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Reaction Dynamics of Continuous Time Random Walker in Heterogeneous Environment

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Reaction Dynamics of Continuous Time Random Walker in Heterogeneous Environment

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요 약. 연속시간 무작위 운동자의 반응이 없을 경우 동력학과 반응이 있는 경우 반응 동력학과의 정확한 상관관계를 보고하였다. 이 상관 관계는 연속시간 무작위 운동자가 그 공간적 위치와 운동의 방향에 따라 다른 운동 성질을 가지는 경우에도 성립한다. 이 결과의 적용범위는 무작위 운동자가 한번에 일정한 거리만 움직이는 경우뿐 아니라 보다 일반적인 경우에도 적용할 수 있으며, 일차원 계와 더불어 등방성을 가지는 다차원 계에도 적용할 수 있다.

주제어: 연속시간 운동자, 반응 동력학, 반응속도, 일반화된 확산방정식

ABSTRACT. We report an exact relation between the survival probability, the revisit time distribution, and the reaction-free propagator of the continuous time random walker. The relation holds even for such a general case where the random walker has a distinct jump dynamics at each lattice site, which may be dependent also on the direction of the jump. The application range of the obtained relation is not limited to the nearest neighbor hopping in the bulk lattice either. The result is applicable to a higher dimensional system with the spherical symmetry as well as it is to the one-dimensional system.

Keywords: Continuous Time Random Walker, Reaction Dynamics, Reaction Kinetics, Generalized Diffusion Equation

Stochastic processes are ubiquitous inbiological, chemical, and physical system. Continuous time random walk (CTRW) has served as a convenient mathematical model to describe a wide variety of stochastic processes.[1-5] Recently, generalizations of CTRW were made to encompass the situation where the random walker suffers a reaction.[6]

The continuous time random walker (CTRW) model has been used to describe a wide range of stochastic transport phenomena. The CTRW is characterized by the waiting time distribution $\psi(t)dt$, which denotes the probability that a random walker that arrived at a lattice site at time 0 jump to one of adjacent lattice sites between t and $t+dt$. At times much longer than the mean waiting time, the dynamics of CTRW model satisfies the well-known universal transport equations such as the diffusion equation and the Fokker-Planck equation irrespective of the detailed functional form of $\psi(t)$. On the other hand, when $t \leq \langle t_w \rangle$, the dynamics of the CTRW deviates from the universal transport equations and it depends on the detailed functional form of $\psi(t)$ without any universality. It is known that transport in arbitrary heterogeneous media can be mapped onto the CTRW model, and the mean waiting time, $<t_w>$ increases with the heterogeneity of the medium in which the transport of CTRW occurs. Therefore, the dynamics of the CTRW reduces to the universal diffusion later in more heterogeneous environment. A couple of decades ago, Kenkre *et al.* obtained a generalized master equation that provide the exact description for the dynamics of the CTRW from the short time regime, which, of course, reduces to the universal diffusion equation at long times. Recently, for a specific model of CTRW, Klafter and coworkers obtained the fractional Fokker-Planck equation that describes anomalous diffusion in the presence of external force field.

However, the rigorous 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 conventional approach, the effects of the reaction at the boundary were taken into account merely by imposing either the absorbing boundary condition (ABC) or the radiation boundary condition (RBC) on the hydrodynamic limit transport equation, of which validity has been a controversial issue.[7] The result of the conventional approach with the ABC has an unphysical singularity at time 0,[8] and Naqvi, Mork, and Waldenstrøm showed that, in thehydrodynamic limit, the Brownian motion in the presence of an absorbing sphere reduces to the conventional approach with the RBC instead of the ABC.[9] Nevertheless, van Kampen and Oppenheim showed that the ABC rather than the RBC gives thecorrect hydrodynamic description of random walk in the presence of a reaction at a boundary.[10]

In the present work, we investigate the dynamics of CTRW model in the presence of boundary, without introducing phenomenological boundary conditions such as ABC or RBC. We consider a general CTRW model in which the random walker has a distinct jump dynamics at each lattice site, which may be dependent also on the direction and the distance to the destination site of the jump. The only constraint in this model is that the random walker at boundary can jump back to the nearest neighbor site only unless it suffers a reaction at the boundary. For the general model, we derive an exact relation of the survival probability and the distribution of the n-th arrival time to the boundary to the reaction-free propagator of the random walker. The result is applicable to a higher dimensional system with the spherical symmetry as well as it is to the one-dimensional system.

At first, we consider a random walk on a one dimensional lattice in the presence of a boundary at the leftmost site labeled as site 0. The other lattice sites are denoted by the series of increasing positive integer, n from left to right. The number of lattice sites can be arbitrary. Let a random walker is created at $n=m$ initially. Subsequently the random walker repeats a jump process in the lattice until it arrives at the boundary, site 0. At site 0, the random walker either suffers a reaction or escapes back to site 1 and repeat the jump process again. In our model, except when it is located at boundary, the random walker can jump to any sites in the lattice. The dynamics of the random walker can be completely specified by a set of waiting time distribution function, $\psi_{nm}(t)$, where $\psi_{nm}(t)dt$ is the probability that a random walker makes a jump from site n to site m in time interval $(t, t+dt)$ given that the random walker arrived at site n at time 0. For all site n except site 0, $\psi_{nm}(t)$ satisfies the normalization condition: $\sum_{m\neq n}\int_0^\infty dt\psi_{nm}(t)=1$. In the absence of a reaction process at site 0, the dynamics of the random walker at the boundary is completely specified by $\psi_{01}(t)$, which satisfies $\int_0^\infty dt\psi_0(t)=1$ with $\psi_0(t)=\psi_{01}(t)$. In the presence of a reaction process at boundary, in addition to $\psi_{01}(t)$, we need to introduce the reaction waiting time distribution $\phi(t)dt$, which denotes the probability that the random walker undergoes a reaction in time interval $(t,t+dt)$ given that the random walker arrives at the boundary at time 0. For the latter case, the normalization condition at site 0 is given by $\int_0^\infty dt\psi_0(t)=1$ with $\psi_0(t)$ being $\psi_{01}(t)+\phi(t)$.

For the general CTRW model, we will first derive the relation of the k-th revisit time distribution and the Greens function in the absence of a reaction process. The first arrival time distribution $h_0(t|m)dt$ denotes the probability that the random walker initially located at site m arrives at site 0 in time interval $(t,t+dt)$. In comparison, the Greens function $G_0(t|m)$ denotes the probability that we find the random walker at site 0 given that the random walker was initially at site m. If $\hat{x}(u)$ denotes the Laplace transform of $x(t)$ with ubeing the Laplace variable, the Greens function can be represented as:

$$\hat{G}_0(u|m) = \hat{\Phi}_0(u)\sum_{k=1}^{\infty}\hat{f}_k(u|m) \qquad (1)$$

where $\Phi_0(t)$ is the probability that the random walker arrived at the boundary at time 0 does not jump until time t and $f_k(t|m)dt$ denotes the probability that the random walker initially located at m arrives k times at site 0 in time interval $(t,t-dt)$. $\Phi_0(t)$ is related to $\psi_0(t)$ by $\Phi_0(t) = \int_t^{\infty} d\tau\psi_{01}(\tau)$, which reads as

$$\hat{\Phi}_0(u) = \frac{1-\hat{\psi}_{01}(u)}{u} \qquad (2)$$

in Laplace domain. In turn, $f_k(t|m)$ can be represented in terms of $h_0(t|n)$ as:

$$\hat{f}_k(u|m) = \hat{h}_0(u|m)[\hat{\psi}_{01}(u)\hat{h}_0(u|1)]^{k-1} \qquad (3)$$

Substituting Eq. (3) into Eq. (1), we obtain

$$\hat{G}_0(u|m) = \frac{\hat{\Phi}_0(u)\hat{h}_0(u|1)}{1-\hat{\psi}_{01}(u)\hat{h}_0(u|1)} \qquad (4)$$

From Eq. (4), we can also express h_0 in terms of G_0 as follows:

$$\hat{h}_0(u|m) = \frac{\hat{G}_0(u|m)}{\hat{\Phi}_0(u)+\hat{\psi}_{01}(u)\hat{G}_0(u|1)} \qquad (5)$$

By noting that $\hat{G}_0(u|0)=\hat{\Phi}_0(u)+\hat{\psi}_{01}(u)\hat{G}_0(u|1)$, we recover the well-known relation from Eq. (5) as:

$$\hat{h}_0(u|m) = \frac{\hat{G}_0(u|m)}{\hat{G}_0(u|0)} \qquad (6)$$

Note that Eq. (6) holds always in the absence of reaction as far as the jump of the random walker is a renewal process.

Now let us consider the situation in which the random walker suffers a reaction at the boundary. If $S(t|m)$ denotes the survival probability of the random walker initially located at site m, the reaction rate, $-\partial S(t|m)\partial t$, is given by

$$\hat{S}(u|m) = \frac{-\hat{\phi}(u)\hat{h}_0(u|m)}{1-\hat{\psi}_{01}(u)\hat{h}_0(u|1)} \qquad (7)$$

so that we have the expression for the survival probability as:

$$\hat{S}(u|m) = \frac{1}{u}\left[1-\frac{-\hat{\phi}(u)\hat{h}_0(u|m)}{1-\hat{\psi}_{01}(u)\hat{h}_0(u|1)}\right] \qquad (8)$$

Eqs. (3)-(5) and (8) constitute the key results of the present paper with the well known equation, given by Eq. (6).

One of the important advantages of this approach is that it 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. This is because the correlation between jump events becomes negligible in a time much longer than the average sojourn time. However, the average sojourn time increases with the heterogeneity in the environment so that it can be comparable to or even longer than the observation time-scale in strongly heterogeneous or 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,[3,17] or when the average sojourn time is infinite, the exact result never reduces to that of the conventional Smoluchowski approach based on the Poisson transport model or its simple generalizations, even at asymptotically long times.

We finish this letter by noting that the obtained results is applicable to a higher dimensional system with the spherical symmetry as well as it is to the one-dimensional system.

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