Comment on "Path Summation Formulation of the Master Equation"

The Green's function for a random walker on a lattice that starts at time $t_0 = 0$ at state i and reaches at time t state j, $G_{ji}(t)$, can be found by various approaches. For spatially invariant systems, a recursion relation finds the Green's function in Laplace-Fourier domains in terms of the basic input probability density functions (PDFs) [1]. For arbitrarily inhomogeneous bounded systems in discrete space, the solution for the Laplace transform Green's function inverts the matrix of transition rates with $(-s)$ added to the diagonal elements (s is the Laplace transform argument). For the general case, the elements of the inverted matrix are not known analytically. A different approach expresses the Green's function as a sum over all relevant paths, e.g., [2]. If one chooses to sum over paths, as was recently done when calculating the Green's function for one-dimensional arbitrarily inhomogeneous lattices with L states [3], associating a combinatorial factor with each path is difficult. Only the product of the combinatorial factor and the path PDF in time is relevant in Green's function calculation. In higher dimensions, the combinatorial factor associated with a path becomes harder to compute.

A recent Letter claims to make a progress in summing over paths of a random walker in an arbitrarily inhomogeneous lattice in d dimensions [4]. We believe this claim is unjustified; although Eq. (13) correctly expresses the Green's function as a sum over all possible relevant paths, one cannot plug in it Eq. (9) or Eq. (16) for a general case, and perform a summation, because combinatorial factors for paths are not given, or discussed, in [4]. (In this Comment, we refer to the numbered equations that appear in [4].) (The only case for which one can calculate the Green's function by summing over paths without worrying about combinatorial factors is for a lattice with two states, where each path appears once.)

To illustrate our point, and to highlight the way to solve the problem in $1d$, consider a $1d$ four-state lattice with transition rate k_{ji} connecting state i to state j, and $K_i = \sum_j k_{ji}$. Say that the Laplace space Green's function $\bar{G}_{41}(s)$ is required. Using Eq. (13), $\bar{G}_{41}(s) = \sum_{\{x(n;s)\}} \bar{\prod}_n[x(n; s)]$. How to find expressions for the $\bar{\prod}_n[x(n; s)]$? For this, ideas given in [3] are used and briefly sketched below. First, the values $n = 0, 1, 2$, do not contribute to the sum, because the random walker must perform at least 3 jumps to reach state 4 from state 1. (Similarly, all even values of n do not contribute to the sum.) For $n = 3$, the path $x(3; s)$ is just the path of direct transitions, and it is denoted by $x(3; s) = (1, 2, 3, 4; s)$. Thus, $\bar{\prod}_3[x(3; s)]$ is obtained using Eq. (9). For $n = 5$, there are 3 distinct paths that contribute to the ensemble of paths $\{x(5; s)\}$,

$$\{x(5; s)\} = \{(1, 2, 1, 2, 3, 4; s), \quad (1, 2, 3, 2, 3, 4; s),$$
$$(1, 2, 3, 4, 3, 4; s)\},$$

and accordingly,

$$\bar{\prod}_5[x(5; s)] = \bar{\prod}_3[x(3; s)]\left(\frac{k_{21}k_{12}}{(s + K_1)(s + K_2)}\right.$$
$$+ \frac{k_{32}k_{23}}{(s + K_2)(s + K_3)}$$
$$\left. + \frac{k_{43}k_{34}}{(s + K_3)(s + K_4)}\right).$$

The large parentheses above are defined as $\bar{h}(1, s; 4)$. The next nonvanishing term in the series, $\bar{\prod}_7[x(7; s)]$, is even more interesting, as it is built from degenerate paths; there are 2 paths with degeneracy 2 and additionally 4 paths with degeneracy 1. $\bar{\prod}_7[x(7; s)]$ can be expressed by the recursion relation, $\bar{\prod}_7[x(7; s)] = \bar{\prod}_5[x(5; s)] \times \bar{h}(1, s; 4) - \bar{\prod}_3[x(3; s)]\bar{h}(2, s; 4)$, where $\bar{h}(2, s; 4) = k_{21}k_{12}k_{43}k_{34}\prod_{i=1}^4(s + K_i)^{-1}$. This sort of recursion relation holds true for every odd n, leading to $\bar{G}_{41}(s) = \bar{\prod}_3[x(3; s)]/[1 - \bar{h}(1, s; 4) + \bar{h}(2, s; 4)]$. Thus, $\bar{G}_{41}(s)$ cannot be approximated by the numerator, which represents the only path of direct transitions connecting states 1 and 4; it is the denominator, which is built from all paths with back transitions and their associate degeneracy, that gives the correct decaying rates and equilibrium probability. Finally, note that for the four-state chain, a complementary analysis shows that the number of paths associated with $\prod_n[x(n; t)]$ scales as $(1 + \phi)^{n/2}$, where ϕ $(= 1.618 \dots)$ is the golden ratio. This sort of complementary analysis can be useful when extending to higher dimensions the treatment given here and in [3] for $1d$ for calculations of Green's functions and related approximations.

O. Flomenbom,[1,*] J. Klafter,[2,†] and R. J. Silbey[1,‡]
[1]Department of Chemistry
　Massachusetts Institute of Technology
　Cambridge, Massachusetts 02139, USA
[2]School of Chemistry
　Raymond & Beverly Sackler Faculty of Exact Sciences
　Tel Aviv University
　Ramat Aviv, Tel Aviv 69978, Israel

　*Electronic address: flomenbo@mit.edu
　†Electronic address: klafter@post.tau.ac.il
　‡Electronic address: silbey@mit.edu
[1] E. W. Montroll and G. H. Weiss, J. Math. Phys. (N.Y.) **6**, 167 (1965); H. Scher and M. Lax, Phys. Rev. B **7**, 4491 (1973).
[2] R. D. Mattuck, *A Guide to Feynman Diagrams in the Many-Body Problem* (McGraw-Hill, New York, 1976).
[3] O. Flomenbom and J. Klafter, Phys. Rev. Lett. **95**, 098105 (2005).
[4] S. X. Sun, Phys. Rev. Lett. **96**, 210602 (2006).