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Subdiffusion-limited reactions

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Abstract

We consider the coagulation dynamics $A + A \to A$ and the annihilation dynamics $A + A \to 0$ for particles moving subdiffusively in one dimension, both on a lattice and in a continuum. The analysis combines the "anomalous kinetics" and "anomalous diffusion" problems, each of which leads to interesting dynamics separately and to even more interesting dynamics in combination. We calculate both short-time and long-time concentrations, and compare and contrast the continuous and discrete cases. Our analysis is based on the fractional diffusion equation and its discrete analog.

1. Introduction

Diffusion-limited reactions in low-dimensional geometries have been studied intensely because they exhibit "anomalous kinetics", that is, behavior different from that predicted by the laws of mass action in well-stirred systems [1]. Among the simplest and most extensively studied are single species diffusion-limited coagulation ($A + A \to A$ or $A + A \rightleftharpoons A$) [2] and annihilation ($A + A \to 0$) [2,3]. These reactions, which show anomalous behavior in one dimension, are of particular theoretical interest because they lend themselves to *exact* solution in one dimension. Exact one-dimensional solutions can be obtained for diffusion in continuous [2,4–9] as well as in discrete [2,11–13] systems. A particularly elegant solution of the coagulation problem is provided by the method of intervals. This method focuses on the diffusive evolution of empty intervals, that is, of intervals that contain no particles [2,6–8,10]. The empty interval equation turns out to be linear and hence exactly solvable. Originally developed for continuous systems, the method has been extended to discrete lattices [11–13]. The method of intervals cannot be directly adapted to the annihilation reaction, but a new formalism, the method of odd/even intervals which keeps track of the parity (even or odd) of the number of particles in an interval, has recently been developed [8,9]. Again, the odd/even interval equation turns out to be linear and hence exactly solvable.

The anomalies of the $A + A$ problem in one dimension are typically displayed in two ways: one is through the time dependence of the reactant

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concentration $c(t)$, which for the $A+A\to A$ and the $A+A\to 0$ reactions in infinite systems decays asymptotically as $t^{-1/2}$ instead of the law of mass action decay t^{-1}; the other is through the interparticle distribution function $p(x,t)$, which is the (conditional) probability density for finding the nearest particle at a distance x on one side of a given particle. This function scales as $x/t^{1/2}$, in typical diffusive fashion. In one dimension a gap develops around each particle that leads to a more ordered spatial distribution than the exponential distribution implicit in well-stirred systems and "explains" the relative slowing down of the reaction.

In a parallel development, the problem of "anomalous diffusion" has also attracted a great deal of attention [14–16]. The universally accepted characterization of anomalous (as in "not ordinary") diffusion is through the mean squared displacement of a process $x(t)$ for large t,

$$x^2(t)\sim\frac{2K_\alpha}{\Gamma(1+\alpha)}t^\alpha. \tag{1}$$

Ordinary diffusion ($\alpha=1$, $K_1\equiv D$) follows Gaussian statistics and Fick's second law for the probability density for finding the process at x at time t,

$$\frac{\partial}{\partial t}P(x,t)=D\frac{\partial^2}{\partial x^2}P(x,t), \tag{2}$$

leading to linear growth of $\langle x^2(t)\rangle$ with time. Anomalous diffusion is characterized by a nonlinear dependence. If $0<\alpha<1$ the process is subdiffusive or dispersive; if $\alpha>1$ it is superdiffusive. Anomalous diffusion is associated with many physical systems and is not due to any single universal cause, but it is certainly ubiquitous. Nor is anomalous diffusion modeled in a universal way; among the more successful approaches to the subdiffusive problem, which is the case we consider in this work, have been continuous time random walks with non-Poissonian waiting time distributions [14], and fractional dynamics approaches in which the diffusion equation (2) is replaced by the generalized diffusion equation [15–21]

$$\frac{\partial}{\partial t}P(x,t)=K_\alpha\,{}_0D_t^{1-\alpha}\frac{\partial^2}{\partial x^2}P(x,t), \tag{3}$$

where ${}_0D_t^{1-\alpha}$ is the Riemann–Liouville operator,

$${}_0D_t^{1-\alpha}P(x,t)=\frac{1}{\Gamma(\alpha)}\frac{\partial}{\partial t}\int_0^t \mathrm{d}\tau\frac{P(x,\tau)}{(t-\tau)^{1-\alpha}}, \tag{4}$$

and K_α is the generalized diffusion coefficient that appears in Eq. (1). Some limitations of this description and some connections between the generalized diffusion equation and continuous random walk formulations have been discussed recently [22,23].

In this paper we consider a combination of these two phenomena, namely, the kinetics of $A+A$ reactions of particles that move subdiffusively in one dimension [24]. Some aspects of this problem have also been considered using the waiting time distribution approach [25,26]. Those solutions require approximations relating the reactant concentration to the distinct number of sites visited by a particle [25], or the waiting time distributions for single particles to the waiting time distributions for relative motion [26]. Here we adapt the fractional dynamics approach to the problem and take advantage of the fact that the resulting generalized diffusion equations can be solved in closed form [24]. We consider both coagulation and annihilation reactions.

In Section 2 we develop the fractional diffusion equations from which one obtains the concentration of reactant as a function of time. For the coagulation reaction we generalize the empty interval method [2,6] and, for the annihilation reaction, the odd/even interval method [8,9]. The solutions are presented in Section 3. Sections 2 and 3 deal with kinetics on continuum one-dimensional systems; in Section 4 we extend the analysis to reactions on a lattice. The differences between the continuum and discrete results are most pronounced at early times (long-time differences are due to finite size effects that get pushed to longer times if one deals with larger systems). We conclude with a recapitulation in Section 5.

2. Evolution equations for subdiffusive particles

2.1. Empty interval method for coagulation reaction

Consider first the coagulation reaction $A+A\to A$ when the particles move by ordinary

diffusion. The probability distribution function for the position x of any *one A* particle *in the absence of reaction* obeys the diffusion equation (2). The coagulation problem can be formulated in terms of the probability $E(x,t)$ that an interval of length x is empty of particles at time t. This "empty interval" function obeys the diffusion equation [2,6]

$$\frac{\partial}{\partial t}E(x,t) = 2D\frac{\partial^2}{\partial x^2}E(x,t). \tag{5}$$

The derivation of this equation is straightforward and recognizes that an empty interval is shortened or lengthened by movement of particles in and out at either end according to the dynamics described by Eq. (2).

It is instructive to recall this derivation as given in [6,7]. The reasoning is more transparent if the diffusion processes that lead to the change $\partial E(x,t)/\partial t$ are described on a lattice with lattice spacing Δx and sites labeled by integers. In this lattice $E_n(t)$ gives the probability that sites 1–n, for example, are empty at time t. Since the event E_{n+1} contains the event E_n, the probability that sites 1–n are empty but that there is a particle at site $n+1$ is $E_{n+1} - E_n$. The particles move randomly to the nearest lattice site with a hopping rate $2D/(\Delta x)^2$, the rate $D/(\Delta x)^2$ to the right being equal to the rate to the left. If the particle at $n+1$ moves to site n in a short time interval Δt, E_n will decrease by $[D/(\Delta x)^2](E_n - E_{n+1})\Delta t$. On the other hand, E_n may increase by the departure of a particle at site n to site $n+1$; the associated increase is $[D/(\Delta x)^2](E_{n-1} - E_n)\Delta t$. The same entry and exit processes can take place at the other end of the interval. Combining these four processes then gives for the change in E_n:

$$\frac{\Delta E_n}{\Delta t} = \frac{2D}{(\Delta x)^2}(E_{n+1} - 2E_n + E_{n-1}). \tag{6}$$

The coagulation reaction fixes the boundary condition. Coagulation involves adjacent occupied sites and either of the two particles hopping onto the other, thereby disappearing. Two adjacent sites can both be occupied, or one can be occupied and the other empty (probability $2(E_1 - E_2)$ because this can occur in two ways) or both can be empty (probability E_2). Since this covers all possibilities, the probability that two adjacent sites are occupied is therefore $1 - 2E_1 + E_2$. The change in E_1 is thus

$$\frac{\Delta E_1}{\Delta t} = \frac{2D}{(\Delta x)^2}(1 - 2E_1 + E_2), \tag{7}$$

and for this equation to fit the pattern of Eq. (6) it is necessary to require the boundary condition

$$E_0 = 0. \tag{8}$$

Letting $x = n\Delta x$ and both Δx and $\Delta t \to 0$ then leads to the continuous equation (5) with the boundary condition

$$E(0,t) = 0. \tag{9}$$

The other boundary condition requires that the population of particles be non-vanishing:

$$E(\infty,t) = 0. \tag{10}$$

The empty interval dynamics is thus essentially the same as that of individual particles in the absence of reaction, but with different boundary conditions and a diffusion coefficient $2D$ that reflects the fact that the relative motion of two diffusive particles involves twice the diffusion coefficient of each particle alone.

The connection between the empty interval function and the observables of interest is obtained as follows [6,7]. Back in the discrete formulation, the probability that a site is occupied (i.e. not empty) is $1 - E_1$, and the concentration of particles is therefore

$$c(t) = \frac{(1 - E_1)}{\Delta x} \quad \to \quad c(t) = -\left.\frac{\partial E(x,t)}{\partial x}\right|_{x=0}, \tag{11}$$

where we have exhibited the continuum limit. The interparticle distribution function $p_n(t)$ is the probability that the nearest neighbor to one side of a given particle is n lattice spacings away. This probability is related to E_n by

$$E_n = c\Delta x \sum_{k=n+1}^{\infty}\sum_{m=k}^{\infty} p_m. \tag{12}$$

The first sum insures that the next neighbor is at least k sites away and the second that k is at least $n+1$. The normalization takes into account that the average distance between the particles is the reciprocal of the concentration,

$$\langle n\Delta x\rangle = \sum_{n=1}^{\infty} np_n\Delta x = \frac{1}{c}. \tag{13}$$

Eq. (12) can be inverted:

$$c\,p_n = \frac{(E_{n+1} - 2E_n + E_{n-1})}{\Delta x} \quad \rightarrow$$
$$c(t)\,p(x,t) = \frac{\partial^2 E(x,t)}{\partial x^2}, \tag{14}$$

where again we have exhibited the continuum limit.

The construction of the kinetic equation for $E(x,t)$ for subdiffusive particles proceeds along arguments analogous to those used in the diffusive case. Again, one follows the motion of the particles in and out at the ends of the empty interval according to the dynamics (3). However, for particles that move subdiffusively, the concept of a hopping rate (steps per unit time) is not defined because the number of steps performed up to time t by a subdiffusive particle goes as t^{α} with $\alpha < 1$ [23]. Therefore, the derivation of the empty interval equation must be adjusted accordingly. Proceeding as above in the discrete formulation, we see that the probability that sites 1–n are empty but that there is a particle at site $n+1$ is still $E_{n+1} - E_n$. However, the rate of decrease of E_n due to a particle that moves from site $n+1$ to site n is now described by the generalized diffusion process implicit in Eq. (3), that is, $[K_{\alpha\,0}D_t^{1-\alpha}/(\Delta x)^2](E_n - E_{n+1})\Delta t$. Collecting arrival and departure processes at both ends of the interval then leads to the equation

$$\frac{\Delta E_n}{\Delta t} = \frac{2K_{\alpha\,0}D_t^{1-\alpha}}{(\Delta x)^2}(E_{n+1} - 2E_n + E_{n-1}). \tag{15}$$

In the continuum limit this then becomes

$$\frac{\partial}{\partial t}E(x,t) = 2K_{\alpha\,0}D_t^{1-\alpha}\frac{\partial^2}{\partial x^2}E(x,t). \tag{16}$$

The boundary conditions are exactly as before, Eqs. (9) and (10), as are the relations (11) and (14) to the observables.

2.2. Odd/even interval method for annihilation reaction

The empty interval method cannot be applied to the annihilation reaction $A + A \rightarrow 0$ because annihilation leads to a discontinuous growth of empty intervals. However, recently a new method of odd/even intervals has been introduced that leads to exact solution in the diffusion-limited case. It is based on the construction of an equation for $r(x,t)$, the probability that an arbitrary interval of length x contains an even number of particles at time t [8,9]. This probability does not change if two particles inside the interval react since this process does not change the even/odd parity of the interval. Because $r(x,t)$ changes only by the movement of particles in or out of the ends of the interval, arguments similar to those that lead to Eq. (5) lead to the same equation for $r(x,t)$. This procedure can again be directly extended to the subdiffusive problem, and $r(x,t)$ satisfies the same fractional diffusion equation as $E(x,t)$:

$$\frac{\partial}{\partial t}r(x,t) = 2K_{\alpha\,0}D_t^{1-\alpha}\frac{\partial^2}{\partial x^2}r(x,t). \tag{17}$$

One boundary condition is the same as for $E(x,t)$ and is obtained via the same arguments used earlier:

$$r(0,t) = 1. \tag{18}$$

The other boundary condition in general differs from that of the empty interval method and depends on the initial condition. In particular, it is determined by the parity of total initial number of particles. This parity never changes. A random initial placement leads to an equal probability that the system forever contain an even or and odd number of particles, so that

$$r(\infty,t) = \frac{1}{2}. \tag{19}$$

The concentration of particles is related to $r(x,t)$ precisely as in Eq. (11):

$$c(t) = -\left.\frac{\partial r(x,t)}{\partial x}\right|_{x=0}. \tag{20}$$

3. Solution of the fractional diffusion equations and subdiffusive reaction kinetics

3.1. Coagulation reaction

The solution of Eq. (5) with boundary conditions (9) and (10) can be written as [18]

$$E(x,t) = \int_0^\infty \mathrm{d}y[W(x-y,t) - W(-x-y,t)]E(y,0) + \int_0^{t(x/\sqrt{2K_\alpha})^{-2/\alpha}} \omega_{\alpha/2}(\eta)\,\mathrm{d}\eta, \tag{21}$$

where

$$W(x,t) = \frac{1}{\sqrt{8K_\alpha t^\alpha}} H_{11}^{10}\left[\frac{|x|}{\sqrt{2K_\alpha t^\alpha}}\,\middle|\,\begin{matrix}(1-\frac{\alpha}{2},\frac{\alpha}{2})\\(0,1)\end{matrix}\right], \tag{22}$$

$$\omega_\beta(x) = \frac{1}{\beta x^2} H_{11}^{10}\left[\frac{1}{x}\,\middle|\,\begin{matrix}(-1,1)\\(-1/\beta,1/\beta)\end{matrix}\right], \tag{23}$$

and H is the Fox H-function [15,16,18,27]. Taking into account that in Laplace transform space (indicated by a tilde over the function and the letter u as variable)

$$\widetilde{W}(x,u) = \frac{u^{\alpha/2-1}}{\sqrt{8K_\alpha}} \exp\left[\frac{u^{\alpha/2}}{\sqrt{2K_\alpha}}|x|\right] \tag{24}$$

and $\widetilde{\omega}_\beta(u) = \exp(-u^\beta)$, the solution $E(x,t)$ in Laplace space adopts a much simpler form

$$\widetilde{E}(x,u) = \frac{s}{2u}\int_0^\infty \mathrm{d}y(\mathrm{e}^{-|x-y|s} - \mathrm{e}^{-|x+y|s})E(y,0) + \frac{1}{u}\exp(-xs), \tag{25}$$

where

$$s \equiv \frac{u^{\alpha/2}}{\sqrt{2K_\alpha}}. \tag{26}$$

From Eqs. (11) and (25) one finds

$$\widetilde{c}(u) = \frac{s}{u}[1 - s\widehat{E}(s,0)], \tag{27}$$

where

$$\widehat{E}(v,t) = \int_0^\infty \mathrm{d}x\mathrm{e}^{-vx}E(x,t)$$

is the *spatial* Laplace transform of $E(x,t)$. Equivalently, from Eq. (14) one obtains

$$\widetilde{c}(u) = \frac{\lambda}{u}[1 - \widehat{p}(s,0)], \tag{28}$$

where $\lambda \equiv c(0)$ and $\widehat{p}(u,0)$ is the *spatial* Laplace transform of the initial interparticle distribution function $p(x,0)$.

A commonly considered initial interparticle distribution is the random (Poisson) distribution of average concentration λ, for which $E(x,0) = \mathrm{e}^{-\lambda x}$ and $p_0(x) = \lambda\mathrm{e}^{-\lambda x}$. For this initial distribution either Eq. (27) or Eq. (28) can be used to obtain

$$\widetilde{c}(u) = \frac{\lambda}{u + \lambda\sqrt{2K_\alpha}u^{1-\alpha/2}} \tag{29}$$

and $c(t)$ is given in closed form in terms of the Mittag–Leffler function [16,28] of parameter $\alpha/2$:

$$c(t) = \lambda E_{\alpha/2}\left(-\lambda\sqrt{2K_\alpha}t^{\alpha/2}\right). \tag{30}$$

The Mittag–Leffler function can be calculated by the series expansion [16,28]

$$E_\alpha(z) = \sum_{k=0}^\infty \frac{z^k}{\Gamma(k\alpha+1)}. \tag{31}$$

When $\alpha = 1$ one recovers the usual result for diffusion-limited coagulation [4,5] since the Mittag–Leffler function of parameter $1/2$ is $E_{1/2}(-x) = \exp(x^2)\mathrm{erfc}(x)$.

Another initial particle distribution of interest is an ordered or periodic arrangement, $p(x,0) = \delta(x - 1/\lambda)$. In this case Eq. (28) leads to

$$\widetilde{c}(u) = \frac{\lambda}{u}\left[1 - \exp\left(-\frac{u^{\alpha/2}}{\lambda\sqrt{2K_\alpha}}\right)\right] \tag{32}$$

and $c(t)$ is given in terms of the Fox H-function $H_{1,1}^{1,0}$ [7,18,27]:

$$\frac{c(t)}{\lambda} = 1 - H_{11}^{10}\left[\frac{1}{\lambda\sqrt{2K_\alpha t^\alpha}}\,\middle|\,\begin{matrix}(1,\frac{\alpha}{2})\\(0,1)\end{matrix}\right]. \tag{33}$$

For normal ($\alpha = 1$) diffusive particles one recovers the usual result for diffusion-limited coagulation [5] since

$$H_{11}^{10}\left[z\,\middle|\,\begin{matrix}(1,\frac{1}{2})\\(0,1)\end{matrix}\right] = \mathrm{erfc}\left(\frac{z}{2}\right).$$

It is useful to exhibit explicitly the long-time and short-time behaviors of the particle concentration. The long-time behavior can be extracted via Tauberian theorems from the small-u behavior *independent of initial condition* and therefore in particular common to both of the initial conditions considered above,

$$\widetilde{c}(u) \sim \frac{u^{-\alpha/2-1}}{\sqrt{2K_\alpha}}, \tag{34}$$

from which it follows that

$$c(t) \sim \frac{t^{-\alpha/2}}{\sqrt{2K_\alpha}\Gamma\left(1-\frac{\alpha}{2}\right)}. \tag{35}$$

For diffusive particles ($\alpha = 1$) one recovers the well-known result $c(t) \sim t^{-1/2}$. The short-time behavior of the particle concentration is, not surprisingly, markedly different for the two initial conditions. For the random initial condition an expansion of Eq. (30) using (31) gives

$$\frac{c(t)}{\lambda} = 1 - \frac{\lambda\sqrt{2K_\alpha}}{\Gamma(1+\frac{\alpha}{2})} t^{\alpha/2} + \cdots \tag{36}$$

Notice that this implies an infinite initial reaction rate because $\mathrm{d}c(t)/\mathrm{d}t \to \infty$ for $t \to 0$, a reflection of the fact that a random distribution of particles includes a large probability of proximate particles. On the other hand, using the asymptotic expression of the Fox H-function $H^{1,0}_{1,1}$ for large argument [18,27] in the solution for the periodic initial distribution of particles, Eq. (33), one finds

$$\frac{c(t)}{\lambda} = 1 - \frac{1}{\sqrt{\pi(2-\alpha)}}\left(\frac{\alpha}{2}\right)^{1/(\alpha-2)} z^{1/(\alpha-2)} \times \exp\left[-\frac{2-\alpha}{2}\left(\frac{\alpha}{2}\right)^{\alpha/(2-\alpha)} z^{2/(2-\alpha)}\right] + \cdots, \tag{37}$$

where $z = [\lambda(2K_\alpha t^\alpha)^{1/2}]^{-1}$. In this case $\mathrm{d}c(t)/\mathrm{d}t \to 0$ for $t \to 0$, since initially there are no proximate particles.

The curves in Fig. 1 shows the time evolution of the concentration $c(t)$ for the coagulation reaction and the two initial conditions considered here. The differences at early times are evident, as is the coalescence of the curves into a single asymptotic form at long times.

The time-asymptotic form of the empty interval function can be used to obtain the asymptotic behavior of the interparticle distribution function via Eq. (14). From Eq. (25) one deduces that

$$\frac{\partial^2}{\partial x^2}\widetilde{E}(x,u) = \frac{s^3}{2u}\int_0^\infty \mathrm{d}y(\mathrm{e}^{-|x-y|s} - \mathrm{e}^{-|x+y|s})E(y,0) + \frac{s^2}{u}\mathrm{e}^{-xs}, \tag{38}$$

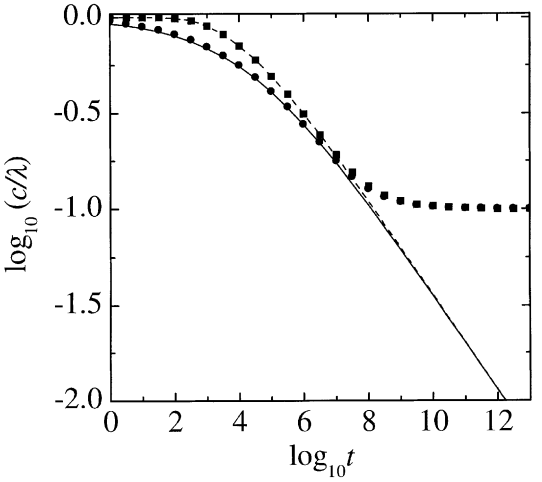

Fig. 1. Logarithm of the survival probability $c(t)/\lambda$ for coagulation dynamics of subdiffusive particles with $\alpha = 1/2$, $K_\alpha = 1$, and initial concentration $\lambda = 1/20$, versus the logarithm of time. The initial arrangements of the particles are Poissonian (solid line and circles) and periodic (broken line and squares). The lines are the continuum solutions given by Eqs. (30) and (33). The symbols are the on-lattice solutions for a finite lattice with $L = 200$ and $\Delta x = 1$ with periodic boundary conditions.

which for $u \to 0$ reduces to

$$\frac{\partial^2}{\partial x^2}\widetilde{E}(x,u) \sim \frac{s^2}{u}\mathrm{e}^{-xs}. \tag{39}$$

From Eq. (14) and the fact that the inverse transform of (39) can be expressed in terms of a Fox H-function, one finds

$$c(t)\,p(x,t) \sim \frac{1}{x^2} H^{10}_{11}\left[\frac{x}{\sqrt{2K_\alpha}t^{\alpha/2}}\middle|\begin{matrix}(1,\frac{\alpha}{2})\\(2,1)\end{matrix}\right], \tag{40}$$

which in combination with Eq. (35) immediately leads to

$$p(x,t) \sim \frac{\Gamma(1-\frac{\alpha}{2})}{\sqrt{2K_\alpha}t^{\alpha/2}} H^{10}_{11}\left[\frac{x}{\sqrt{2K_\alpha}t^{\alpha/2}}\middle|\begin{matrix}(1-\alpha,\frac{\alpha}{2})\\(0,1)\end{matrix}\right] \tag{41}$$

for $t \to \infty$. This result is independent of the initial distribution of particles. We can also write this in the scaled form

$$p_\alpha(z) \sim \Gamma^2\left(1-\frac{\alpha}{2}\right) H^{10}_{11}\left[\Gamma\left(1-\frac{\alpha}{2}\right)z\middle|\begin{matrix}(1-\alpha,\frac{\alpha}{2})\\(0,1)\end{matrix}\right], \tag{42}$$

where $z \equiv c(t)x$ is the scaled interparticle distance and $p_\alpha(z)\mathrm{d}z \equiv p(x,t)\mathrm{d}x$. This stationary form is

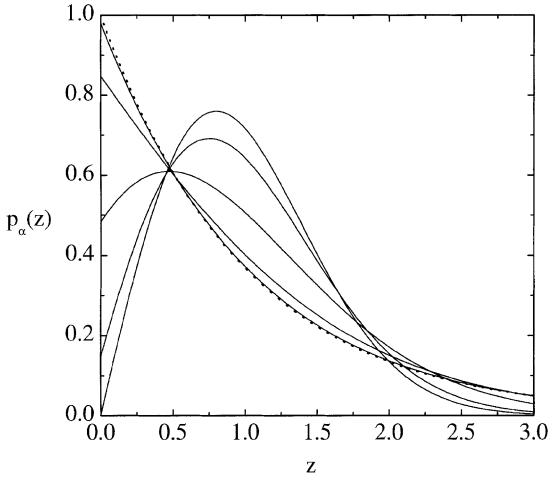

Fig. 2. Long-time scaled interparticle distribution function for the coagulation reaction for several values of the anomalous diffusion exponent. Proceeding upward from lowest to highest curves along the y axis intersection: $\alpha = 1, 0.95, 0.8, 0.5, 0.2$. Note that the distribution for $\alpha = 0.2$ on this scale is nearly indistinguishable from the completely random distribution $\exp(-z)$ (dotted curve).

shown in Fig. 2 for several values of the diffusion exponent α.

The interparticle distribution function conveys the interesting "anomalies" of the problem most clearly. For a random distribution of particles on a line this distribution is exponential. In particular, the most probable interparticle gaps are the smallest. For diffusion-limited reactions on a line it is well known that the scaled distribution deviates in two ways from the exponential behavior. First, a gap develops around each particle, and the distribution vanishes near the origin (see $\alpha = 1$ curve in the figure), indicating an "effective repulsion" of particles. Second, the probability of large gaps decays much more rapidly than exponentially: the decay goes as a power of $\exp(-z^2/2)$. In the subdiffusive case decreasing α leads to the diminution of the gap around each particle, that is, to a weakening of the effective repulsion and to a behavior that appears closer to that of a random distribution in the short-interparticle-distance behavior. This is evident in the progression of the curves with decreasing α shown in the figure. Furthermore, the probability of large gaps decays as a power of $\exp(-x^{2/(2-\alpha)})$, thus neatly interpolating between the purely random exponential decay state as $\alpha \to 0$ (since then $p(x,t) \to c(t)e^{-c(t)x}$) and the more ordered state corresponding to diffusive particles at $\alpha = 1$.

3.2. Annihilation reaction

It is straightforward to deduce that the solution $r(x,t)$ of Eq. (17) with initial condition $r(x,0) = \frac{1}{2} + E(x,0)/2$ and boundary conditions (18) and (19) is simply $r(x,t) = \frac{1}{2} + E(x,t)/2$ where $E(x,t)$ is the solution found in the previous section. We can therefore here rewrite Eq. (27) for the Laplace transform of the concentration of particle undergoing the annihilation reaction as

$$\widetilde{c}(u) = \frac{s}{u}[1 - s\widehat{r}(s,0)], \tag{43}$$

where $\widehat{r}(v,t)$ is the *spatial* Laplace transform of $r(x,t)$.

For a random initial distribution of mean concentration λ the initial distribution is $r(x,0) = \frac{1}{2} + \frac{1}{2}e^{-2\lambda x}$ (note that this goes to 1/2 as $x \to \infty$ since there is an equal probability that we start with an even or odd number of particles, and it goes to 0 as $x \to 1$ since zero particles is an even number). Hence

$$\widetilde{c}(u) = \frac{\lambda}{u + 2\lambda\sqrt{2K_\alpha}u^{1-\alpha/2}}, \tag{44}$$

which can be inverted analytically to yield

$$c(t) = \lambda E_{\alpha/2}\left(-2\lambda\sqrt{2K_\alpha}t^{\alpha/2}\right). \tag{45}$$

Comparing this result with Eq. (30) for the coagulation reaction we see that the rate of change of the concentration for annihilation is exactly twice that for coagulation at all times, a result that has been noted for ordinary diffusion [8,9].

For a periodic initial distribution with separation $1/\lambda$ between particles we have

$$r(x,0) = \begin{cases} 2j + 1 - \lambda x, & 2j/\lambda \leqslant x \leqslant (2j+1)/\lambda, \\ -2j - 1 + \lambda x, & (2j+1)/\lambda \leqslant x \leqslant (2j+2)/\lambda. \end{cases} \tag{46}$$

This is a periodic function of period $2/\lambda$, so that [29]

$$\widehat{r}(u,0)=\frac{\int_0^{2/\lambda}\mathrm{d}x\,\mathrm{e}^{-ux}r(x,0)}{1-\mathrm{e}^{-2u/\lambda}}. \tag{47}$$

Carrying out this integral and substituting into Eq. (43) immediately leads to

$$\widetilde{c}(u)=\frac{\lambda}{u}\tanh\left(\frac{s}{2\lambda}\right)=\frac{\lambda}{u}\left[\frac{1-\exp\left(-\frac{u^{\alpha/2}}{\lambda\sqrt{2K_\alpha}}\right)}{1+\exp\left(-\frac{u^{\alpha/2}}{\lambda\sqrt{2K_\alpha}}\right)}\right], \tag{48}$$

where we have written the second equality to make comparison with Eq. (32) more apparent. We have not been able to invert this expression analytically to find $c(t)$ in closed form.

Fig. 3 shows the temporal evolution of $c(t)$ for the two initial conditions when $\alpha=1/2$. The evolution for a periodic initial distribution has been obtained by numerically inverting Eq. (48).

The long-time behavior is again seen to be independent of initial condition and can be obtained directly from Eq. (43). Since $\widehat{r}(s,0)\to(2s)^{-1}$ when $s\to 0$, it follows that as $u\to 0$,

$$\widetilde{c}(u)\sim\frac{u^{-\alpha/2-1}}{2\sqrt{2K_\alpha}} \tag{49}$$

which in turn implies that

$$c(t)\sim\frac{t^{-\alpha/2}}{2\sqrt{2K_\alpha}\Gamma\left(1-\frac{\alpha}{2}\right)}, \tag{50}$$

when $t\to\infty$. Comparison with Eq. (35) shows that at long times the concentration for the annihilation reaction is exactly half that of the coagulation reaction. This is in agreement with the general result obtained above comparing the rates of change of the concentrations. The short-time behaviors for the two initial conditions are different, as already evident in Fig. 3. For the random initial condition an expansion of Eq. (45) leads to

$$\frac{c(t)}{\lambda}=1-\frac{2\lambda\sqrt{2K_\alpha}}{\Gamma(1+\frac{\alpha}{2})}t^{\alpha/2}+\cdots \tag{51}$$

[compare with Eq. (36)]. For the periodic initial condition, expansion of the denominator of Eq. (48) for large u and comparison with Eq. (32) leads to

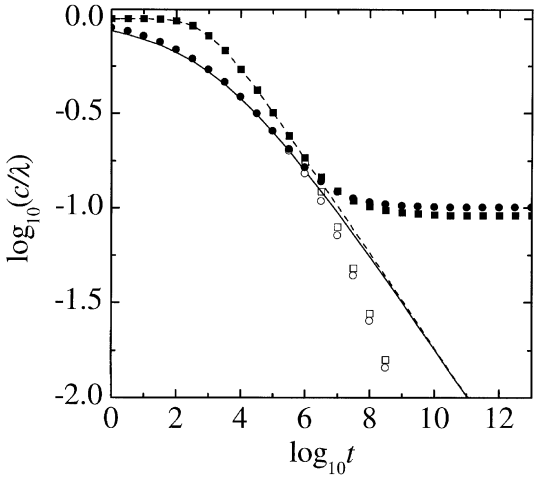

Fig. 3. Logarithm of the survival probability $c(t)/\lambda$ for annihilation dynamics of subdiffusive particles with $\alpha=1/2$, $K_\alpha=1$, and initial concentration $\lambda=1/20$, versus the logarithm of time. The initial arrangements of the particles are Poissonian (solid line and circles) and periodic (broken line and squares). The lines are the continuum solutions given by Eq. (45) and by the numerical inversion of Eq. (48). The symbols are the on-lattice solutions for a finite lattice with $L=220$ (filled symbols) and $L=200$ (open symbols) with periodic boundary conditions and $\Delta x=1$. Note that with these values of L and λ the initial number of particles and hence the total number of particles is odd (filled symbols) or even (open symbols) at all times.

$$\frac{c(t)}{\lambda}=1-\frac{2}{\sqrt{\pi(2-\alpha)}}\left(\frac{\alpha}{2}\right)^{1/(\alpha-2)}z^{1/(\alpha-2)}\times\exp\left[-\frac{(2-\alpha)}{2}\left(\frac{\alpha}{2}\right)^{\alpha/(2-\alpha)}z^{2/(2-\alpha)}\right]+\cdots, \tag{52}$$

where again $z=[\lambda(2K_\alpha t^\alpha)^{1/2}]^{-1}$ [compare with Eq. (37)].

4. Reactions in a lattice

It is sometimes convenient not to carry out the continuous limit in the formulation of the reaction kinetics for coagulation or annihilation reactions. Not only may the actual physical system be discrete, but simulations usually involve discrete lattices, and finite reactant size effects (i.e., small distance scale effects) are more appropriately dealt with through discrete formulations [10–13].

Indeed, a discrete viewpoint was the starting point of the continuum equations considered in the previous section. Furthermore, the discrete formulation allows consideration of different reaction rules such as $A\emptyset A \to AAA$ [12].

The hierarchy of differential-difference equations on a lattice of L sites is

$$I_0(t) = 1,$$

$$\frac{\mathrm{d}I_n}{\mathrm{d}t} = a\,{}_0D_t^{1-\alpha}[I_{n+1}(t) - 2I_n(t) + I_{n-1}(t)], \quad 1 \leqslant n \leqslant L-1, \tag{53}$$

for $n = 1, 2, \ldots,$ where $a \equiv 2K_\alpha/(\Delta x)^2$, $I_n(t) \equiv E(x_n = n\Delta x, t)$ for the coagulation reaction, and $I_n(t) \equiv r(x_n = n\Delta x, t)$ for the annihilation reaction. The other boundary condition, at $n = L$, depends on which reaction is under consideration and will be stated below. The discrete form [6]

$$c(t) = \frac{1 - I_1(t)}{\Delta x} \tag{54}$$

was already introduced in Eq. (11). From here on, we take $\Delta x = 1$.

4.1. Coagulation in a segment

The problem of the coagulation dynamics in a discrete segment has been solved for the normal diffusive case [10–13]. Here we present the solution for the coagulation process of subdiffusive particles on a chain of L sites with periodic boundary conditions, which is described by the hierarchy (53) together with the additional boundary condition

$$I_L(t) = 0. \tag{55}$$

We solve this set of equations by means of the ansatz

$$I_n(t) = \sum_\omega b_n(\omega) E_\alpha(-a\omega t^\alpha) \tag{56}$$

which is closely related to the method of separation of variables for the subdiffusive fractional differential equation [16,20]. Again, E_α is the Mittag–Leffler function of parameter α. Taking into account that

$$\frac{\mathrm{d}}{\mathrm{d}t} E_\alpha(-\beta t^\alpha) = -\beta\,{}_0D_t^{1-\alpha} E_\alpha(-\beta t^\alpha), \tag{57}$$

the resulting eigenvalue problem can be solved in the same way as for normal diffusion [11,12]. Notice that $E_\alpha(x) = \mathrm{e}^x$ for $\alpha = 1$ so that the ansatz (56) takes the well-known form for normal diffusive particles (for which $\alpha = 1$). The full solution is

$$I_n(t) = \left(1 - \frac{n}{L}\right) + \sum_{m=0}^{L-1} A_m \times \sin\left(m\frac{\pi}{L}(n-L)\right) E_\alpha(-a\omega_m t) \tag{58}$$

with

$$\omega_m = 2[1 - \cos(m\pi/L)]. \tag{59}$$

The coefficients A_m are determined from the initial conditions.

For an initially random distribution of particles of concentration λ we have $I_n(0) = (1-\lambda)^n$ for $n = 0, 1, \ldots, L-1$, so that

$$A_m(t) = -\frac{2}{m\pi} \frac{(1-\lambda)^L m^2\pi^2 + (-1)^m L^2 [\ln(1-\lambda)]^2}{m^2\pi^2 + L^2[\ln(1-\lambda)]^2}. \tag{60}$$

For an initially periodic distribution of particles separated by $1/\lambda$ lattice sites we have $I_n(0) = 1 - \lambda n$ for $\lambda n \leqslant 1$ and $I_n(0) = 0$ for $\lambda n \geqslant 1$. In this case

$$A_m(t) = (-1)^{m+1} \frac{2\lambda L \sin(m\pi/\lambda L)}{m^2\pi^2}. \tag{61}$$

Fig. 1 shows the decay of the concentration $c(t)$ given by Eq. (54) with (58) when the initial distribution of subdiffusive particles on the lattice is random and when it is periodic. At longer times both solutions approach those of the continuum equations and would do so more clearly if we were to exhibit the solutions to our difference equations for larger lattices. The marked deviation of the lattice solution from the continuous asymptotic $t^{-\alpha/2}$ decay occurs when the concentration on the lattice approaches its asymptotic (minimum) value of one particle on the entire lattice, $c(t \to \infty) = 1/L$. Using the continuum solution, this can be estimated to occur at time $t_\times$ such that $c(t_\times) = 1/L$. In the figure this separation of solutions clearly does occur when $c/\lambda = 1/\lambda L = 0.1$, i.e., when $\log_{10}(c/\lambda) = -1.0$.

While the long-time behaviors of the discrete and continuous solutions coincide (independently of initial condition) until the reactant concentration is extremely low, the short-time behavior of the two solutions is expected to differ, especially when the initial distribution of particles is random. The difference has been established for particles undergoing normal diffusion [13]. To determine the short-time behavior on the lattice we assume that the lattice is initially full, so that $I_n(0) = 0$ for $n \geqslant 1$. (The reasoning follows along the same lines for an arbitrary concentration of particles, but the equations are more cumbersome.) Taking the time Laplace transform of Eq. (53) gives

$$\widetilde{I}_{n+1}(u) - \left(2 + \frac{u^\alpha}{a}\right)\widetilde{I}_n(u) + \widetilde{I}_{n-1}(u) = 0, \quad n \geqslant 1. \tag{62}$$

This set of difference equations must be solved with the boundary conditions $\widetilde{I}_0(u) = 1/u$ and $\widetilde{I}_L(u) = 0$. Since we are interested in the short-time (large-u) behavior, we can set $L \to \infty$ without appreciably affecting the outcome. With these boundary conditions we essentially follow the procedure of [13] to find

$$\widetilde{I}_n(u) = \frac{1}{2^n u}\left[2 + \frac{u^\alpha}{a} - \left(\frac{u^{2\alpha}}{a^2} + 4\frac{u^\alpha}{a}\right)^{1/2}\right]^n. \tag{63}$$

In particular, $\widetilde{I}_1(u) = a/u^{1+\alpha} + \cdots$ for $u \to \infty$, so that with the help of appropriate Tauberian theorems we find that $I_1(t) = at^\alpha/\Gamma(1+\alpha) + \cdots$ for $t \to 0$. Using Eq. (54), we calculate the short-time behavior of the reactant concentration

$$\frac{c(t)}{\lambda} = 1 - \frac{2K_\alpha \lambda^2}{\Gamma(1+\alpha)} t^\alpha + \cdots \tag{64}$$

Note that with an initially full lattice there is no distinction between an initially random and initially periodic distribution of particles. For an arbitrary random initial concentration one still finds that $c(t)/\lambda - 1 \sim t^\alpha$. Comparison with Eq. (36) shows that at short times, as in the case of normal diffusion [13], the concentration on a lattice decays more slowly than in the continuum. This is not easily visible on the scale of Fig. 1.

4.2. Annihilation in a segment

Now consider the annihilation reaction $A + A \to 0$ and suppose that initially there are N particles on a segment of length L. The hierarchy (53) is now augmented with the second boundary condition

$$I_L(t) = \begin{cases} 1, & N = \text{even}, \\ 0, & N = \text{odd}, \end{cases} \tag{65}$$

where we note that now $I_n(t) \equiv r(x_n = n\Delta x, t)$. This condition is of course a result of the fact that the reaction does not change the parity of the number of surviving particles. We proceed as in the coagulation problem and write the solution as

$$I_n(t) = I_n^* + \sum_{m=0}^{L-1} A_m \sin\left(m\frac{\pi}{L}(n-L)\right) E_\alpha(-a\omega_m t), \tag{66}$$

where

$$I_n^* = I_n(\infty) = \begin{cases} 1, & N = \text{even}, \\ 1 - \frac{n}{L}, & N = \text{odd}, \end{cases} \tag{67}$$

ω_m is given in Eq. (59), and the A_m are coefficients determined from the initial conditions.

For a random initial condition of particle concentration λ we have $I_n(0) = \frac{1}{2} + \frac{1}{2}(1-2\lambda)^n$ for $n = 0, 1, \ldots, L-1$, so that

$$\begin{aligned} A_m(t) = \frac{1}{m\pi}\{&[(-1)^N - (1-2\lambda)^L]m^2\pi^2 \\ &+ [1 - (-1)^{m+N}]L^2[\ln(1-2\lambda)]^2\}/ \\ &\{m^2\pi^2 + L^2[\ln(1-2\lambda)]^2\}. \end{aligned} \tag{68}$$

For a periodic initial distribution with particle separation $1/\lambda$ we have

$$I_n(0) = \begin{cases} 2j+1-\lambda n, & 2j/\lambda \leqslant n \leqslant (2j+1)/\lambda, \\ -2j-1+\lambda n, & (2j+1)/\lambda \leqslant n \leqslant (2j+2)/\lambda, \end{cases} \tag{69}$$

which leads to

$$\begin{aligned} A_m(t) = (-1)^N\left[1 - (-1)^N(-1)^m\right]^2 \frac{\lambda L}{m^2\pi^2} \\ \times \tan\left(\frac{m\pi}{2\lambda L}\right). \end{aligned} \tag{70}$$

Fig. 3 shows the evolution of the concentration as given by Eq. (54) with (66) for a random initial distribution (circles) and a periodic initial distribution (squares). A number of points are noteworthy. First, the solution of course decays to a finite constant (one particle remaining) when there is initially an odd number of particles in the system, and to zero when the initial number of particles is even. The deviation of the solutions on a finite segment from those in an infinite continuum again set in around the time when $c = 1/L$ (strictly speaking around $2/L$ for the even case). Note that in the continuum solution one does not distinguish between the even and odd particle number cases: the boundary condition (19) is an average of the two, and so the continuum curves should be compared to the average of the discrete ones for the two boundary conditions.

5. Conclusions

We have considered the coagulation dynamics $A + A \to A$ and the annihilation dynamics $A + A \to 0$ for particles moving subdiffusively in one dimension. This scenario combines the "anomalous kinetics" and "anomalous diffusion" problems, each of which leads to interesting dynamics separately and to even more interesting dynamics in combination. The fractional diffusion equation plays a central role in our analysis and allows the exact calculation of the density $c(t)$ within this formulation. We have calculated $c(t)$ explicitly for all times for the coagulation reaction in a one-dimensional continuum for two initial distributions, a random (Poisson) distribution and a periodic distribution. This calculation is based on the empty interval method. Using the odd/even interval formulation, we have also obtained an explicit solution for the annihilation reaction with a random initial distribution. For a periodic initial distribution we are only able to calculate the Laplace transform of $c(t)$ analytically and must perform the inversion numerically.

For the coagulation reaction the empty interval method also leads to an explicit solution for the interparticle distribution function $p(x,t)$. At long times we find a universal expression for this distribution (i.e., one independent of initial distribution), in terms of a single scaled variable. Anomalous diffusion is characterized by the exponent α introduced in Eq. (1), ordinary diffusion corresponding to $\alpha = 1$. Deviations from ordinary diffusion lead to a curious interplay. On the one hand, with decreasing α (and hence increasingly subdiffusive motion) the decay of the particle density towards extinction becomes increasingly slower and in this sense increasingly different from law of mass action behavior. On the other hand, for the coagulation reaction the spatial distribution of initially randomly distributed reactants remains more Poissonian for all time as α decreases; indeed, as α deviates from unity the relatively empty regions around each particle that are tantamount to (and indeed explain) anomalous kinetics in the usual diffusion-limited case become more populated.

We have also considered the problem of subdiffusion-limited reaction on discrete lattices. We have presented a hierarchy of differential-difference equations for the empty interval probability $I_n(t) \equiv E(x_n, t)$ and the even/odd interval probability $I_n(t) \equiv r(x_n, t)$, and have expressed the solutions $I_n(t)$ as a superposition of subdiffusive modes whose decay is governed by the Mittag–Leffler function in the same way that the exponential function governs the decay of ordinary diffusive modes. As in ordinary diffusion [13], the associated concentrations $c(t)$ differ from the continuum solutions at early times. At long times the lattice solutions deviate from those of the continuum systems when there is only a small number of particles (one or two) remaining in the system.

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