Subdiffusion-Limited $A + A$ Reactions

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We consider the coagulation dynamics $A + A \rightarrow A$ and $A + A \rightleftharpoons A$ and the annihilation dynamics $A + A \rightarrow 0$ 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. Our analysis is based on the fractional diffusion equation.

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Diffusion-limited reactions in constrained 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 ($A + A \rightarrow A$ or $A + A \rightleftharpoons A$) [2] and annihilation ($A + A \rightarrow 0$) [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 [2,4–7]. The anomalies are typically displayed in two ways: one is through the time dependence of the reactant concentration $c(t)$, which for the $A + A \rightarrow A$ and the $A + A \rightarrow 0$ reactions decays as $t^{-1/2}$ in one dimension 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 [8–10]. The universally accepted characterization of anomalous (as in “not ordinary”) diffusion is through the mean squared displacement of a process $x(t)$ for large $t$,

$$\langle x^2(t) \rangle \sim \frac{2K_a}{\Gamma(1+\alpha)} t^{\alpha}. \quad (1)$$

Ordinary diffusion ($\alpha = 1, K_1 = D$) follows Gaussian statistics and Fick’s second law 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 have been continuous time random walks with non-Poissonian waiting time distributions [8], and fractional dynamics approaches in which the diffusion equation is replaced by a generalized diffusion equation [9,10]. Some connections between these two approaches have recently been clarified [11].

In this Letter, we consider a combination of these two phenomena, namely, the (one-dimensional) kinetics of $A + A$ reactions of particles that move subdiffusively. We pose two questions: (1) How does the reactant concentration evolve in time? (2) How does the interparticle distribution function evolve in space and time? Some aspects of this problem have been considered previously using the waiting time distribution approach [12,13]. The solutions require approximations relating the reactant concentration to the distinct number of sites visited by a particle [12], or the waiting time distributions for single particles to the waiting time distributions for relative motion [13]. Here we adopt 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. We consider both coagulation and annihilation reactions.

Consider first the coagulation reaction $A + A \rightarrow A$ when the particles move by ordinary diffusion. The probability distribution function for the position $y$ of any one $A$ particle in the absence of reaction obeys the diffusion equation

$$\frac{\partial}{\partial t} P(y,t) = D \frac{\partial^2}{\partial y^2} P(y,t). \quad (2)$$

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 for a diffusion-limited reaction (i.e., one with immediate reaction upon encounter) obeys the diffusion equation [2]

$$\frac{\partial}{\partial t} E(x,t) = 2D \frac{\partial^2}{\partial x^2} E(x,t). \quad (3)$$

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). The empty interval dynamics is thus essentially the same as that of individual particles in the absence of reaction, but with a diffusion coefficient $2D$ that reflects the fact that the relative

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motion of two diffusive particles involves twice the diffusion coefficient of each particle alone. The coalescence reaction implies the boundary condition \( E(0, t) = 1 \), and \( E(\infty, t) = 0 \) as long as the concentration is nonvanishing.

From \( E(x, t) \) one obtains the concentration of particles [14]
\[
c(t) = -\frac{\partial E(x, t)}{\partial x} \bigg|_{x=0},
\]
and the interparticle distribution function
\[
p(x, t) = \frac{1}{c(t)} \frac{\partial^2 E(x, t)}{\partial x^2}.
\]
Equation (3) and the boundary conditions can readily be generalized in a number of ways [15], in particular to reversible coagulation \((A + A = A)\) [2] and nucleation [14] and even to processes with three-site interactions [16].

The motion of a subdiffusive particle (in the absence of reaction) is described by the fractional diffusion equation [17–20]
\[
\frac{\partial}{\partial t} P(y, t) = D_1^{1-\alpha} K_\alpha \frac{\partial^2}{\partial y^2} P(y, t),
\]
where \( D_1^{1-\alpha} \) is the Riemann-Liouville operator:
\[
D_1^{1-\alpha} P(y, t) = \frac{1}{\Gamma(\alpha)} \frac{\partial}{\partial t} \int_0^t d\tau \frac{P(y, \tau)}{(t-\tau)^{1-\alpha}},
\]
and \( K_\alpha \) is the generalized diffusion coefficient that appears in Eq. (1). Some limitations of this description have been discussed recently [11].

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 of the ends of the empty interval according to the dynamics (6). This readily leads to the fractional diffusion evolution equation for the empty intervals for subdiffusion-limited reactions
\[
\frac{\partial}{\partial t} E(x, t) = D_1^{1-\alpha} 2K_\alpha \frac{\partial^2}{\partial x^2} E(x, t).
\]

The solution of Eq. (8) with the boundary conditions \( E(0, t) = 1 \) and \( E(\infty, t) = 0 \) can be expressed in terms of the Fox H functions [18]. In Laplace transform space (indicated by a tilde over the function) the solution is
\[
\tilde{E}(x, u) = \frac{s}{2u} \int_0^\infty dy [e^{-|x-y|s} - e^{-|x+y|s}] E(y, 0)
+ \frac{1}{u} \exp[-sx],
\]
where \( s = u^{\alpha/2}/\sqrt{2K_\alpha} \). From Eqs. (4) and (9) one finds
\[
\tilde{c}(u) = \frac{\lambda}{u} \left[ 1 - \tilde{p}_0 \left( \frac{u^{\alpha/2}}{\sqrt{2K_\alpha}} \right) \right],
\]
where \( \lambda = c(0) \) and \( \tilde{p}_0(s) \) is the spatial Laplace transform of the initial interparticle distribution function \( p_0(x) = p(x, 0) \).

A commonly considered initial interparticle distribution is the random (Poisson) distribution of average concentration \( \lambda, p_0(x) = \lambda e^{-\lambda x} \). For this initial distribution \( \tilde{c}(u) = \lambda/(u + \lambda \sqrt{2K_\alpha} u^{1-\alpha/2}) \) and \( c(t) \) is given in closed form in terms of the Mittag-Leffler function [10,21] of parameter \( \alpha/2 \):
\[
c(t) = \lambda E_{\alpha/2}(-\lambda \sqrt{2K_\alpha} t^{\alpha/2}).
\]
When \( \alpha = 1 \) one recovers the usual result for diffusion-limited coagulation [4,5] since the Mittag-Leffler function of parameter 1/2 is \( E_{1/2}(-x) = \exp(x^2) \text{erfc}(x) \).

The \( u \to 0 \) expansions of Eqs. (9) and (10) are readily seen to be independent of the initial distribution \( p_0(x) \) and can be Laplace inverted to yield the asymptotic results for large \( t \):
\[
c(t) \sim \frac{t^{-\alpha/2}}{\sqrt{2K_\alpha} \Gamma(1 - \frac{\alpha}{2})}
\]
and
\[
p(x, t) c(t) \sim \frac{1}{x^2} H_1^{10} \left[ \frac{x}{\sqrt{2K_\alpha} t^{\alpha/2}} \right] \left[ (1, \frac{\alpha}{2}) \right].
\]
where \( H \) is the Fox H function [9,10,18,22]. Furthermore, with Eqs. (12) and (13) we find
\[
p_\alpha(z) \sim \Gamma(1 - \frac{\alpha}{2}) \left[ (1 - \frac{\alpha}{2}) z \right] \left. \right|_{(0, 1)}
\]
where \( z = c(t)x \) is the scaled interparticle distance and \( p_\alpha(z) \, dz = p(x, t) \, dx \). This stationary form is shown in Fig. 1 for several values of the diffusion exponent \( \alpha \).

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 $\alpha$ 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 $\alpha$ shown in the figure. Furthermore, the probability of large gaps decays as a power of $\exp(-x^2/(2-\alpha^2))$, thus neatly interpolating between the purely random exponential decay state as $\alpha \to 0$ [since then $p(x,t) \to c(t) \exp(-c(t)\alpha t)$] and the more ordered state corresponding to diffusive particles at $\alpha = 1$. Note that the congruence of the curves at $z = 1/2$ is not exact although the almost congruence is certainly intriguing [and may be related to the special but physically unclear role played by the initial concentration $c_{eq}/2$ in the reversible coagulation problem that reaches an equilibrium state at concentration $c_{eq}$; see [2] and Eq. (17) et seq.].

The arguments presented so far are applicable to the irreversible coagulation reaction $A + A \rightarrow A$. 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 $t$ [6,7]. Again, 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. (3) lead to exactly the same equation for $r(x,t)$ but with the boundary conditions $r(0,t) = 1$ [as for $E(0,t)$] and $r(\infty,t) = 1/2$. The concentration of particles is related to $r(x,t)$ precisely as in Eq. (4).

The method of odd/even intervals can again be directly extended to the subdiffusive problem, where $r(x,t)$ satisfies the same fractional diffusion equation as $E(x,t)$ with appropriately modified boundary conditions. Closed solution is again possible and, for a random initial distribution with average initial concentration $\lambda$, leads to a form slightly modified from the result (11):

$$c(t) = \lambda E_{\alpha/2}(-2\lambda \sqrt{2K_\alpha \alpha t^{3/2}}).$$

It is appropriate to make contact with the ingenious work of Spouge [5]. He introduced a single formalism to calculate the particle concentration $c(t)$ for both coagulation and annihilation. His approach is based on the probability $a(x,t)$ that two particles, one starting at a distance $x$ from the other, have met by time $t$. In ordinary diffusion this quantity also obeys the diffusion equation with diffusion coefficient $2D$ with appropriate boundary conditions. Again, his method can be generalized to anomalous diffusion and the resulting $a(x,t)$ is [23]

$$a(x,t) = H_{10}^{11} \left[ \frac{x}{\sqrt{2K_\alpha \alpha x^{3/2}}}, (1, \alpha/2) \right],$$

Spouge’s prescription applied to this subdiffusive situation leads, for an initially random distribution, to the results (11) and (15) for coagulation and annihilation, respectively.

The irreversible processes can be generalized in a variety of ways for which the empty interval and the odd/even interval methods have been suitably extended [2,6,7]. In particular, consider the generalization to reversible coagulation, $A + A \rightleftharpoons A$ [2]. For the ordinary diffusion-limited process this generalization is accomplished by subtracting from the right-hand side of Eq. (3) a term proportional to $\partial E(x,t)/\partial x$ that describes the rate of decrease of $E(x,t)$ due to the fact that particles adjacent to either end of an empty interval may give birth to a particle that moves into and therefore shrinks the interval. The same generalization is possible in the subdiffusive case. Assuming that newly created particles move into an empty interval subdiffusively, the evolution equation for $E(x,t)$ is given by

$$\frac{\partial}{\partial t} E(x,t) = D_1 \frac{\partial^2}{\partial x^2} E(x,t) - v_a \frac{\partial}{\partial x} E(x,t),$$

with the same boundary conditions as for Eq. (8). Here $v_a$ is a measure of the birth rate but is itself a rate only when $\alpha = 1$. This equation can be solved by separation of variables [10,19]. The diffusive modes have the same spatial dependence $\varphi_n(x)$ as in the diffusive case, but their temporal evolution is no longer exponential. Instead, it is determined by the Mittag-Leffler function: $E(x,t) = \sum_n \varphi_n(x) e_{eq}(-\lambda_n t)$, where the $\lambda_n$ are the eigenvalues associated with the $\varphi_n(x)$. The equilibrium solution is $E_{eq}(x,t) = \exp(-ux/2K_a)$, which in turn leads to $c_{eq} = v/2K_a$ and $p_{eq}(x) = c_{eq} \exp(-c_{eq}x)$, as in the case of ordinary diffusion [2,15]. However, the approach to equilibrium is algebraic rather than exponential and thus qualitatively different, $c(t) \sim c_{eq} \sim t^{-\alpha}$. An interesting attendant observation involves the dependence of these results on the initial concentration $c(0)$. In the diffusion-limited case the time constant $\tau$ in the exponential decay to equilibrium $\exp(-t/\tau)$ is a function of $c(0)$ for $c(0) < c_{eq} / 2$ and changes to a value independent of $c(0)$ for $c(0) > c_{eq} / 2$ [2]. In the subdiffusive case it is the prefactor of $t^{-\alpha}$ that undergoes exactly the same change.

We have considered the coagulation dynamics $A + A \rightarrow A$ and $A + A \rightleftharpoons A$ and the annihilation dynamics $A + A \rightarrow 0$ 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 $c(t)$ and of the interparticle distribution function $p(x, t)$ within this formulation. Anomalous diffusion is characterized by the exponent $\alpha$ 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 $\alpha$ (and hence increasingly subdiffusive motion) the decay of the particle density towards extinction or towards equilibrium becomes increasingly slower and in this sense increasingly different from law of mass action behavior. On the other hand, the spatial distribution of initially randomly distributed reactants remains more Poissonian for all time as $\alpha$ decreases; indeed, as $\alpha$ 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.

A number of generalizations and further questions that have been considered in the context of diffusion-limited reactions but not for sub diffusion-limited reactions immediately come to mind. They include an analysis of different initial distributions, more detailed consideration of reactions with external input (sources), effective kinetic equations for the density, reactions in statistically inhomogeneous media, and reactions in the presence of external potentials.

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