Anomalous diffusion with linear reaction dynamics: From continuous time random walks to fractional reaction-diffusion equations

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We have revisited the problem of anomalously diffusing species, modeled at the mesoscopic level using continuous time random walks, to include linear reaction dynamics. If a constant proportion of walkers are added or removed instantaneously at the start of each step then the long time asymptotic limit yields a fractional reaction-diffusion equation with a fractional order temporal derivative operating on both the standard diffusion term and a linear reaction kinetics term. If the walkers are added or removed at a constant per capita rate during the waiting time between steps then the long time asymptotic limit has a standard linear reaction kinetics term but a fractional order temporal derivative operating on a nonstandard diffusion term. Results from the above two models are compared with a phenomenological model with standard linear reaction kinetics and a fractional order temporal derivative operating on a standard diffusion term. We have also developed further extensions of the CTRW model to include more general reaction dynamics.

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I. INTRODUCTION

Reaction-diffusion equations have been studied extensively as mathematical models of systems with reactions and diffusion across a wide range of applications including; nerve cell signaling, animal coat patterns, population dispersal, and chemical waves. The generic form of these equations is [1]

$$\frac{\partial \mathbf{n}(\mathbf{x},t)}{\partial t} = \mathbf{D}\nabla^2 \mathbf{n}(\mathbf{x},t) + \mathbf{f}[\mathbf{n}(\mathbf{x},t)], \tag{1}$$

where $\mathbf{n}$ is a vector whose components represent the numbers of a particular species per unit volume. The first term on the right hand side accounts for the spatial diffusion of the species and $\mathbf{D}$ is a diagonal matrix whose elements are the diffusivities of the different species. The second term on the right hand side, a functional of $\mathbf{n}$, accounts for "reactions" that produce or destroy species. This partial differential equation can be motivated by a mesoscopic description based on a coarse grained representation of space with diffusion between cells and reactions within cells [1]. The cells are considered to be arbitrarily small so that the diffusion of reactants within cells is instantaneous. In this case the reactants within cells are homogeously mixed and the production or destruction of particles in the cells is a reaction-limited process that can be modeled according to the law of mass action. The characteristic length scale l_D and time scale τ_D for the mesoscopic description are defined relative to the following physical scales: the characteristic size of a reaction zone δl_R; the characteristic microscopic diffusion time for encounters between reactants $\delta\tau_D$; the microscopic reaction time $\delta\tau_R$; the size of the domain L; the time scale of the experiment T. Explicitly (i) $\delta l_R \ll l_D \ll L$ and (ii) $\delta\tau_D \ll \delta\tau_R \ll \tau_D \ll T$. The length scale l_D and the time scale τ_D are both considered to be arbitrarily small but (in the case of standard Brownian motion) l_D^2/τ_D is finite.

In this mesoscopic description the number density $\mathbf{n}(\mathbf{x},t)$ can be interpreted as an ensemble average over many statistical realizations of the system [1] or as the number density for a particular realization if the number density is sufficiently large. An underlying assumption in the formulation of Eq. (1), is that the diffusion between cells is standard Brownian motion.

Over the past few decades an intensive effort has been put into developing theoretical models for systems with diffusive motion that cannot be modeled as standard Brownian motion [2–4]. The signature of this anomalous diffusion is that the mean square displacement of the diffusing species $\langle(\Delta x)^2\rangle$ scales as a nonlinear power law in time, ie., $\langle(\Delta x)^2\rangle \sim t^\alpha$. Faster than linear scaling ($\alpha > 1$) is referred to as superdiffusion and slower than linear scaling ($0 < \alpha < 1$) is referred to as subdiffusion. In recent years the additional motivation for these studies has been stimulated by experimental measurements of subdiffusion in porous media [5], glass forming materials [6], biological media [7,8], and Monte Carlo studies of subdiffusion in materials with trapping or binding sites [9]. One of the most successful theoretical paradigms to emerge from this research has been fractional calculus models for anomalous diffusion justified at a mesoscopic level by continuous time random walks (CTRWs) [3,4,10]. In the CTRW model anomalous subdiffusion arises when the asymptotic long time limit of the waiting time probability density function is heavy tailed, ie., $\psi(t) \sim t^{-\alpha-1}$ with $0 < \alpha < 1$. The evolution equation for the concentration of nonre-

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acting species undergoing subdiffusion can then be modeled using a fractional diffusion equation which differs from the conventional diffusion equation in that it has a fractional order temporal derivative acting on the spatial Laplacian.

In recent years reaction terms have been incorporated with anomalous subdiffusion in the CTRW-fractional calculus paradigm yielding so called fractional reaction-diffusion equations [11–22]. Most of these studies posit a fractional order temporal derivative acting on the spatial Laplacian with standard classical rate equations for the reaction terms [11–15,18,20–23]. However, some studies consider the fractional temporal order derivative to operate on both the Laplacian and classical rate equation reaction terms [16,17,19]. These two models produce very different Turing patterns in two-species activator-inhibitor systems [24]. In the absence of experimental results to validate either model we have been led to reconsider the theoretical foundations of the models. Both models were obtained from balance equations for CTRWs with source or sink terms. In the original model introduced by Henry and Wearne [11] the source or sink term was convolved with the survival probability for random walkers. The heuristic interpretation was that the concentration of walkers at x and t is composed of walkers coming from other positions x' at earlier times $t'<t$, plus walkers that were added by reactions at location x at earlier times $t'<t$ and then survived there, minus walkers removed by reactions at location x at earlier times $t'<t$ that would otherwise have survived at this location had they not been removed. The replacement of this source or sink term with standard reaction rate kinetics (see, e.g., Refs. [12,14,20,22]) is then *ad hoc*. The model introduced by Seki, Wojcik, and Tachiya [16,17] was for the particular problem of geminate recombination and the extension to other reaction rate kinetics [19] is again *ad hoc*. Very recently, Sokolov, Schmidt, and Sagués [25] revisted the problem of reactions with subdiffusion, and in the case of a monomolecular conversion $A\rightarrow B$, they found that the fractional reaction-diffusion equation includes the effects of the reactions in both an additive reaction term and a nonstandard diffusion term. The latter cannot be represented by a temporal fractional order derivative operating on a standard diffusion term.

Here we have revisited the CTRW model to allow for the addition or removal of species via one of three different linear processes: (i) Walkers are added or removed via a source/sink term with linear reaction rate kinetics in the generalized CTRW model introduced by Henry and Wearne [11]. The long time asymptotic limit is a fractional reaction-diffusion equation with standard linear reaction kinetics and a fractional order temporal derivative operating on a standard diffusion term. (ii) A constant proportion of walkers is added or removed instaneously at the start of each step. In this case the long time asymptotic description in terms of fractional reaction-diffusion equations yields a fractional order temporal derivative operating on both the diffusion term and a linear reaction kinetics term. (iii) Walkers are added or removed at a constant per capita rate during the waiting time before a step is made. Here the long time asymptotic limit in terms of fractional reaction-diffusion equations can be represented with standard linear reaction kinetics but a fractional order temporal derivative operating on a nonstandard diffusion term.

A subdiffusive CTRW model for case (ii) with a linear degradation term was considered recently by Hornung, Berkowitz, and Barkai [26]. Here we have formulated the CTRW in terms of a fractional diffusion equation with a fractional order temporal derivative operating on both the (Laplacian) diffusion term and the (linear) reaction term. In case (iii) we obtain similar CTRW results to those recently reported by Sokolov, Schmidt, and Sagués [25] but we have represented the long time asymptotics by a fractional reaction diffusion equation with a linear reaction term and a temporal order fractional derivative operating on a nonstandard diffusion term.

We have obtained explicit solutions for the three fractional reaction-diffusion equations considered in these models. The different solutions are informative of different physical processes involving anomalous diffusion with linear reaction dynamics.

The remainder of these notes are organized as follows. In Sec. II we summarize the CTRW formalism for (possibly anomalous) diffusion. Most of this material up to the formulation of the master equation appears elsewhere but we have revisited it here to clarify the subsequent extension to include source and sink terms. In Sec. III we introduce linear reaction dynamics into the CTRW formalism according to the different processes outlined above and we derive the appropriate fractional reaction-diffusion equations for the long time asymptotic behavior. In Sec. IV we outline further extensions of the CTRW model to include more general reaction dynamics. In Sec. V we present explicit solutions of the fractional reaction-diffusion equations resulting from the different linear models. In Sec. VI we discuss the results.

II. CONTINUOUS TIME RANDOM WALKS

The continuous time random walk (CTRW) was introduced by Montroll and Weiss [27], and Scher and Lax [28], as a generalization of the standard random walk introduced by Pearson in 1905 [29]. In Pearson's formulation the random walk consists of a sequence of equal length steps taken at regular time intervals. In the CTRW the waiting times between successive steps and the length of the steps are both random variables with the associated probability density $\Psi(x,t)$ for the particle to step a distance x after waiting a time t. In the original formulation by Montroll and Weiss [27] the walk was considered to have taken place on a discrete lattice.

A fundamental quantity to calculate is the conditional probability density $p(x,t|x_0,0)$ that a walker starting from position x_0 at time $t=0$ is at position x at time t. First it is useful to consider the conditional probability density $q_n(x,t|x_0,0)$ that a walker starting at x_0 at time zero arrives at position x at time t after n steps. This latter probability density satisfies the recursion equation [28]

$$q_{n+1}(x,t|x_0,0)=\sum_{x'}\int_0^t \Psi(x-x',t-t')q_n(x',t'|x_0,0)dt', \tag{2}$$

where $\Psi(x-x',t-t')$ is the probability density that a random walker jumps a distance $x-x'$ after waiting a time $t-t'$ in a

single step. Note that the sum over x' includes the possibility $x'=x$. The initial condition that the walker is at x_0 at time zero

$$q_0(x,t|x_0,0) = \delta_{x,x_0}\delta(t) \tag{3}$$

satisfies the normalization

$$\sum_{x'} \int_0^\infty q_0(x',t'|x_0,0)dt' = 1. \tag{4}$$

The conditional probability density $q(x,t|x_0,0)$ that a walker arrives at position x at time t after any number of steps is given by

$$q(x,t|x_0,0) = \sum_{n=0}^{\infty} q_n(x,t|x_0,0). \tag{5}$$

Note that we can write

$$\sum_{n=0}^{\infty} q_n(x,t|x_0,0) = q_0(x,t|x_0,0) + \sum_{n=0}^{\infty} q_{n+1}(x,t|x_0,0),$$

so that, after performing a summation over n, the recursion relation (2), can be written as [28,30]

$$q(x,t|x_0,0) = \sum_{x'} \int_0^t \Psi(x',t')q(x-x',t-t'|x_0,0)dt' + \delta(t)\delta_{x,x_0}. \tag{6}$$

In the remainder it is supposed that the probability density $\Psi(x,t)$ decouples in space and time, i.e.,

$$\Psi(x,t) = \psi(t)\lambda(x), \tag{7}$$

where $\psi(t)$ is the waiting time probability density given by

$$\psi(t) = \sum_{x'} \Psi(x',t) \tag{8}$$

and $\lambda(x)$ is the step length probability density given by

$$\lambda(x) = \int_0^\infty \Psi(x,t')dt'. \tag{9}$$

It is also useful to define the survival probability distribution $\Phi(t)$ that the walker does not take a step in time interval t

$$\Phi(t) = 1 - \int_0^t \psi(t')dt' = \int_t^\infty \psi(t')dt'. \tag{10}$$

The conditional probability density $p(x,t|x_0,0)$ that a walker starting from the origin at time zero is at position x at time t is equivalent to the probability density that the walker arrived at x at any earlier time t' and thereafter did not take a step, i.e. [27,28,30],

$$p(x,t|x_0,0) = \int_0^t q(x,t-t'|x_0,0)\Phi(t')dt'. \tag{11}$$

The results in Eqs. (6) and (11) can be combined using Laplace transforms to yield the master equation for the probability density $p(x,t|x_0,0)$. The Laplace transform of Eq. (11) yields

$$\hat{p}(x,u|x_0,0) = \hat{q}(x,u|x_0,0)\hat{\Phi}(u), \tag{12}$$

and the Laplace transform of Eq. (6) yields

$$\hat{q}(x,u|x_0,0) = \sum_{x'} \hat{\Psi}(x',u)\hat{q}(x-x',u|x_0,0) + \delta_{x,x_0}. \tag{13}$$

We can combine these two results to obtain

$$\hat{p}(x,u|x_0,0) = \sum_{x'} \hat{\Psi}(x',u)\hat{\Phi}(u)\hat{q}(x-x',u|x_0,0) + \hat{\Phi}(u)\delta_{x,x_0},$$

$$= \sum_{x'} \hat{\Psi}(x',u)\hat{p}(x-x',u|x_0,0) + \hat{\Phi}(u)\delta_{x,x_0}. \tag{14}$$

The inverse Laplace transform of Eq. (14) now yields the master equation [30]

$$p(x,t|x_0,0) = \Phi(t)\delta_{x,x_0} + \sum_{x'} \int_0^t p(x',t'|x_0,0) \times \Psi(x-x',t-t')dt'. \tag{15}$$

Most of the recent literature on CTRWs take Eq. (15), or the continuum version [31]

$$p(x,t|x_0,0) = \Phi(t)\delta_{x,x_0} + \int_0^t \psi(t-t') \times \left[\int_{-\infty}^{\infty} \lambda(x-x')p(x',t'|x_0,0)dx'\right]dt' \tag{16}$$

as the starting point for further analysis. For example Maindardi and co-workers [31] motivate this equation on probability arguments with the interpretation that the first term expresses the persistence of a walker at the initial position and the second term is the contribution from a walker being at point x' at time t' and then jumping to x and t after waiting a time $t-t'$.

It follows from Eq. (15), that if there is an initial concentration of $c(x_0,0|x_0,0)$ random walkers at $x=x_0$ at time $t=0$ and if these walkers do not interact then the expected concentration $c(x,t|x_0,0)$ at position x and time t is given by

$$\frac{c(x,t|x_0,0)}{c(x_0,0|x_0,0)} = \Phi(t)\delta_{x,x_0} + \sum_{x'} \int_0^t \frac{c(x',t'|x_0,0)}{c(x_0,0|x_0,0)} \times \Psi(x-x',t-t')dt'. \tag{17}$$

After multiplying by the initial concentration we have

$$c(x,t|x_0,0) = \Phi(t)c(x_0,0|x_0,0)\delta_{x,x_0} + \sum_{x'} \int_0^t c(x',t'|x_0,0) \times \Psi(x-x',t-t')dt'. \tag{18}$$

Now suppose that we have a different initial concentration at each possible starting point x_0 and sum over all possible starting points then

$$\sum_{x_0} c(x,t|x_0,0) = \sum_{x_0} \Phi(t)c(x_0,0|x_0,0)\delta_{x,x_0} + \sum_{x'} \int_0^t \sum_{x_0} c(x',t'|x_0,0)\Psi(x-x',t-t')dt' \tag{19}$$

$$= \Phi(t)c(x,0|x,0) + \sum_{x'} \int_0^t \sum_{x_0} c(x',t'|x_0,0) \times \Psi(x-x',t-t')dt'. \tag{20}$$

We now identify the number density

$$n(x,t) = \sum_{x_0} c(x,t|x_0,0) \tag{21}$$

as the total expected concentration of walkers at position x and time t (independent of their starting locations) and

$$n(x,0) = c(x,0|x,0) \tag{22}$$

as the initial concentration of walkers at x. The result in Eq. (20) can now be written as

$$n(x,t) = \Phi(t)n(x,0) + \sum_{x'} \int_0^t n(x',t')\Psi(x-x',t-t')dt'. \tag{23}$$

III. CONTINUOUS TIME RANDOM WALKS WITH SUBDIFFUSION AND LINEAR REACTION KINETICS

In earlier work [11] we considered an extension of the conservation equation (23) to incorporate sources and sinks as follows:

$$n(x,t) = \Phi(t)n(x,0) + \sum_{x'} \int_0^t n(x',t')\Psi(x-x',t-t')dt' + \int_0^t \Phi(t-t')s(x,t')dt'. \tag{24}$$

The heuristic interpretation of the additional source/sink term was that it represents the net contribution to the concentration of walkers at x and t due to (i) walkers added at x at time $t' < t$ that then do not jump from x over the time $(t-t')$ and (ii) walkers removed at x at time $t' < t$ that would not otherwise have jumped from x during the time $(t-t')$. Thus walkers with survival characteristics represented through $\Phi(t)$ are added or removed from the system at a rate $s(x,t)$. If the source/sink term arises from reactions among the walkers, then it is tempting to replace $s(x,t)$ with $f[n(x,t)]$, the standard reaction rate kinetics from the law of mass action. However, the resulting phenomenological model has not been justified at the mesoscopic level of the random walks and the physical interpretation is not clear. Nevertheless one of the appealing features of this model is that the asymptotic long time limit yields a fractional reaction-diffusion equation [11] that only differs from the standard reaction-diffusion equation through a fractional temporal order derivative operating on the standard spatial Laplacian. This model can thus be derived phenomenologically from the standard conservation law for reaction-diffusion processes [32] by replacing the general flux transport with a fractional temporal order derivative operating on the gradient of the concentration—a time fractional Fickian process [33]. Similarly the space fractional diffusion equation [34] can be reconciled with a space fractional Fickian process [35]. In the models below we have attempted to move beyond a phenomenological description by incorporating the physical basis of the source/sink terms at the level of the random walks.

A. Instantaneous creation and annihilation processes

In this subsection we consider a simple extension of the standard CTRW model to include the instantaneous addition or removal of a fixed proportion of the walkers at the start of the waiting time before they take their next step. A subdiffusive CTRW formulation of this problem in the case of removals (physically representing the degradation of morphogens) was considered recently by Hornung, Berkowitz, and Barkai [26]. In the derivation below we show that the CTRW for this problem can be formulated as a fractional reaction-diffusion equation. One of the appealing features of this representation is that it provides a ready comparison between standard reaction-diffusion equations and the corresponding problem with anomalous diffusion. Another appealing feature is that standard mathematical methods for partial differential equations and the mathematical tools of fractional calculus can be employed to provide the asymptotic long time behaviour of this problem without further approximation.

The probability density for walkers to arrive at position x at time t at the end of their $(n+1)$th step, given that a fixed proportion are added or removed instantaneously (at the start or end of the step), is now given by

$$q_{n+1}(x,t) = \int_0^t \sum_{x'} [q_n(x',t') \pm kq_n(x',t')]\psi(t-t')\lambda(x-x')dt'. \tag{25}$$

Here we have increased $(+)$ or reduced $(-)$ the walkers that arrived after n steps by a constant proportion $k \in (0,1)$. We could of course write $r=(1\pm k)$ and then

$$q_{n+1}(x,t) = r\int_0^t \sum_{x'} q_n(x',t')\psi(t-t')\lambda(x-x')dt'. \tag{26}$$

Similar to Eq. (6) we can now sum over n to obtain

$$q(x,t) = r\sum_{x'} \int_0^t \psi(t-t')\lambda(x-x')q(x',t')dt' + \delta(t)\delta_{x,x_0}, \tag{27}$$

where we have included the initial condition that walkers are starting at x_0.

We now consider the probability density for walkers to be at x at time t. This is given by

$$p(x,t) = r\int_0^t \Phi(t-t')q(x,t')dt', \tag{28}$$

i.e., the walkers at x at time t are those that arrived there at an earlier time $t<t'$ and then did not jump away, increased or reduced by the constant fraction of arrivals that were added or removed by the source/sink term. Note that in the case $r=1-k$, Eq. (28) can be written as [26]

$$p(x,t) = \int_0^t \Pi(t-t')q(x,t')dt' \tag{29}$$

with

$$\Pi(t) = 1-(1-k)\int_0^t \psi(t')dt' - k\int_0^t \psi_R(t')dt' \tag{30}$$

and $\psi_R(t)=\delta(t)$. In this representation, $\psi_R(t)$ is a degradation time density (taken to be instantateous here) and k can be considered as the probability for degradation to occur, so that $\Pi(t)$ is the probability that the walker survives at position x and does not degrade during the time interval t.

It follows from Eq. (27) that we can also write

$$p(x,t) = r\int_0^t \Phi(t-t')\delta_{x,x_0}\delta(t')dt' + r^2\int_0^t \Phi(t-t') \times\left(\sum_{x'}\int_0^{t'} \psi(t'-t'')\lambda(x-x')q(x',t'')dt''\right)dt'. \tag{31}$$

We can combine the results of Eqs. (28) and (31) as in the derivation of the master equation (15) to obtain

$$p(x,t) = r\Phi(t)\delta_{x,x_0} + r\sum_{x'}\int_0^t p(x',t')\psi(t-t')\lambda(x-x')dt'. \tag{32}$$

Allowing for walkers starting from different initial positions and proceeding through steps similar to those leading to Eq. (23) we have the following equation for the number density:

$$n(x,t) = r\Phi(t)n(x,0) + r\sum_{x'}\int_0^t n(x',t')\psi(t-t')\lambda(x-x')dt'. \tag{33}$$

The fractional reaction diffusion equation in Henry and Wearne [11] was derived after a spatial Fourier transform and temporal Laplace transform of the master equation (24), with asymptotic expansions for small values of the Fourier and Laplace variables, followed by inverse transforms using the definition of the Riemann-Liouville fractional derivative. We follow this approach here starting with the new balance equation (33). The Fourier-Laplace transform of Eq. (33) with Fourier variable q and Laplace variable u yields

$$\hat{\hat{n}}(q,u) = r\hat{\Phi}(u)\hat{n}(q,0) + r\hat{\psi}(u)\hat{\lambda}(q)\hat{\hat{n}}(q,u). \tag{34}$$

The Laplace transform of the survival probability (10), can be written as

$$\hat{\Phi}(u) = \frac{1}{u} - \frac{\hat{\psi}(u)}{u} \tag{35}$$

and the small q asymptotic expansion of the step length density is given by

$$\hat{\lambda}(q) \sim 1 - \frac{q^2\sigma^2}{2} + O(q^4) \tag{36}$$

with

$$\sigma^2 = \int r^2\lambda(r)dr \tag{37}$$

finite. We can thus approximate Eq. (34) as

$$u\hat{\hat{n}}(q,u) = r[1-\hat{\psi}(u)]\hat{n}(q,0) + ru\hat{\psi}(u)\left(1-\frac{q^2\sigma^2}{2}\right)\hat{\hat{n}}(q,u). \tag{38}$$

We now consider asymptotic small u results for a heavy tailed waiting time density

$$\psi(t) \sim \frac{\kappa}{\tau_D}\left(\frac{t}{\tau_D}\right)^{-\alpha-1} \tag{39}$$

that is characteristic of anomalous subdiffusion (see, e.g., Ref. [3]). In this expression κ is a dimensionless constant and τ_D is the characteristic mesoscopic time scale. The asymptotic Laplace transform for this density function is obtained from a Tauberian (Abelian) theorem [36,37] as

$$\hat{\psi}(u) \sim 1 - \frac{\kappa\Gamma(1-\alpha)}{\alpha}\tau_D^\alpha u^\alpha. \tag{40}$$

The asymptotic results in Eqs. (39) and (40) apply for times $t \gg \tau_D$. We now substitute the above expansion into Eq. (38) to arrive at

$$u\hat{\hat{n}}(q,u) = r\frac{\kappa\Gamma(1-\alpha)}{\alpha}\tau_D^\alpha u^\alpha\hat{n}(q,0) + ru\left(1-\frac{\kappa\Gamma(1-\alpha)}{\alpha}\tau_D^\alpha u^\alpha\right) \times\left(1-\frac{q^2\sigma^2}{2}\right)\hat{\hat{n}}(q,u). \tag{41}$$

If we rearrange this equation and retain only leading order terms then

$$u\hat{\hat{n}}(q,u) - \hat{n}(q,0) = -\frac{\alpha}{\kappa\Gamma(1-\alpha)\tau_D^\alpha}u^{1-\alpha} \times\left(\frac{1-r}{r}\hat{n}(q,u) + \frac{q^2\sigma^2}{2}\hat{\hat{n}}(q,u)\right). \tag{42}$$

The above equation can also be derived without long time asymptotics in the special case where the waiting time density is given by the derivative of a Mittag-Leffler function [38]. The inverse Laplace transform and inverse Fourier transform of Eq. (42) now yields

$$\frac{\partial n}{\partial t} = D(\alpha)\mathcal{D}^{1-\alpha}\frac{\partial^2 n}{\partial x^2} + \frac{\alpha}{\kappa\Gamma(1-\alpha)\tau_D^\alpha}\left(\frac{r-1}{r}\right)\mathcal{D}^{1-\alpha}n, \tag{43}$$

with the diffusivity

$$D(\alpha) = \frac{\sigma^2 \alpha}{2\kappa\Gamma(1-\alpha)\tau_D^{\alpha}} \tag{44}$$

and we use the notation

$$\mathcal{D}^{1-\alpha}[y(x,t)] = \frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}} y(x,t) + \mathcal{L}^{-1}\left\{ \frac{\partial^{-\alpha}}{\partial t^{-\alpha}} y\,(x,t)\big|_{t=0} \right\}, \quad 0 < \alpha < 1, \tag{45}$$

where

$$\frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}} y(x,t) \tag{46}$$

is the Riemann-Liouville fractional derivative defined as the ordinary derivative of the Riemann-Liouville fractional integral

$$\mathcal{D}^{-\alpha}[y(x,t)] = \frac{\partial^{-\alpha}}{\partial t^{-\alpha}} y(x,t) = \frac{1}{\Gamma(\alpha)} \int_0^t \frac{y(x,t)}{(t-s)^{1-\alpha}} ds, \quad 0 < \alpha < 1. \tag{47}$$

Note that the operator $\mathcal{D}^{\gamma}$ has a different definition depending on whether γ is positive, Eq. (45), or negative, Eq. (47) (see Appendix A). Note too that the inverse Laplace transform of the fractional integral evaluated at time zero, which appears in the operator $\mathcal{D}^{1-\alpha}$ in Eq. (45), will cancel in Eq. (43) if the method of Laplace transforms is applied to find the solution.

The fractional reaction-diffusion equation (43), has a fractional order temporal derivative operating on both the diffusion term and a linear kinetics reaction term. Before leaving this section we note that Eq. (42) for the Fourier-Laplace representation of the CTRW is consistent with Eq. 10 in Ref. [26]. However after representing Eq. (40) by a fractional reaction-diffusion equation in Eq. (43) we can find an explicit solution in this space-time domain without further approximation (see Sec. V.). By comparison, the authors of Ref. [26] obtain an approximate space-time representation of Eq. (10) (see Sec. IV of Ref. [39]).

B. Noninstantaneous creation and annihilation processes

We now consider an extension of the CTRW model to include the addition or removal of walkers at a constant per capita rate during the times that they wait before taking their next step. The CTRW model in this case is similar to that recently formulated [25] for monomolecular conversions. The probability density for arrivals at the end of the $(n+1)$th step in this case is given by

$$q_{n+1}(x,t) = \int_0^t \sum_{x'} [q_n(x',t') e^{\pm k(t-t')}] \psi(t-t') \lambda(x-x') dt'. \tag{48}$$

The exponential factor accounts for the constant per capita increase $(+)$ or decrease $(-)$ during time intervals $t-t'$. In the usual way after summing over n we have

$$q(x,t) = \sum_{x'} \int_0^t \psi(t-t') \lambda(x-x') q(x',t') e^{\pm k(t-t')} dt' + \delta(t)\delta_{x,x_0}. \tag{49}$$

The probability for walkers to be at x at time t is now given by

$$p(x,t) = \int_0^t \Phi(t-t') q(x,t') e^{\pm k(t-t')} dt' \tag{50}$$

$$= \int_0^t \Phi(t-t') e^{\pm k(t-t')} \left(\sum_{x'} \int_0^{t'} \psi(t'-t'') \times \lambda(x-x') q(x',t'') e^{\pm k(t'-t'')} dt'' \right) dt' + \int^t \Phi(t-t') e^{\pm k(t-t')} \delta_{x,x_0} \delta(t') dt' \tag{51}$$

$$= \Phi(t) e^{\pm kt} \delta_{x,x_0} + \sum_{x'} \int_0^t p(x',t') e^{\pm k(t-t')} \times \psi(t-t') \lambda(x-x') dt'. \tag{52}$$

The concentration balance equation in this case is

$$n(x,t) = \Phi(t) e^{\pm kt} n(x,0) + \sum_{x'} \int_0^t n(x',t') e^{\pm k(t-t')} \times \psi(t-t') \lambda(x-x') dt'. \tag{53}$$

and the Fourier-Laplace transform of the balance equation results in

$$\hat{\hat{n}}(q,u) = \hat{\Phi}(u \mp k) \hat{n}(q,0) + \hat{\psi}(u \mp k) \hat{\lambda}(q) \hat{\hat{n}}(q,u). \tag{54}$$

From the result in Eq. (35) we can rewrite the above equation as

$$(u \mp k)\hat{\hat{n}}(q,u) = [1 - \hat{\psi}(u \mp k)] \hat{n}(q,0) + (u \mp k) \hat{\lambda}(q) \hat{\psi}(u \mp k) \hat{\hat{n}}(q,u). \tag{55}$$

In the case of anomalous sub-diffusion we use the asymptotic results in Eqs. (36) and (40) to obtain

$$u\hat{\hat{n}}(q,u) - \hat{n}(q,0) = -\frac{\alpha}{\kappa\Gamma(1-\alpha)\tau_D^{\alpha}} (u \mp k)^{1-\alpha} \frac{q^2\sigma^2}{2} \hat{\hat{n}}(q,u) \pm k\hat{\hat{n}}(q,u) \tag{56}$$

and then after taking the inverse Fourier and Laplace transforms

$$\frac{\partial n(x,t)}{\partial t} = \mathcal{L}^{-1}\left\{ D(\alpha)(u \mp k)^{1-\alpha} \frac{\partial^2 \hat{n}(x,u)}{\partial x^2} \right\} \pm k n(x,t), \tag{57}$$

where it remains to evaluate the inverse Laplace transform represented by the operator $\mathcal{L}^{-1}\{\cdots\}$. This step follows from the identity

$$\mathcal{L}^{-1}\{u^{1-\alpha}\hat{y}(u)\} = \mathcal{D}^{1-\alpha}y(t) \tag{58}$$

together with the shift theorem

$$\mathcal{L}^{-1}\{z(u \pm k)\} = e^{\mp kt}z(t) \tag{59}$$

so that finally we have

$$\frac{\partial n}{\partial t} = e^{\pm kt}D(\alpha)\mathcal{D}^{1-\alpha}\left(e^{\mp kt}\frac{\partial^2 n}{\partial x^2}\right) \pm kn. \tag{60}$$

We note in passing that we can use Leibniz's formula extended to fractional derivatives [40] to rewrite the above equation as

$$\frac{\partial n}{\partial t} = e^{\pm kt}D(\alpha)\sum_{j=0}^{\infty}\binom{1-\alpha}{j}[\mathcal{D}^j e^{\mp kt}]\left[\mathcal{D}^{1-\alpha-j}\frac{\partial^2 n}{\partial x^2}\right] \pm kn \tag{61}$$

or, equivalently,

$$\frac{\partial n}{\partial t} = D(\alpha)\left[\mathcal{D}^{1-\alpha}\frac{\partial^2 n}{\partial x^2}\right] \pm kn + D(\alpha)\sum_{j=0}^{\infty}\frac{\Gamma(2-\alpha)}{\Gamma(1-\alpha-j)(j+1)!}(\mp k)^{j+1}\left[\mathcal{D}^{-\alpha-j}\frac{\partial^2 n}{\partial x^2}\right]. \tag{62}$$

IV. CONTINUOUS TIME RANDOM WALKS WITH SUBDIFFUSION AND GENERAL REACTION KINETICS

A. Instantaneous creation and annihilation processes

In this subsection we consider arbitrary reaction kinetics coupled with the CTRW model to include the instantaneous addition or removal of walkers at the start of the waiting times between steps. The general equation for the density for walkers to arrive at position x at time t at the end of their $(n+1)$th step in this case can be written

$$q_{n+1}(x,t) = \int_0^t \sum_{x'}[q_n(x',t') + s_n(x',t')]\psi(t-t')\lambda(x-x')dt', \tag{63}$$

where $s_n(x,t)$ is the density for walkers that are added and/or removed at the start of the waiting time for the $(n+1)$th step.

If we identify $s(x,t)=\Sigma_{n=0}^{\infty}s_n(x,t)$ then the arrival density is given by

$$q(x,t) = \sum_{x'}\int_0^t \psi(t-t')\lambda(x-x')[q(x',t') + s(x',t')]dt' + \delta(t)\delta_{x,x_0}. \tag{64}$$

The density for a random walker to be at x at time t is now

$$p(x,t) = \int_0^t \Phi(t-t')[q(x,t') + s(x,t')]dt' \tag{65}$$

and the balance equation for the concentration of walkers at x and t becomes

$$n(x,t) = \Phi(t)n(x_0,t) + \sum_{x'}\int_0^t \psi(t-t')\lambda(x-x')n(x',t')dt' + \int_0^t \Phi(t-t')s(x,t')dt'. \tag{66}$$

The asymptotic long time behaviour is then governed by the nonhomogeneous fractional diffusion equation

$$\frac{\partial n}{\partial t} = D(\alpha)\mathcal{D}^{1-\alpha}\left[\frac{\partial^2 n}{\partial x^2}\right] + s(x,t). \tag{67}$$

The above balance equation (66) leading to the nonhomogeneous fractional diffusion equation (67) was motivated by heuristic arguments in Ref. [11]. We could consider these equations with any source or sink term for $s(x,t)$ including reaction terms

$$s(x,t) = f[n(x,t)] \tag{68}$$

but the physical interpretation of this is not clear. For example, in the case of linear reaction dynamics $f(n(x,t) = \pm kn(x,t)$ we have

$$\frac{\partial n}{\partial t} = D(\alpha)\mathcal{D}^{1-\alpha}\left[\frac{\partial^2 n}{\partial x^2}\right] \pm kn(x,t), \tag{69}$$

but this does not equate with the fractional reaction diffusion equation (43), corresponding to the CTRW model with linear reaction dynamics $s(x,t)=\Sigma_{n=0}^{\infty}\pm kq_n(x,t)=\pm kq(x,t)$ that we considered in Sec. III A. To further highlight the difference between the two models it is useful to compare the balance equations directly. Note that we can rewrite the balance equation (33) as

$$n(x,t) = \Phi(t)n(x,0) + \sum_{x'}\int_0^t \psi(t-t')\lambda(x-x')n(x',t')dt' + \frac{r-1}{r}n(x,t). \tag{70}$$

Thus the source term $s(x,t)$ in the general balance equation (66) corresponding to this model is given by equating

$$\int_0^t \Phi(t-t')s(x,t')dt' = \frac{r-1}{r}n(x,t). \tag{71}$$

It is a simple matter to solve this equation for $s(x,t)$ by the method of Laplace transforms. Explicitly we have

$$\hat{s}(x,u) = \frac{r-1}{r}\frac{\hat{n}(x,u)}{\hat{\Phi}(u)} \tag{72}$$

and then after using the asymptotic results in Eqs. (35) and (40) we have

$$s(x,t) = \frac{r-1}{r}\frac{\alpha}{\kappa\Gamma(1-\alpha)\tau_D^{\alpha}}\mathcal{D}^{1-\alpha}n, \tag{73}$$

so that Eq. (43) is again seen as a special case of Eq. (67).

B. Noninstantaneous creation and annihilation processes

In this subsection we consider arbitrary time dependent creation and annihilation processes coupled with the CTRW model to include the non-instantaneous addition or removal of walkers during the waiting times between steps. There are two generalizations as follows.

1. General linear model

In the preceding model for non-instantaneous reactions the proportion of particles and density surviving each step was modeled by the exponential function arising from constant per capita creation and annihilation processes. Here we consider a more general balance equation in which the proportion surviving in each step is any non-negative function $f(t)$. In this case the balance equation can be written as

$$n(x,t) = \Phi(t)f(t)n(x,0) + \sum_{x'} \int_0^t n(x',t')\psi(t-t')\lambda(x-x') \times f(t-t')dt'. \tag{74}$$

Taking the Fourier-Laplace transform of Eq. (74) and using Eq. (36) we find

$$\hat{\hat{n}}(q,u)(1-\mathcal{L}\{\psi(t)f(t)\}(u)) = \mathcal{L}\{\Phi(t)f(t)\}(u)\hat{n}(q,0) - q^2\frac{\sigma^2}{2}\mathcal{L}\{\psi(t)f(t)\}(u)\hat{\hat{n}}(q,u). \tag{75}$$

This equation can be simplified by exploiting relationships between the transforms $\mathcal{L}\{\Phi(t)f(t)\}(u)$ and $\mathcal{L}\{\psi(t)f(t)\}(u)$. First we note

$$\frac{d}{dt}(\Phi(t)f(t)) = -\psi(t)f(t) + f'(t)\Phi(t), \tag{76}$$

where we have used the identity

$$\frac{d\Phi}{dt} = \frac{d}{dt}\left(\int_t^\infty \psi(t')dt'\right) = -\psi(t). \tag{77}$$

Now taking the Laplace transform of Eq. (76) we find

$$u\mathcal{L}\{\Phi(t)f(t)\}(u) - \Phi(0)f(0) = -\mathcal{L}\{\psi(t)f(t)\}(u) + \mathcal{L}\{\Phi(t)f'(t)\}(u) \tag{78}$$

or

$$-\mathcal{L}\{\psi(t)f(t)\}(u) = u\mathcal{L}\{\Phi(t)f(t)\}(u) - f(0) - \mathcal{L}\{\Phi(t)f'(t)\}(u) \tag{79}$$

noting $\Phi(0)=1$. Equation (75) then becomes after some manipulation and inverting the Fourier transform

$$\mathcal{L}\left\{\frac{\partial n}{\partial t}\right\}(u) = \frac{\sigma^2}{2}\frac{\mathcal{L}\{\psi(t)f(t)\}(u)}{\mathcal{L}\{\Phi(t)f(t)\}(u)}\frac{\partial^2 \hat{n}}{\partial x^2} + \frac{\mathcal{L}\{\Phi(t)f'(t)\}(u) + f(0) - 1}{\mathcal{L}\{\Phi(t)f(t)\}(u)}\hat{n}. \tag{80}$$

To simplify further requires detailed information about the small u behaviour of the three transforms $\mathcal{L}\{\Phi(t)f(t)\}(u)$, $\mathcal{L}\{\psi(t)f(t)\}(u)$, and $\mathcal{L}\{\Phi(t)f'(t)\}(u)$. In the case of $f(t)=e^{kt}$, the coefficient of $\hat{n}$ simplifies to k and the ratio $\mathcal{L}\{\psi(t)f(t)\}\times(u)/\mathcal{L}\{\Phi(t)f(t)\}(u)$ simplifies to $\mathcal{L}\{\psi(t)\}(u-k)/\mathcal{L}\{\Phi(t)\}(u-k)$ which can be further simplified given the form of $\psi(t)$.

2. General reaction-kinetics model

We finally consider the extension of the CTRW model for general reaction-kinetic equations for reactions between the end of the nth step and the end of the $(n+1)$th step, i.e.,

$$\frac{\partial q_n}{\partial t} = f(q_n). \tag{81}$$

In this general case we can integrate over the time interval $t-t'$ to write the arrival density after the $(n+1)$th step as

$$q_{n+1}(x,t) = \int_0^t \sum_{x'} F^{-1}\{F[q_n(x,t')] + (t-t')\}\psi(t-t') \times \lambda(x-x')dt', \tag{82}$$

where

$$F'(q_n) = \frac{1}{f(q_n)}. \tag{83}$$

We can also write

$$p(x,t) = \int_0^t \Phi(t-t')F^{-1}\{F[q(x,t')] + (t-t')\}dt', \tag{84}$$

where $q(x,t)=\Sigma_{n=0}^{\infty}q_n(x,t)$ but it is not clear how to obtain the balance equation from Eqs. (82) and (84) except in the special linear case $f(q_n)=\pm kq_n$.

V. COMPARISON OF FRACTIONAL REACTION-DIFFUSION EQUATION MODELS

In this section we present solutions to the three model systems.

Model I:

$$\frac{\partial n}{\partial t} = D(\alpha)\mathcal{D}^{1-\alpha}\left[\frac{\partial^2 n}{\partial x^2}\right] \pm kn. \tag{85}$$

Model II:

$$\frac{\partial n}{\partial t} = D(\alpha)\mathcal{D}^{1-\alpha}\left[\frac{\partial^2 n}{\partial x^2}\right] \pm \frac{k}{1\pm k}\left(\frac{\alpha}{\kappa\Gamma(1-\alpha)\tau_D^\alpha}\right)\mathcal{D}^{1-\alpha}n. \tag{86}$$

Model III:

$$\frac{\partial n}{\partial t} = D(\alpha)e^{\pm kt}\mathcal{D}^{1-\alpha}\left(e^{\mp kt}\frac{\partial^2 n}{\partial x^2}\right) \pm kn. \tag{87}$$

In the infinite domain (Greens solution) the initial condition is taken to be the delta function, i.e., $n(x,0)=\delta(x)$. It is convenient to rewrite the models I and II equations (85) and (86) in the form

$$\frac{\partial n}{\partial t} = D(\alpha)\mathcal{D}^{1-\alpha}\frac{\partial^2 n}{\partial x^2} + K\mathcal{D}^{1-\beta}n, \tag{88}$$

where $\beta=1$ and $K=\pm k$ in model I and $\beta=\alpha$ and $K=\pm\frac{k}{(1\pm k)}\left(\frac{\alpha}{k\Gamma(1-\alpha)\tau_D^{\alpha}}\right)$ in model II. The solutions to the two models can thus be constructed as special cases of Eq. (88). As a further simplification we also write model III, Eq. (87), as

$$\frac{\partial n}{\partial t} = e^{Kt}D(\alpha)\mathcal{D}^{1-\alpha}\left(e^{-Kt}\frac{\partial^2 n}{\partial x^2}\right) + Kn, \tag{89}$$

where $K=\pm k$.

A. Solution model I and II

From Appendix B we have the infinite domain (Green's solution) of Eq. (88) given by

$$n(x,t) = \frac{1}{\sqrt{4\pi Dt^{\alpha}}}\sum_{j=0}^{\infty}\frac{(Kt^{\beta})^j}{j!} \times H_{1,2}^{2,0}\left[\frac{x^2}{4Dt^{\alpha}}\middle|\begin{matrix}\left(1-\frac{\alpha}{2}+\beta j,\alpha\right) & \\ (0,1) & \left(\frac{1}{2}+j,1\right)\end{matrix}\right]. \tag{90}$$

For model I we set $\beta=1$ and $K=\pm k$ to give

$$n(x,t) = \frac{1}{\sqrt{4\pi Dt^{\alpha}}}\sum_{j=0}^{\infty}\frac{(\pm kt)^j}{j!} \times H_{1,2}^{2,0}\left[\frac{x^2}{4Dt^{\alpha}}\middle|\begin{matrix}\left(1-\frac{\alpha}{2}+j,\alpha\right) & \\ (0,1) & \left(\frac{1}{2}+j,1\right)\end{matrix}\right] \tag{91}$$

and for model II we set $\beta=\alpha$ and $K=\pm k^*$ to give

$$n(x,t) = \frac{1}{\sqrt{4\pi Dt^{\alpha}}}\sum_{j=0}^{\infty}\frac{(\pm k^* t^{\alpha})^j}{j!} \times H_{1,2}^{2,0}\left[\frac{x^2}{4Dt^{\alpha}}\middle|\begin{matrix}\left(1-\frac{\alpha}{2}+\alpha j,\alpha\right) & \\ (0,1) & \left(\frac{1}{2}+j,1\right)\end{matrix}\right], \tag{92}$$

where

$$\pm k^* = \frac{\pm k}{1\pm k}\frac{\alpha}{\Gamma(1-\alpha)}. \tag{93}$$

B. Solution model III

To find the solution to Eq. (89) we first make the substitution

$$n(x,t) = e^{Kt}y(x,t) \tag{94}$$

noting that n and y have the same initial condition. Equation (89) then becomes after simplifing

$$\frac{\partial y}{\partial t} = D\mathcal{D}^{1-\alpha}\frac{\partial^2 y}{\partial x^2} \tag{95}$$

which is the fractional diffusion equation. Equation (95) has the solution in the infinite domain [3]

$$y(x,t) = \frac{1}{\sqrt{4\pi Dt^{\alpha}}} \times H_{1,2}^{2,0}\left[\frac{x^2}{4Dt^{\alpha}}\middle|\begin{matrix}\left(1-\frac{\alpha}{2},\alpha\right) & \\ (0,1) & \left(\frac{1}{2},1\right)\end{matrix}\right]. \tag{96}$$

The solution of model III in the infinite domain is then (with $K=\pm k$)

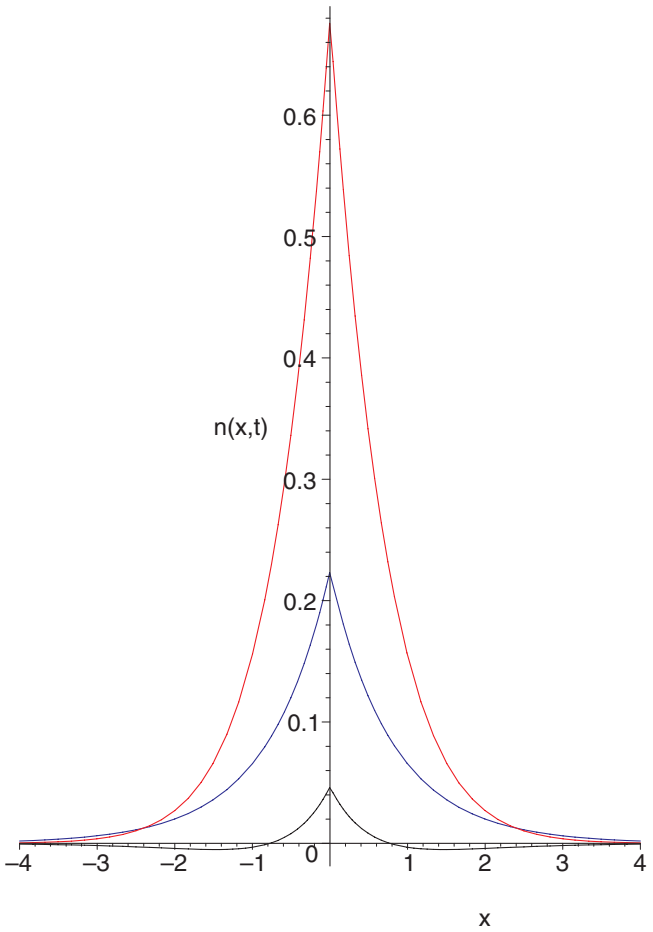

FIG. 1. (Color online) The infinite solution for model I at the dimensionless times $t=0.1$ (red), 1.0 (blue), and 5.0 (black) with $K=-1$, $D=1$, and $\alpha=1/2$. The peak height decreases with increasing time.

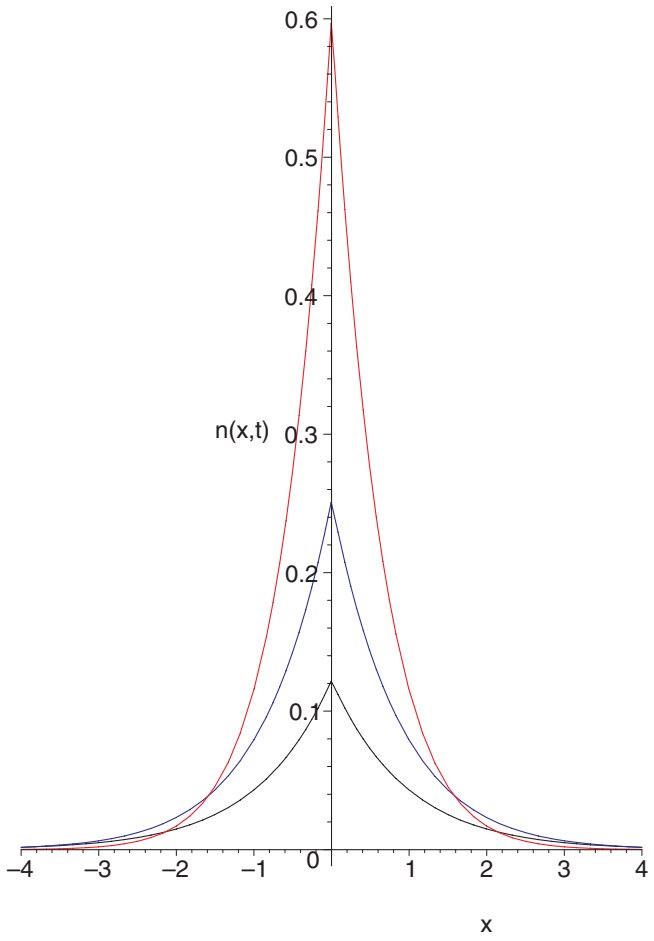

FIG. 2. (Color online) The infinite solution for model II at the dimensionless times $t=0.1$ (red), 1.0 (blue), and 5.0 (black) with $K=-1$, $D=1$, and $\alpha=1/2$. The peak height decreases with increasing time.

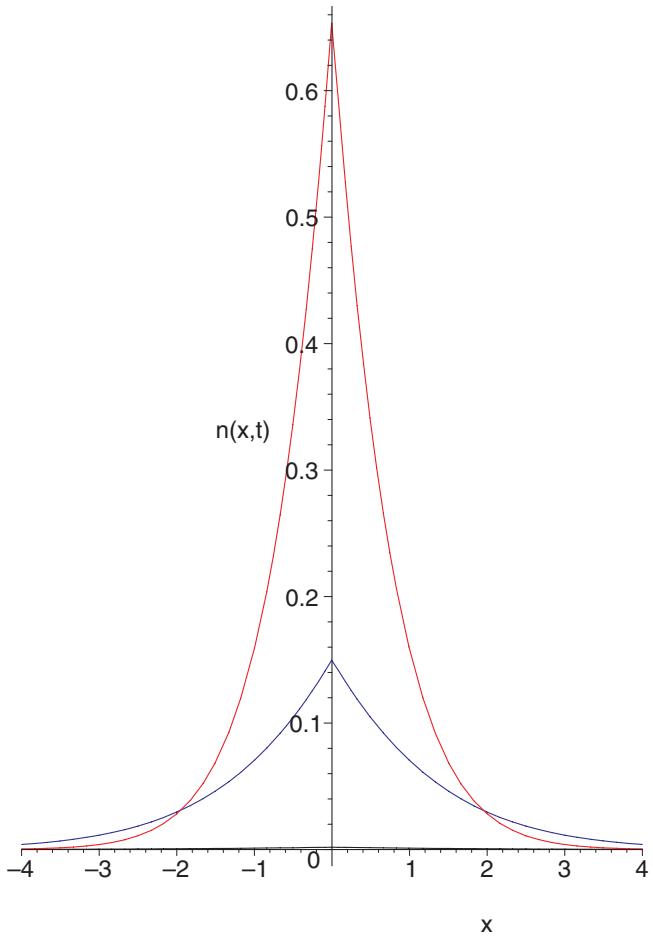

FIG. 3. (Color online) The infinite solution for model III at the dimensionless times $t=0.1$ (red), 1.0 (blue), and 5.0 (black) with $K=-1$, $D=1$, and $\alpha=1/2$. The peak height decreases with increasing time. The profile at $t=5.0$ lies along the x axis.

$$n(x,t) = \frac{e^{\pm kt}}{\sqrt{4\pi D t^{\alpha}}} \times H_{1,2}^{2,0}\left[\frac{x^2}{4Dt^{\alpha}} \middle| \begin{matrix} \left(1-\frac{\alpha}{2},\alpha\right) & \\ (0,1) & \left(\frac{1}{2},1\right) \end{matrix} \right]. \quad (97)$$

C. Particular results and moments

In Figs. 1–3 the infinite domain solution of the equations of models I, II, and III [Eqs. (88) and (89)] are shown at various times in the case $\alpha=1/2$, $K=-1$, and $D=1$. Note that in the case of model I the solution has become negative and hence is physically unrealistic at $t\approx 5$ (Figs. 1 and 4). The reason for this is simply that the reaction term in this model is attempting to remove more walkers than there are available to jump. The solution (Figs. 2 and 3) in the case of the other two models is always positive because we only ever attempt to remove a fraction of the walkers that are available. The solution in the case of model III decays to zero more rapidly than in the case of model II.

In Figs. 5 and 6, the zeroth order and second order moments are given for each model which are

$$\langle x^{(0)}(t)\rangle = \begin{cases} e^{Kt}, & \text{models I, III,} \\ E_{\alpha,1}(Kt^{\alpha}), & \text{model II} \end{cases} \quad (98)$$

and

$$\langle x^{(2)}(t)\rangle = \begin{cases} 2Dt^{\alpha}E_{1,\alpha}(Kt), & \text{model I,} \\ 2Dt^{\alpha}E_{\alpha,1}(Kt^{\alpha}), & \text{model II,} \\ \dfrac{2Dt^{\alpha}}{\Gamma(1+\alpha)}e^{Kt}, & \text{model III,} \end{cases} \quad (99)$$

where $E_{\alpha,\beta}(z)$ is the generalized Mittag-Leffler function (see Appendix B).

In Figs. 7–9 the infinite domain solution of the equations of models I, II, and III [Eqs. (88) and (89)] are shown at various times in the case $\alpha=1/2$, $K=1$, and $D=1$. Note thatin the case of model I the solution does not become negative as it did previously (Fig. 7).

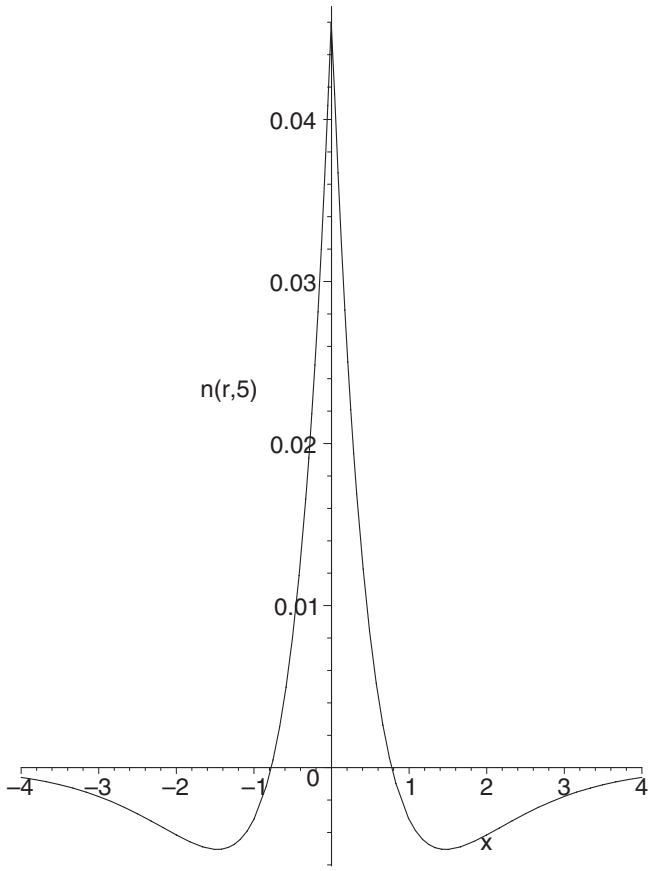

FIG. 4. The infinite solution for model I at the dimensionless time $t=5.0$ with $K=-1$, $D=1$, and $\alpha=1/2$.

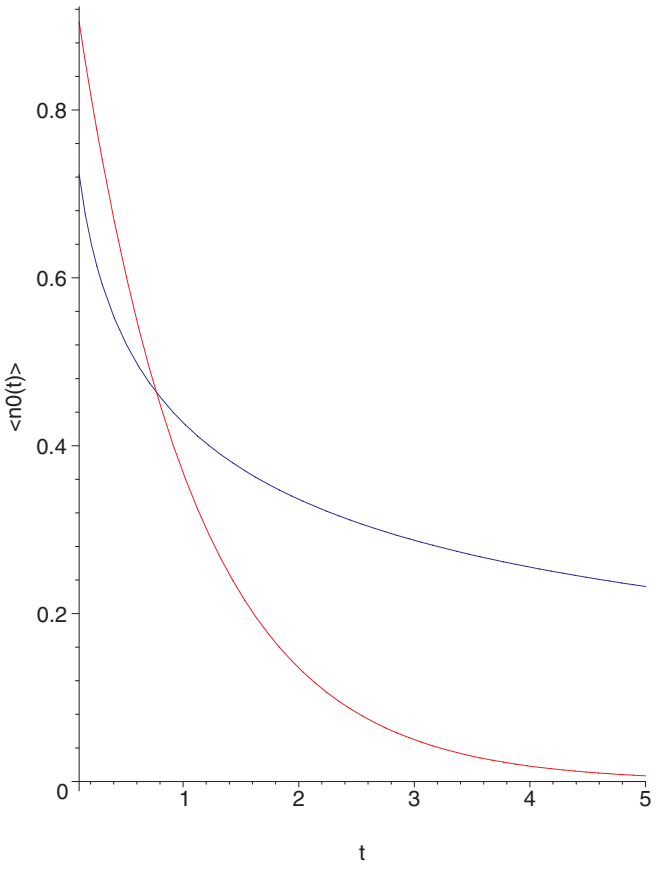

FIG. 5. (Color online) The zeroth order moments of the infinite solution for models I and III (red), and model II (blue) with $K=-1$, $D=1$, and $\alpha=1/2$. The result for model II is the upper curve at $t=5$.

VI. SUMMARY AND DISCUSSION

In this paper we revisited the CTRW model for anomalously diffusing particles to incorporate linear reaction dynamics in a mesoscopic level description. The primary motivation for this work was to relate the reaction terms in fractional order reaction-diffusion equations to physical processes in a mesoscopic description and where possible to elucidate different solutions characteristic of these different physical processes. Three different model systems were explored in detail. Model I was based on an earlier CTRW balance equation that we originally motivated with heuristic arguments in Ref. [11]. In this model a fraction of the walkers are added or removed at a constant rate in time, independent of the diffusion process. This leads to a fractional reaction-diffusion equation with linear reaction dynamics added to a standard fractional diffusion term, i.e., a fractional order temporal differential operator $\mathcal{D}^{1-\alpha}$, operating on the Laplacian diffusion term. If the reaction term is negative in this model then the solution becomes negative (so that the model breaks down). This compares with the standard reaction diffusion equation with negative linear reaction kinetics where the solution remains positive for all times. This is a clear demonstration that in anomalous subdiffusion with reactions the removal of walkers cannot be performed independent of the diffusion process.

In model II a constant proportion of the available walkers are added or removed instantaneously at the start of each jump. In this case the CTRW model leads to a fractional reaction diffusion equation with a fractional order temporal differential operator $\mathcal{D}^{1-\alpha}$ operating on both the Laplacian diffusion term and a linear reaction dynamics term. This model is special case of the fractional reaction-diffusion model proposed by Yuste, Acedi, and Lindenberg [19] for general (possibly nonlinear) reaction kinetics. The model does not yield unphysical negative solutions but it does not recover the mean field reaction kinetics equation for homogeneous concentrations.

In model III the available walkers are added or removed at a constant rate during the time interval between steps. A similar CTRW model was formulated recently for monomolecular reactions [25]. The resultant fractional reaction-diffusion equation that we derived from the CTRW model in this case has a linear reaction dynamics term added to a nonstandard fractional diffusion term, explicitly, $e^{\pm kt}D(\alpha)\mathcal{D}^{1-\alpha}\left(e^{\mp kt}\frac{\partial^2 n}{\partial x^2}\right)$. This model equation does not lead to unphysical negative solutions and it recovers the mean field reaction kinetics equation for homogeneous concentrations.

The development of fractional reaction diffusion equations as models for anomalous subdiffusion with nonlinear reaction kinetics remains an open problem. While it is a simple matter to generalize the above fractional reaction-diffusion equations by replacing the linear reaction dynamics term in each case by a nonlinear reaction term the physical

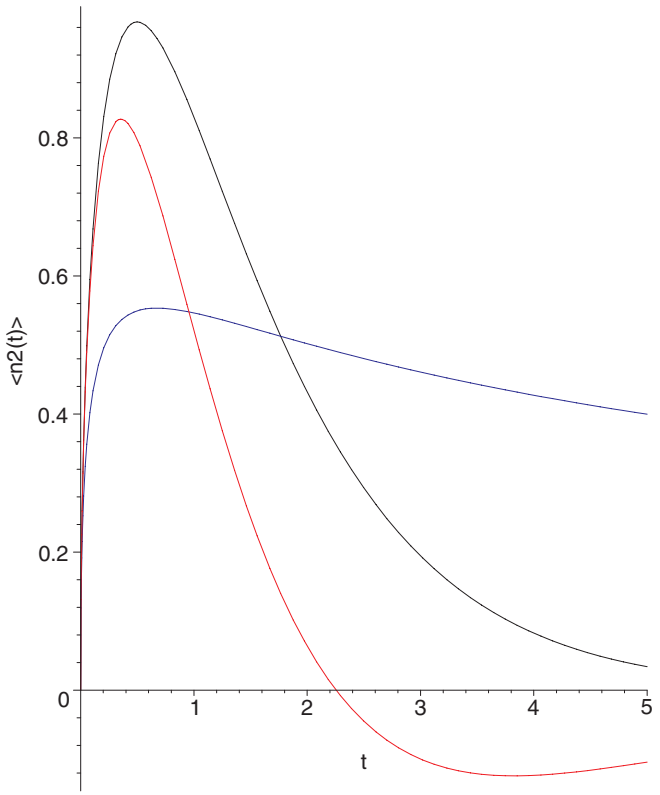

FIG. 6. (Color online) The second order moments of the infinite solution for models I (red), II (blue), and III (black) with $K=-1$, $D=1$, and $\alpha=1/2$. At $t=5$ the result for model II is the upper curve and the result for model I is the lower curve.

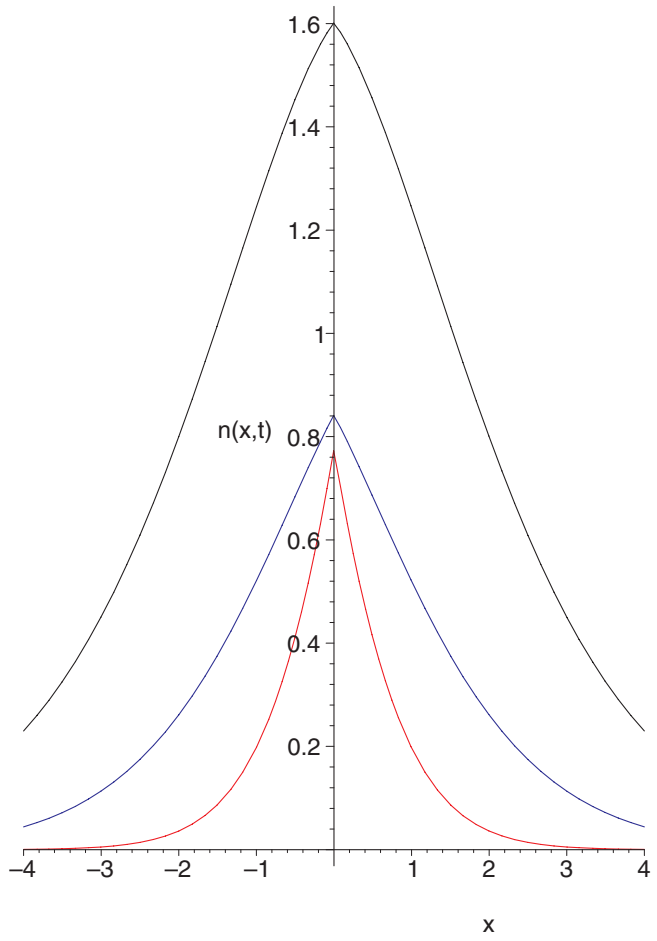

FIG. 7. (Color online) The infinite solution for model I at the dimensionless times $t=0.1$ (red), 1.0 (blue), and 5.0 (black) with $K=1$, $D=1$, and $\alpha=1/2$. The peak height increases with increasing time.

meaning of this is not clear and it may lead to unphysical behavior. This is because the simplification in the CTRW models that results from replacing $\Sigma_n f(q_n)$ with $f(\Sigma_n q_n)$ does not apply if $f(q_n)$ is a nonlinear function. The explicit linear solutions and the physical interpretation of the linear models in this paper provides a useful guide for future theoretical and computational studies.

ACKNOWLEDGMENTS

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APPENDIX A: RIEMANN-LIOUVILLE FRACTIONAL OPERATORS

The Riemann-Liouville fractional integral is given by

$$\frac{\partial^{-\alpha}}{\partial t^{-\alpha}} y(x,t) = \frac{1}{\Gamma(\alpha)} \int_0^t \frac{y(x,t)}{(t-s)^{1-\alpha}} ds, \quad \alpha > 0. \tag{A1}$$

and the Riemann-Liouville fractional derivative is given by

$$\frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}} y(x,t) = \frac{\partial}{\partial t} \frac{1}{\Gamma(\alpha)} \int_0^t \frac{y(x,t)}{(t-s)^{1-\alpha}} ds \tag{A2}$$

for $0<\alpha<1$. In the paper we have introduced the related operators for $0<\alpha<1$,

$$\mathcal{D}^{1-\alpha}[y(x,t)] = \frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}} y(x,t) + \mathcal{L}^{-1}\left\{ \frac{\partial^{-\alpha}}{\partial t^{-\alpha}} y\,(x,t)|_{t=0} \right\} \tag{A3}$$

and

$$\mathcal{D}^{-\alpha} = \frac{\partial^{-\alpha}}{\partial t^{-\alpha}} y(x,t). \tag{A4}$$

APPENDIX B: SOLUTION OF LINEAR FRACTIONAL REACTION DIFFUSION EQUATIONS

In this appendix we consider the infinite domain (Green's solution) for the general linear fractional reaction-diffusion equation given by

$$\frac{\partial n}{\partial t} = D(\alpha)\mathcal{D}^{1-\alpha}\frac{\partial^2 n}{\partial x^2} + K\mathcal{D}^{1-\beta} n, \tag{B1}$$

where the fractional order temporal differential operator $\mathcal{D}^{1-\alpha}$ is defined in the paper in Eq. (45).

To solve models I and II we use an approach similar to that recently described by Langlands for modified fractional

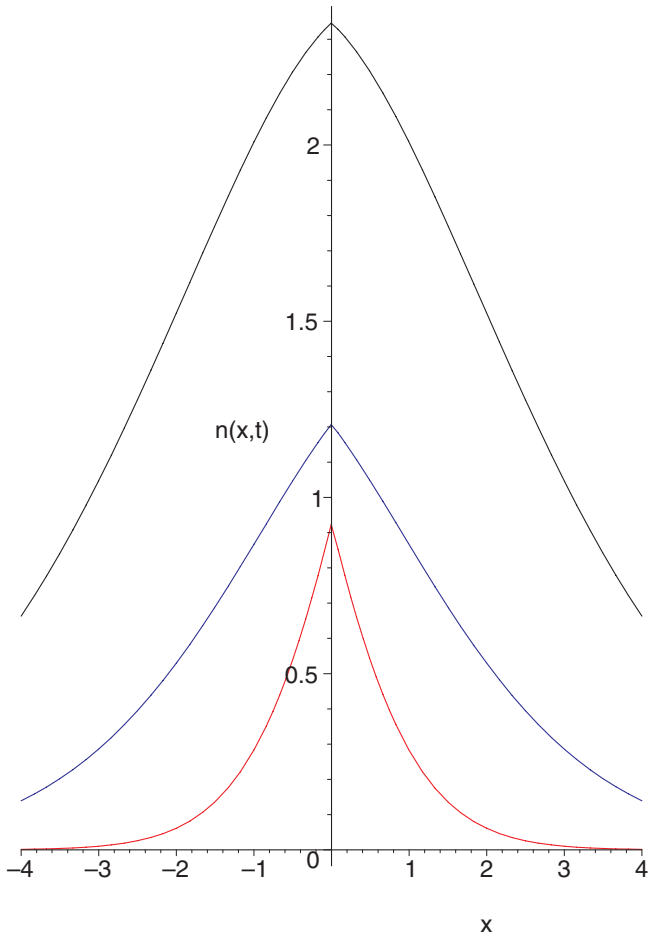

FIG. 8. (Color online) The infinite solution for model II at the dimensionless times $t=0.1$ (red), 1.0 (blue), and 2.0 (black) with $K=1$, $D=1$, and $\alpha=1/2$. The peak height increases with increasing time.

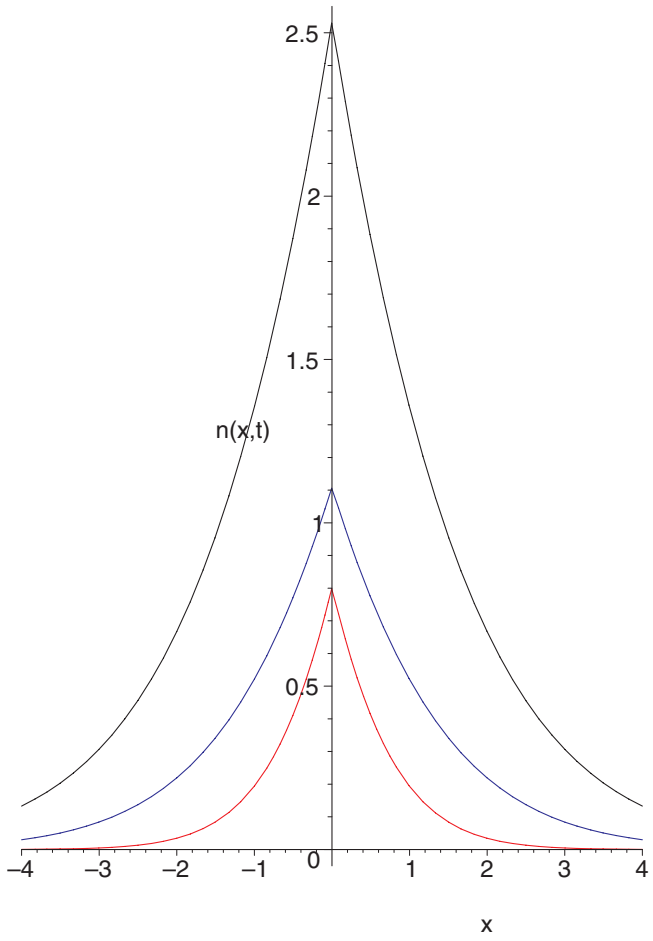

FIG. 9. (Color online) The infinite solution for model III at the dimensionless times $t=0.1$ (red), 1.0 (blue), and 2.0 (black) with $K=1$, $D=1$, and $\alpha=1/2$. The peak height increases with increasing time.

diffusion equations [41]. First we take the Fourier-Laplace transform of Eq. (88)

$$u\hat{\hat{n}} - \hat{n}(q,0) = -D(\alpha)q^2u^{1-\alpha}\hat{\hat{n}} + Ku^{1-\beta}\hat{\hat{n}} \tag{B2}$$

which upon solving for $\hat{\hat{n}}$ gives

$$\hat{\hat{n}}(q,u) = \frac{u^{\alpha-1}\hat{n}(q,0)}{u^\alpha + Dq^2 - Ku^{\alpha-\beta}}. \tag{B3}$$

This can be rewritten in the form (taking into account the initial condition)

$$\hat{\hat{n}}(q,u) = \sum_{j=0}^{\infty} \frac{K^j}{j!}\frac{j!u^{\alpha-[1+(\beta-\alpha)j]}}{(u^\alpha + Dq^2)^{j+1}}. \tag{B4}$$

Now from Podlubny [42] we have the Laplace transform of involving the derivative of the Mittag-Leffler function is

$$\mathcal{L}\{t^{\alpha j+\beta-1}E^{(j)}_{\alpha,\beta}(-at^\alpha)\}(u) = \frac{j!u^{\alpha-\beta}}{(u^\alpha + a)^{j+1}}, \tag{B5}$$

where the derivative of the Mittag-Leffler function is given by

$$E^{(j)}_{\alpha,\beta}(y) = \frac{d^jE_{\alpha,\beta}(y)}{dy^j} = \sum_{n=0}^{\infty}\frac{(j+n)!y^n}{n!\Gamma[\alpha(j+n)+\beta]}. \tag{B6}$$

Setting $a=q^2$, and $\beta=1+(\beta-\alpha)j$ in Eq. (B5) we can then invert the Laplace transform in Eq. (B4) to give

$$\hat{n}(q,t) = \sum_{j=0}^{\infty}\frac{(Kt^\beta)^j}{j!}E^{(j)}_{\alpha,1+(\beta-\alpha)j}(-q^2Dt^\alpha). \tag{B7}$$

To invert the Fourier transform we note that the derivative of the Mittag-Leffler function in Eq. (B6) can be written as a Fox function (see, e.g., Ref. [3])

$$E^{(j)}_{\alpha,\beta}(y) = H^{1,1}_{1,2}\left[-y\left|\begin{matrix}(-j,1)\\(0,1)\end{matrix}\quad\begin{matrix}\\[1-(\alpha j+\beta),\alpha]\end{matrix}\right.\right]. \tag{B8}$$

So to invert the transform in Eq. (B7) we need only to invert, for each j, the term

$$\hat{h}_j(q,t) = E^{(j)}_{\alpha,1+(\beta-\alpha)j}(-Dq^2t^\alpha) = H^{1,1}_{1,2}\left[Dq^2t^\alpha \left| \begin{matrix} (-j,1) \\ (0,1) \end{matrix} \quad \begin{matrix} \\ (-\beta j,\alpha) \end{matrix} \right.\right]. \tag{B9}$$

To invert the Fourier transform we use the following relation between the Mellin transform of a Fourier transformed function and its Mellin transform in the case of an even function $f(x)$

$$\mathcal{M}\{\mathcal{F}[f(x)](q)\}(z) = 2\Gamma(z)\cos\left(\frac{\pi z}{2}\right)\mathcal{M}\{f(x)\}(1-z). \tag{B10}$$

So to invert the Fourier transform $\hat{h}_j(q,t)$ in Eq. (B9) we need to first evaluate its Mellin transform to find the Mellin transform of $h_j(x,t)$ using Eq. (B10). The Mellin transform then need only be inverted to find the Fourier inverse $h_j(x,t)$.

Taking the Mellin transform of Eq. (B9) using the Mellin transform of a Fox function [43], the identity [44]

$$\mathcal{M}\{\phi(ax^p)\}(z) = \frac{1}{p}a^{-z/p}\mathcal{M}\{\phi(x)\}\left(\frac{z}{p}\right), \quad p>0,\ a>0 \tag{B11}$$

and Eq. (B10) we find

$$\mathcal{M}\{h_j(x,t)\}(z) = \frac{1}{2}\frac{1}{\sqrt{4\pi Dt^\alpha}}\left(\frac{1}{\sqrt{4Dt^\alpha}}\right)^{-z}\frac{\Gamma\left(\frac{z}{2}\right)\Gamma\left(\frac{1}{2}+j+\frac{z}{2}\right)}{\Gamma\left(1-\frac{\alpha}{2}+\beta j+\frac{\alpha z}{2}\right)}. \tag{B12}$$

Inverting the Mellin transform Eq. (B12) and noting $x=|x|$ we find

$$h_j(x,t) = \frac{1}{2}\frac{1}{\sqrt{4\pi Dt^\alpha}} \times H^{2,0}_{1,2}\left[\frac{|x|}{\sqrt{4Dt^\alpha}} \left| \begin{matrix} \left(1-\frac{\alpha}{2}+\beta j,\frac{\alpha}{2}\right) \\ \left(0,\frac{1}{2}\right) \end{matrix} \quad \begin{matrix} \\ \left(\frac{1}{2}+j,\frac{1}{2}\right) \end{matrix} \right.\right]. \tag{B13}$$

Using the identity

$$H^{m,n}_{p,q}\left[x \left| \begin{matrix} (a_p,\alpha_p) \\ (b_q,\beta_q) \end{matrix} \right.\right] = cH^{m,n}_{p,q}\left[x^c \left| \begin{matrix} (a_p,c\alpha_p) \\ (b_q,c\beta_q) \end{matrix} \right.\right] \tag{B14}$$

with $c=\frac{1}{2}$ we arrive at the expression for $h_j(x,t)$:

$$h_j(x,t) = \frac{1}{\sqrt{4\pi Dt^\alpha}} \times H^{2,0}_{1,2}\left[\frac{x^2}{4Dt^\alpha} \left| \begin{matrix} \left(1-\frac{\alpha}{2}+\beta j,\alpha\right) \\ (0,1) \end{matrix} \quad \begin{matrix} \\ \left(\frac{1}{2}+j,1\right) \end{matrix} \right.\right]. \tag{B15}$$

The infinite domain (Green's solution) of Eq. (88) by Eqs. (B7) and (B15),

$$n(x,t) = \frac{1}{\sqrt{4\pi Dt^\alpha}}\sum_{j=0}^{\infty}\frac{(Kt^\beta)^j}{j!} \times H^{2,0}_{1,2}\left[\frac{x^2}{4Dt^\alpha} \left| \begin{matrix} \left(1-\frac{\alpha}{2}+\beta j,\alpha\right) \\ (0,1) \end{matrix} \quad \begin{matrix} \\ \left(\frac{1}{2}+j,1\right) \end{matrix} \right.\right]. \tag{B16}$$

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