \hat{\mathsf{G}}(x, z|0)\hat{S}(u|r_0)\}dx, \qquad (r > 0), \tag{11}$$

with $\hat{\lambda}(u) = \lim_{\epsilon\to 0}[\sigma\hat{\phi}(u)/\epsilon]$ and $z = u\sigma^2/\hat{D}(u)$. In passing to the small ϵ limit, it is natural to assume that the reaction probability $\phi(t)dt$, and hence $\hat{\phi}(u)$, are proportional to the size of reaction zone, ϵ, so that $\hat{\lambda}(u)$ is a finite quantity in the small ϵ limit. On the other hand, if $\hat{\phi}(u)$ is set constant in ϵ, $\hat{\lambda}(u)$ diverges in the small ϵ limit, and Eq. (10) becomes $\hat{S}^{\infty}(u|r_0) = -\hat{\mathsf{G}}(0, z|x_0)/\hat{\mathsf{G}}(0, z|0)$, independent of reaction and transport properties at the boundary.

Equations (10) and (11) reduce to the conventional Smoluchowski result, when the reaction and the transport at the boundary are the independent Poisson processes whose sojourn time distributions are given by $\phi^0(t) = k_0 e^{-k_0 t}$, and $\psi_0^0(t) = k_d e^{-k_d t}$ with $\epsilon k_0 \equiv \kappa$, and $\epsilon^2 k_d \equiv D$, provided that the sojourn time distribution for the transport in the bulk is given by $\psi(t) = 2k_d e^{-2k_d t}$. For this model, Eq. (10) yields $\hat{S}(u|r_0) = \lambda^{SM}\hat{\mathsf{G}}(0, z_0|x_0)/[1 + \lambda^{SM}\hat{\mathsf{G}}(0, z_0|0)] \equiv \hat{S}^{SM}(u|r_0)$ with $\lambda^{SM} = (\kappa\sigma/D)$ and $z_0 = u\sigma^2/D$, which is the same as the Smoluchowski result with the RBC. On the other hand, if k_0 and k_d are set constant in ϵ, we obtain $\hat{S}(u|r_0) = \hat{\mathsf{G}}(0, z_0|x_0)/\hat{\mathsf{G}}(0, z_0|0)$, which is the Smoluchowski result with the ABC, in accordance with [13]. Note that, for the just-mentioned Poisson model, the transport Eq. (2), in the presence of a boundary, is the same as that in the absence of a boundary, or $\mathsf{R}(u) \cong R_0 = 1/2 + O(\epsilon)$ as assumed in the conventional approach. The assumption holds for a Poisson sojourn time distribution ψ_0^0 if $\psi(t) = 2\psi_0^0(t)\int_t^\infty d\tau\,\psi_0^0(\tau)$, and if the reaction and transport at the boundary are independent of each other, $\psi_0^{nr}(t) = \psi_0^0(t)\int_t^\infty d\tau\,\phi^0(\tau)$.

In general, the transport at the boundary can be much different from that in the bulk because of possibly distinct physicochemical environments at the boundary, in which case $\hat{\mathsf{R}}_0(u)$ can be much different from R_0. For example, for a general Poisson model having $\phi^0(t) = k_0 e^{-k_0 t}$, $\psi_0^0(t) = k_0^{nr}e^{-k_0^{nr}t}$, and $\psi(t) = 2k_d e^{-2k_d t}$ with $\epsilon k_0 \equiv \kappa_0$, $\epsilon^2 k_0^{nr} \equiv \kappa_0^{nr}$, and $\epsilon^2 k_d \equiv D_0$, we get $\hat{\mathsf{R}}(u) = k_0^{nr}/(2k_d)$, which is different from R_0 unless k_0^{nr} is $2R_0 k_d$. The survival probability $\hat{S}^P$ of this Poisson model is similar to $\hat{S}^{SM}$ given above but with λ^{SM} replaced by $\lambda^P \equiv \kappa\sigma/\kappa_0^{nr}$, and the ultimate escape probability of the Poisson model $S_\infty^P(r_0)[\equiv \lim_{t\to\infty}S^P(t|r_0)] = 1 - \lim_{z\to 0}\lambda^P\hat{\mathsf{G}}(0, z|x_0)/[1 + \lambda^P\hat{\mathsf{G}}(0, z|0)]$ is independent of the diffusion constant D, in contrast to the prediction of the Smoluchowski approach, but dependent only on the dynamics at the boundary, through κ and κ_0^{nr}. Equation (10) indicates that, for a general model, the ultimate escape probability $S_\infty(r_0)[\equiv \lim_{t\to\infty}S(t|r_0)]$ is independent of the transport property in bulk media, but dependent only on the dynamics at the boundary through $\hat{\lambda}(0) = \lim_{\epsilon\to 0}[\sigma\hat{\phi}(0)/\epsilon]$, and on the geometric properties of the system, such as the external field and the spatial dimension through the small z limit of $\hat{\mathsf{G}}(0, z|x_0)$.

As expected, the relaxation of $S(t|r_0)$ to $S_\infty(t)$ depends on the transport property ψ in the bulk through $\hat{D}(u)$; however, there are two qualitatively different phases of the asymptotic relaxation behavior. When the average sojourn time $\langle t_w\rangle[\equiv \int_0^\infty dt\, t\psi(t)]$ is finite, we have $\hat{D}(u) \cong \hat{D}(0) = \epsilon^2/2\langle t_w\rangle$, and $\hat{\lambda}(u) \cong \hat{\lambda}(0)$ in the small u limit so that the relaxation behavior becomes qualitatively the same as S^P of the Poisson model at long times. This is because the effects of the correlation between the jump events described by a non-Poisson sojourn time distribution ψ becomes negligible at long times $t \gg \langle t_w \rangle$. Therefore, at such long times, the relaxation behavior is not sensitive to the details of ψ; only the first moment $\langle t_w \rangle$ of ψ determines the time scale of the relaxation. On the other hand, when the observation time scale is not long compared to $\langle t_w \rangle$, the relaxation behavior is dependent on the details of the correlation between jump events described by $\psi(t)$, as given by Eq. (10). Especially when $\langle t_w \rangle$ becomes infinite, the correlation between the jumps persists forever, and the long time asymptotic relaxation never reduces to that of the Poisson model. For example, let us consider the reaction system in a linear external potential given by $\beta U(r) = -br/\sigma$ with b being a characteristic constant proportional to the external force. For this model, the expression for $\hat{\mathsf{G}}(x, u|x_0)$ is obtained as

$$\hat{\mathsf{G}}(x, z|x_0) = \frac{\exp[b(x - x_0)]}{2z\sqrt{b^2 + z}}[(\sqrt{b^2 + z} - b)^2 e^{-\sqrt{b^2+z}(x+x_0)} + ze^{-\sqrt{b^2+z}|x-x_0|}], \tag{12}$$

and the asymptotic behavior of $S(t|r_0)$ is obtained from Eq. (10) as $S(t|r_0) \approx S_\infty(r_0) + R_\infty(r_0)[(\lambda + b + |b|)^{-1} + (r_0/\sigma)]\xi(t)$, where $\lambda = \lim_{\epsilon\to 0}(\sigma/\epsilon)^{-1}\hat{\phi}(0)$, $R_\infty(r_0) = 1 - S_\infty(r_0) = \exp[-(b + |b|)x_0]/[1 + \lambda^{-1}(|b| + b)]$, and $\hat{\xi}(u) = (\sqrt{b^2 + z} - |b|)/u$, with $z = u\sigma^2/\hat{D}(u)$. When there exists a finite $\langle t_w \rangle$, the asymptotic relaxation function $\xi(t)$ is obtained as $\xi(t) \approx \exp(-\tau)\tau^{-3/2}/2\sqrt{\pi}$ with $\tau = tb^2 D_0/\sigma^2$ $(b \neq 0)$ and $D_0 \cong 2^{-1}\epsilon^2/\langle t_w \rangle$. In contrast, when $\langle t_w \rangle$ is infinite, we obtain $\xi(t) = (\sigma/\epsilon)^2 \int_t^\infty dt\, \psi(t)$ $(b \neq 0)$, which is dependent on the details of $\psi(t)$ [26].

For the pseudofirst order reaction model in which a number N of mutually independent random walkers in an initial equilibrium distribution are competing to react with a target particle fixed at the boundary, we obtain the exact expression $S(t|eq)$ for the survival probability of the target molecule: $S(t|eq) = \exp[-(N/V)\int_0^t d\tau\, k(\tau)]$, with V being the volume of system, and $\hat{k}(u) = -\sigma\hat{\lambda}(u)\exp[-\beta U(0)]/z[1 + \hat{\lambda}(u)\hat{\mathsf{G}}(0, z|0)]$ in the small ϵ limit. As $\hat{S}$ is related to $\hat{h}$, $\hat{k}(u)$ is also related to $\hat{h}$ through $\hat{k}(u) = \hat{k}_D(u)\hat{\lambda}(u)e^{-\beta U(0)}\hat{S}(u|0)$ with $\hat{k}_D(u) = \hat{D}(u)/\sigma$. The relations of $\hat{S}$ and $\hat{k}(u)$ to $\hat{h}$ provide efficient methods to calculate $S(t)$ and $k(t)$ in a complex system, because h can be obtained much more easily from computer simulation than S and k.

In this Letter, we derived the exact dynamics of CTRW in the presence of a reaction at a boundary. We found that the ultimate escape probability is independent of the transport mechanism in contradiction to the conventional approach, that the relaxation behavior reduces to that of the Poisson model in a time much longer than a characteristic time scale $\langle t_w \rangle$ of the transport, when the observation time scale is smaller than $\langle t_w \rangle$, the relaxation behavior is not universal, but is dependent on the details of the sojourn time distribution $\psi(t)$. We note that these results can be generalized to a higher dimension in a straightforward manner.

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