1
Subdiffusion Limited Reactions

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1.1
Introduction

Anomalous diffusion processes are ubiquitous in nature [1–6]. Their occurrence is usually associated with complex systems that induce spatial and/or temporal correlations in the diffusion process. The signature of normal diffusion is the linear asymptotic dependence of the mean square displacement of the diffusing entity (hereafter called "the particle") on time, $\langle r^2 \rangle \sim t$, $t \to \infty$. The signature of anomalous diffusion is a non-linear dependence on time. In particular, if the growth with time is sublinear, so that

$$\langle r^2 \rangle / t \to 0, \quad t \to \infty, \tag{1.1}$$

the particle is said to be subdiffusive . (The process is superdiffusive when the limit goes to infinity.) In this chapter we focus on the important class of subdiffusive processes for which

$$\langle r^2 \rangle \sim t^\gamma, \quad t \to \infty \tag{1.2}$$

and where the (anomalous) diffusion exponent γ satisfies $0 < \gamma < 1$.

An interesting class of diffusive processes are so-called diffusion-limited reactions. These are processes in which diffusion is the dominant mixing mechanism and, furthermore, where the time for reactants to find one another is much longer than the time it takes for a reaction to occur following such an encounter. Therefore, in these systems diffusion is the key factor that determines the spatial distribution of reactants and the resultant reaction rate. Since diffusion is not a particularly effective mixing mechanism, diffusion-limited reactions often present extremely interesting spatial as well as temporal characteristics. In this context it is especially appropriate to point to the pioneering work of Turing on pattern formation in reaction-diffusion systems [7]. Diffusion-limited reactions show up in a vast number of applications

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including not only chemical (see e.g. [8]) but also biological (e.g. [9]), ecological (e.g. [10]) and economic processes (e.g. [11]) that have been studied over many decades.

The question that drives this chapter is the following: what happens if the reaction partners are subdiffusive instead of diffusive? How is the spatial distribution and, specifically, the reaction kinetics, affected by the subdiffusive nature of the reactants? Even more, what happens if the diffusive properties of different reactant species are qualitatively different, for example, if one species diffuses normally but the other is subdiffusive? We will see that the answers to these questions will take us to very diverse scenarios. Some will be answered via straightforward procedures related to the subordination of random processes (see Section 1.3.1), while others are unexpectedly complex and essentially unpredictable on any simple grounds [12–14]. Some will involve an almost automatic extension of normal diffusion results to the subdiffusive regime , while others involve profound qualitative changes (akin to critical phenomena) in the reaction kinetics as one reaches certain critical values of the anomalous diffusion exponents [15–17].

In Section 1.2 we introduce a number of physical scenarios that lead to subdiffusive motion as well as some of the mathematical language used to describe particle motion and chemical reactions in such environments. In Section 1.3 we review two classic reaction-(sub)diffusion problems, namely, the target problem (which involves a static particle in a sea of mobile traps), and the trapping problem (where the traps are static and the particle is mobile). The situation becomes more complicated when all reaction partners are mobile. In Section 1.4 we consider the reaction-(sub)diffusion problems $A + A \rightarrow$ Products and $A + B \rightarrow$ Products when all reactants are mobile and are initially randomly distributed. Sections 1.2-1.4 focus on the time dependence of global concentrations of reactants, $c(t)$, and on results that can be obtained by scaling arguments. There are situations involving non-homogeneous distributions of reactants in which one wishes to focus not only on the global concentrations but on the local (space-dependent) concentrations $c(\mathbf{r}, t)$. An example is the evolution of reaction fronts between initially separated reactants. In Section 1.5 we discuss the various ways in which the evolution of local concentrations has been modeled using reaction-subdiffusion equation approaches, and we illustrate some of these on the analysis of a reaction front. A special challenge presents itself when reacting particles that are all mobile are described by different subdiffusive exponents. Section 1.6 discusses some such reactions and arrives at results for global concentrations on the basis of mutually convergent bounding arguments. Finally, in Section 1.7 we present a brief concluding summary and mention a number of open problems in the reaction-subdiffusion arena.

1.2
Subdiffusion contexts and modeling approaches

Subdiffusive processes arise in diverse contexts, of which we mention only the most ubiquitous.

Subdiffusion describes the way a particle moves through spatially disordered or fractal media [1,5,18,19] (see the contribution by Hoffmann and Prehl in this volume). In such media there are structural irregularities, bottlenecks, and dead ends, that is, impairments to normal diffusion that lead to a mean square displacement given by [5,20]

$$\langle r^2 \rangle \sim t^{2/d_w}, \quad t \to \infty. \tag{1.3}$$

Here $d_w = 2d_f/\widetilde{d}$ is the random walk dimension, d_f and $\widetilde{d}$ being respectively the fractal and spectral dimension of the substrate. This result describes the mean square displacement on both random fractal structures such as percolation clusters and diffusion-limited aggregates, and regular fractals such as Sierpinski gaskets. For d-dimensional Euclidean media, $d = d_f = \widetilde{d}$ and therefore $d_w = 2$ for all d.

Subdiffusion also describes the motion of a particle in a regular lattice with quenched (frozen) disorder [1–5,19] or with dynamical disorder due to correlated (slow) temporal fluctuations of the medium [19,21,22]. Here, although the sites and connectivity are those of a regular lattice, the transition rates from one site to another vary from site to site due to random energy barriers, or potential wells of random depths or, more generally, the presence of a spatially random quenched force field (the Sinai problem) or a time-dependent random force field. Certain distributions of transition rates lead to subdiffusive motion (see Bouchaud's contribution in this volume). For example, suppose that at every node of a d-dimensional lattice there is a potential well of a fixed depth λ drawn from a distribution $p(\lambda)$. Suppose that this distribution behaves as $p(\lambda) \sim \lambda^{-1-\alpha}$ for large λ. If one assumes that the waiting-time distribution for exiting the well of depth λ follows the Arrhenius law, $\psi(t|\lambda) = \lambda^{-1} \exp(-t/\lambda)$, then one finds that

$$\langle r^2 \rangle \sim t^{\gamma}, \quad t \to \infty, \tag{1.4}$$

with $\gamma = 2\alpha/(1 + \alpha)$ for a one-dimensional lattice. For d-dimensional lattices with $d \geq 2$ the anomalous diffusion exponent γ is simply α [1,5]. In Figure 1.1 we show simulation results for $\langle r^2 \rangle$ for one-, two-, and three-dimensional lattices when $\alpha = 1/2$. The anomalous character of the diffusion process in this system is evident.

We note that the contexts mentioned above arise in vastly different physical situations. For instance, fractal media or quenched disorder are invoked in porous glasses, micelle systems, actin networks, intracellular transport, and

geophysical phenomena such as subsurface hydrology or force distributions in static granular media (see the contributions by Kob et al. and Kimmich et al. in this volume). Dynamical disorder is invoked in relaxation processes in polymers and in viscoelastic materials, diffusion of particles in certain turbulent media, electron transfer processes in proteins and, more generally, in the relaxation of any system coupled to a complex (fractal) heat bath. In these systems subdiffusion arises from fluctuations that are not much faster than the transfer rates associated with the transport process of interest. As a result, these dynamical fluctuations may give rise to a distribution of rates that in turn leads to anomalous transport properties.

Since each of these varied processes may be characterized by a subdiffusive mean square displacement, it is clear that this quantity alone can not distinguish between the vastly different underlying mechanisms all of which give rise to the same anomalous behavior in this single measure.

The theoretical and mathematical approaches to the subdiffusion problem, particularly those that lead to results beyond the mean square displacement, are also varied. In fact, the distinctions invoked above do not necessarily lead to different models; in other words, essentially the same model (but with suitably interpreted parameter definitions) may be invoked in situations that are fundamentally different [2–4,19]. For example, it is often assumed that motion
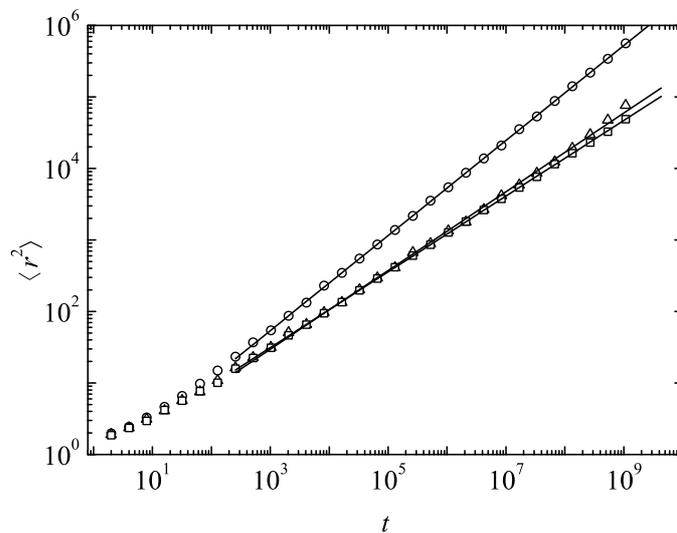

Fig. 1.1 Mean square displacement in one-, two-, and three-dimensional media with quenched disorder as described in the text for $\alpha = 1/2$. The points correspond to times $t = 2^1, 2^2, \ldots, 2^{30}$ for $d = 1$ (circles), $d = 2$ (squares) and $d = 3$ (triangles). The lines are fit to the simulation data from $t = 2^{10}$ to $t = 2^{30}$. The slopes are 0.66 for $d = 1$, 0.53 for $d = 2$ and 0.54 for $d = 3$, in good agreement with the corresponding theoretical anomalous diffusion exponent ($\gamma = 2/3$ for $d = 1$, $\gamma = 1/2$ for $d = 2, 3$).

in a fractal medium can in some sense be represented by motion in a regular medium with quenched disorder. While this is often the case, there are instances where it is not [23]. Here we briefly mention a few approaches, some of which we develop in more detail as needed in later sections. But here we also hasten to add that since subdiffusion is often associated with disorder of some sort, analytic work is difficult, and a great deal of work in this arena has been numerical. This, too, presents difficulties because a subdiffusive process is, by definition, slow, and in many cases it is beyond even current numerical capabilities to arrive at reliable statistics, especially when one is interested in asymptotic behavior, or when the subdiffusive process occurs amidst faster time scale processes. For example, simulations involving reactions between diffusive and subdiffusive particles are notoriously strenuous. This is a typical numerical quandary in problems involving very disparate time scales.

A frequent theoretical starting model for subdiffusive processes is the Continuous Time Random Walk (CTRW) [3, 24] (see the contribution by Gorenflo and Mainardi in this volume). Suppose a walker starts at $t = 0$ at the origin, waits a random time T_1 to make a jump of length X_1, waits a random time T_2 to jump again over distance X_2, etc., with the waiting times between jumps and the lengths of the jumps drawn from a probability distribution function (pdf) $\phi(x, t)$. This defines a CTRW. If the waiting times and jump lengths are independent random variables, then the pdf is a product, $\phi(x, t) = w(x)\psi(t)$, and the probability density $P(x, t)$ that the particle is at x at time t obeys the integral equation

$$P(x, t) = \delta(x)\Psi(t) + \int_0^t dt'\psi(t - t') \int_{-\infty}^{\infty} dx' w(x - x')P(x', t'), \tag{1.5}$$

where $\Psi(t) = \int_t^{\infty} dt'\psi(t')$ is the probability that at time t the particle is still at the origin. Ordinary random walks or ordinary diffusion arise if $w(x)$ has finite variance and $\psi(t)$ has a finite first moment. (Superdiffusion is associated with a $w(x)$ with infinite variance.) Subdiffusion arises if $w(x)$ has finite variance but the time density between jumps decays as a power law at long times [3, 25–27],

$$\psi(t) \sim t^{-1-\gamma}, \quad t \to \infty, \tag{1.6}$$

with $\gamma < 1$ so that the mean time between jumps diverges. Most often the CTRW is assumed to take place on a regular lattice or a Euclidean continuum, and it is then straightforward to deduce that

$$\langle r^2 \rangle \sim \frac{2K}{\Gamma(1 + \gamma)} t^{\gamma}, \quad t \to \infty. \tag{1.7}$$

Here K is the (generalized) diffusion coefficient. One can generalize the discussion to the case where the time at which the observation begins ($t = 0$)

does not coincide with the time at which the walker makes a jump, thus introducing the notion of "aging" [28].

While CTRW models have been applied broadly, they can quickly become analytically onerous. They are then used as a point of departure for the formulation of more tractable coarse-grained models. These latter approaches also facilitate the consideration of force fields and of spatial boundaries, which are difficult to incorporate in the CTRW context. A favorite path to simplify the situation is to follow the route often taken for ordinary random walks, namely, to take a scaling limit in which the variance of the jump lengths and the mean time between jumps vanish in a particular way to arrive at the diffusion equation. The fractional diffusion equation for the probability density associated with a CTRW with an asymptotic power-law jump time distribution has been derived in various ways in the literature [3, 4, 29] (see Part 1 of this volume). A particularly illuminating recent discussion of a scaling approach appears in Reference [30]. One arrives at the equation

$$\frac{\partial}{\partial t} P(x,t) = {}_0 D_t^{1-\gamma} K \frac{\partial^2}{\partial x^2} P(x,t), \tag{1.8}$$

where ${}_0 D_t^{1-\gamma}$ is the Riemann-Liouville operator (see Hilfer's contribution in this volume for more information on this operator)

$$ {}_0 D_t^{1-\gamma} P(x,t) = \frac{1}{\Gamma(\gamma)} \frac{\partial}{\partial t} \int_0^t d\tau \frac{P(x,\tau)}{(t-\tau)^{1-\gamma}} \tag{1.9}$$

and K is the generalized diffusion coefficient that appears in Equation (1.7). Solutions to this equation are well studied, and we will have occasion to invoke the equation in later sections.

A second starting point for subdiffusive processes has been invoked mainly for systems with dynamical disorder. This approach, called fractional Brownian motion [31], starts with a generalized Langevin equation with fluctuations that are, as usual, Gaussian, but whose correlation function includes a slow power-law time decay contribution [19, 21, 22]. Just as the ordinary Langevin equation with Gaussian δ-correlated noise can be recast in the form of the diffusion equation, so the generalized Langevin equation with fractional Gaussian noise can be recast as a fractional diffusion equation, but now with a time-dependent diffusion coefficient [22],

$$\frac{\partial}{\partial t} P(x,t) = \gamma D t^{\gamma-1} \frac{\partial^2}{\partial x^2} P(x,t), \tag{1.10}$$

which also leads to a sublinear mean square displacement. We have mentioned this approach for completeness but do not apply it in our studies.

While we have thus briefly outlined a number of possible approaches to subdiffusion , the problem becomes much more complicated if subdiffusive

particles can also *react*. How to build reactions into any subdiffusive model is as yet far from clear, and different approaches have even produced mutually inconsistent results. In reaction-diffusion problems one is accustomed to simply add a local law of mass action (product) reaction term to the diffusion or random walk equation, which clearly relies on the assumption that these processes are simply additive. Thus, for example, if one considers a bimolecular reaction of the form $A + B \rightarrow C$ in a normal diffusive system one would not hesitate to write the mean field equation for the local concentration $a(x,t)$ of A particles (or, equivalently, the probability density of finding an A particle at x at time t) as

$$\frac{\partial}{\partial t}a(x,t) = D\frac{\partial^2}{\partial x^2}a(x,t) - ka(x,t)b(x,t).$$
(1.11)

However, if the motion of one or both reactants is subdiffusive , it is not at all clear that the reaction contribution can simply be added to a subdiffusion equation this way. In fact, it is now known on the basis of theoretical arguments and numerical simulation results that simple addition of a product term is in general not correct [12,13,32–34]. Fortunately, there are some exact results as well as approximate results that have been supported by numerical simulations that point to more appropriate ways to model reaction-subdiffusion processes [1,5,6,12,13,15,16,32–37]. In the following sections we describe this scenario in more detail.

1.3
Target and trapping problem

The target problem and the trapping problem are the two classic reaction-diffusion scenarios on which rests the broader theory of diffusion-limited reactions. In the *target* (or scavenger) problem a *static particle A* is surrounded by a distribution of *mobile traps B* [6, 38–40] (see Fig. 1.2.a), whereas in the traditional version of the *trapping* problem, a *diffusive (Brownian) particle A* wanders in a medium doped at random with *static traps B* [1, 5, 24, 25] (see Fig. 1.2.b). When a particle and a trap meet, the particle disappears. The trapping problem dates back to Smoluchowski's theory of reaction rates at the beginning of last century [41]. Both are among the most widely investigated and applied problems of non-equilibrium statistical mechanics. The principal quantity of interest is the survival probability $P(t)$ of the A particle as a function of time t. From this survival probability one is able to calculate essentially all other quantities of practical interest. The subdiffusive versions of these two problems, that is, the target problem with subdiffusive traps, and the trapping problem with subdiffusive particles, have also been studied extensively [6, 38–40, 42–50].

1.3.1

Target problem

Whether the traps move diffusively or subdiffusively on a lattice, it can be proved that [38, 50]

$$P(t) = \exp[-cS(t)], \tag{1.12}$$

where c is the concentration of traps and $S(t) \equiv \langle \mathbf{S}(t) \rangle$ is the *mean* number of distinct sites that a random walker visits in time t. In a continuum "number of distinct sites visited" must be understood as the volume that has been generated by a randomly moving spherical particle, that is, the volume of the "Wiener sausage" generated by the spherical particle [51, 52]. For the case of ordinary diffusion one can think of the traps as random walkers taking steps of unit length per unit time in a d-dimensional lattice, and then one has, for large t [24–26],

$$S(t) \sim \begin{cases} \sqrt{\frac{8}{\pi}} t^{1/2}, & d = 1, \\ \omega t / \ln t, & d = 2, \\ \omega t, & d \geq 3. \end{cases} \tag{1.13}$$

The value of the constant ω in each dimension depends on the lattice geometry. For example for a two-dimensional square lattice one has $\omega = \pi$, whereas for a simple-cubic lattice $\omega = 1 - R$, where $R = 0.340537...$ is the probability of a random walker ever returning to his starting point [24, 50]. The expressions are in general valid with modified constant prefactors for walks with a distribution of step lengths and stepping times if the variance of the jump lengths and the mean time between jumps remain finite.
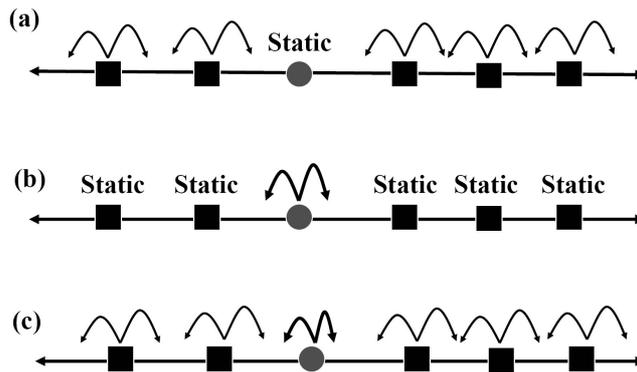

Fig. 1.2 (a) Sketch of the target problem: a static particle (circle) in a sea of diffusive traps (squares). (b) Sketch of the trapping problem: a diffusive particle (circle) in a sea of static traps (squares). (c) Sketch of the generalized problem discussed in 1.6: a diffusive particle (circle) surrounded by a sea of diffusive traps (squares).

In the subdiffusive case one can think of traps that jump over distances of finite variance but with the jump times governed by a waiting time distribution whose long-time behavior is a power law as in (1.6) (CTRW model). The time dependences of the $S(t)$ are now different [6,15,38,45,49,53,54]:

$$S(t) \sim \begin{cases} \Omega t^{\gamma/2}, & d = 1, \\ \Omega t^{\gamma} / \ln t^{\gamma}, & d = 2, \\ \Omega t^{\gamma}, & d \geq 3, \end{cases} \tag{1.14}$$

where the Ω are constants that depend on the geometry of the substrate, the generalized diffusion coefficient, and the anomalous diffusion exponent γ. Note that one can obtain the correct time dependence of the subdiffusive formulas ($\gamma < 1$) from the normal diffusive counterparts by means of the substitution $t \to t^{\gamma}$. This is a manifestation of the "subordination" of the subdiffusive process to the normal diffusive one (the *parent process*) in the sense that the subdiffusive process $X(t)$ can be obtained from a Brownian process $B(n)$ in which its time n (the *operational time*) is conveniently randomized by a stochastic process (the directing process) $n = T(t)$ with non-negative independent increments, i.e., $X(t) = B[n(t)]$ (see more details in [55,56]). Therefore the subdiffusive process can be fully described from its Brownian counterpart. However, in some cases, a rough but easier description of the subdiffusive process can be obtained by means of the simple substitution of $t \to t^{\gamma}$ into the normal diffusive quantities [6,42]. This subordination procedure (or trick) can be understood taking into account that subdiffusion is due to the fact that the number of steps $n(t)$ within a given time interval t typically grows sublinearly with time, $n(t) \sim t^{\gamma}$, as opposed to the normal linear growth typical of ordinary diffusion [55]. Therefore, all properties that depend on time only through the number of steps taken by the random walker behave as they would in ordinary diffusion but with the replacement $t \to t^{\gamma}$. In our case it is clear that the determining factor in the growth of $S(t)$, and hence in the decay of $P(t)$, is the number of steps $n(t)$ taken by the traps up to time t. Finally, for the CTRW model on a fractal one has $S(t) \sim t^{\gamma \tilde{d}/2}$ for $\tilde{d} < 2$, and $S(t) \sim t^{\gamma}$ for $\tilde{d} > 2$ [39].

Many interesting variations and applications of the target problem can be found in the literature. Some recent ones include stochastically gated [50] or evanescent [46] traps, and the target problem on scale-free networks and on small world networks [47].

1.3.2
Trapping problem

The probability that any given site is *not* occupied by a trap is $1 - c$. From the definition of $\mathbf{S}(t)$ one then immediately concludes that the survival probabil-

ity in the trapping problem is

$$P(t) = \left\langle (1-c)^{\mathbf{S}(t)} \right\rangle \equiv \left\langle e^{-\lambda \mathbf{S}(t)} \right\rangle, \tag{1.15}$$

where $\lambda \equiv -\ln(1-c)$. The average in this equation is performed over all realizations of the random walk from time $t = 0$ to time t. This average can not be calculated exactly, and therefore to deal with the trapping problem one typically has to resort to short-time and long-time asymptotic approximations.

The extended Rosenstock approximation or truncated cumulant expansion is the standard approach for estimating the short-time asymptotics of the trapping problem [24, 25, 40, 57, 58]. The cumulant expansion technique allows an alternative expression for the survival probability as an infinite series,

$$P(t) = \exp \left[\sum_{n=1}^{\infty} \frac{(-\lambda)^n \kappa_n}{n!} \right], \tag{1.16}$$

where κ_n, $n = 1, 2, \ldots$, denote the cumulants of $\mathbf{S}(t)$. The first two cumulants are $\kappa_1 = \langle \mathbf{S}(t) \rangle \equiv S(t)$ and $\kappa_2 = \langle \mathbf{S}^2(t) \rangle - \langle \mathbf{S}(t) \rangle^2 \equiv \sigma^2(t)$. If only the first term of the sum in Equation (1.16) is retained, we get the zeroth order Rosenstock approximation

$$P(t) = e^{-\lambda S(t)}. \tag{1.17}$$

The error made in this truncation can be estimated by considering the next term in the exponent in Equation (1.16). One finds that the zeroth order Rosenstock approximation is reasonable for concentrations and times sufficiently small to satisfy the condition $\lambda^2 \sigma^2 \ll 1$. A shortcoming of this approach is that the first moments of $\mathbf{S}(t)$ are known only for a few simple cases [24, 59].

The long-time behavior of the survival probability of the particle in a sea of stationary traps has been studied for diffusive particles in Euclidean media [24, 25, 60] and on fractal substrates [42, 43, 48]. It has also been studied for particles performing a long-tailed CTRW in Euclidean and fractal media [39, 40, 42, 49]. The mathematics leading to the results is too elaborate to reproduce in any abbreviated version, so we simply state the results. For diffusive particles on a Euclidean or fractal medium one finds

$$P(t) \sim \exp \left[-\alpha \lambda^{2/(\tilde{d}+2)} t^{\tilde{d}/(\tilde{d}+2)} \right]. \tag{1.18}$$

where α is a substrate-dependent constant and $\tilde{d}$ is the spectral dimension of the substrate. The difficulties in verifying this result numerically because of the long times it takes to reach this asymptotic behavior are well known [61]. On the other hand, for a particle that performs a long-tailed CTRW the survival probability is given by $P(t) \sim t^{-\gamma}$ [39]. Note that now, at odds with

what we founded for the target problem, one can not arrive at the long-time behavior of $P(t)$ via the simple subordination substitution $t \to t^\gamma$ in the normal diffusive result. This is because the survival probability here is not determined mainly by the number of steps taken by the particle. In fact, the survival probability of the particle is greatest if it takes no steps at all, and the probability that it remains at its initial location up to time t is precisely $\int_t^\infty \psi(\tau) d\tau \sim t^{-\gamma}$.

In Figure 1.3 we show simulation results for the survival probability in a one-dimensional subdiffusive trapping problem where the particle motion is a long-tailed CTRW. We also show the long-time, $P(t) \sim 1/\left[2\Gamma(1-\gamma)\xi^2\right]$, and short-time, $P(t) \sim \exp\left[-2\xi/\Gamma(1+\gamma/2)\right]$, asymptotic results [49]. Here $\xi = \lambda\sqrt{Kt^\gamma}$.

1.4
Two basic reactions

In both the target and the trapping problems discussed in Section 1.3 one of the two particles involved in the reaction (either the one that disappears or the one that survives) was *static*. As a result, the solution of these problems is relatively simple. The problem turns out to be much more difficult when all the
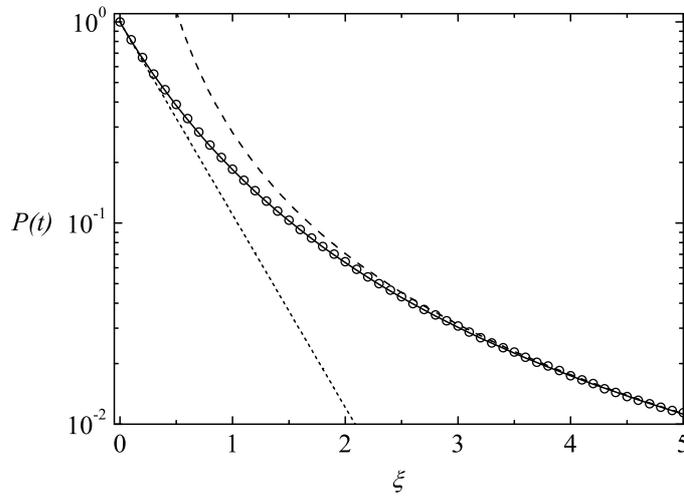

Fig. 1.3 Survival probability $P(t)$ versus $\xi \equiv \lambda\sqrt{Kt^\gamma}$ for the one-dimensional CTRW trapping problem with $\gamma = 1/2$. The symbols are simulation results for $c = 0.01$ and 10^6 realizations. The dashed and dotted lines correspond to the long- and short-time asymptotic approximations, and the solid line represents the numerical estimation of an exact integral representation of $P(t)$ [49].

reacting particles are mobile. In this section we consider two basic reactions of this type. The first is a single-component reaction, $A + A \rightarrow \{A, 0\}$, and the second is a two-component reaction, $A + B \rightarrow 0$.

1.4.1
Annihilation and coalescence reactions

Consider a reactive system in which subdiffusive A particles merge when they meet, $A + A \rightarrow A$ (coalescence reaction). Although we explicitly discuss only the coalescence reaction, all the results of this section are also valid for the annihilation reaction, where both particles disappear upon encounter, $A + A \rightarrow 0$.

For well-stirred systems, the concentration $c(t)$ of particles A follows the classical kinetics equation $dc/dt \sim -c^2$, so that $c(t) \sim 1/t$ independently of the initial concentration $c(0)$. However, when the particles are mixed only by diffusion, a system in low dimensions is not well-stirred and the kinetics is different [1,5]:

$$c(t) \sim \begin{cases} 1/t^{d/2}, & d < 2, \\ 1/t, & d > 2. \end{cases} \tag{1.19}$$

When the particles A are subdiffusive with anomalous diffusion exponent γ, the corresponding result is [6]

$$c(t) \sim \begin{cases} 1/t^{\gamma d/2}, & d < 2, \\ 1/t^{\gamma}, & d > 2. \end{cases} \tag{1.20}$$

Note that this result follows from Equation (1.19) via the subordination replacement $t \rightarrow t^{\gamma}$.

In Figure 1.4 we show simulation results for the concentration $c(t)$ of A particles that react by annihilation or by coalescence, and that diffuse in one- and three-dimensional quenched-disorder lattices as described above Equation (1.4) with $\alpha = 1/2$ (i.e., $\gamma = 2/3$ for $d = 1$ and $\gamma = 1/2$ for $d = 3$). The fitted lines for $d = 1$ [$d = 3$] correspond to the expression $c(t) = 0.88/t^{0.33}$ [c(t)=1.44/$t^{0.49}$] for the coalescence reaction, and to $c(t) = 0.44/t^{0.33}$ [c(t)=0.74/$t^{0.49}$] for the annihilation reaction. Note that, as one would expect, $c_{\text{annihilation}} \simeq c_{\text{coalescence}}/2$.

Equation (1.20) can be justified by means of scaling arguments [1, 5] that involve $S(t)$, the volume swept out by a randomly moving particle (cf. Equation (1.13)). One assumes that the number of particles that a given particle A destroys during time Δt is given approximately by the number of particles inside the volume swept by A during this time, namely, $c(dS/dt)\Delta t$. Recognizing that there is not just a single A in this volume but that there are in fact $c(t)V$ of them, the cV particles inside the volume V will destroy $cV \times c(dS/dt)\Delta t$

particles. Thus, as $\Delta t \to 0$ we have $dc/dt \sim c^2 V dS/dt$, which upon integration immediately leads to $c \sim 1/S$. For $d > 2$ this argument is clear because the random walk is not recurrent, that is, each step essentially brings the particle to a new previously unexplored location. However, for $d \leq 2$ the random walk is recurrent and the argument is less evident. Nevertheless, the same result holds precisely because the exploration of a particle is compact for $d \leq 2$, and thus only the (surviving) sweeping particle remains inside the swept volume $S(t)$, which means that again $c \sim 1/S$. It turns out that this result is valid for normally diffusive as well as subdiffusive particles in Euclidean and fractal substrates [6]. This formula, together with (1.14), explains (1.19) and (1.20). It is worth noting that for the one-dimensional case there are more precise and detailed results obtained by special methods for normal diffusive particles (see, e.g., [5,62]) and also for subdiffusive particles (see, e.g., [63,64]).

In this subsection we have only explicitly considered reactions in Euclidean media. For fractal media the results (1.19) and (1.20) are also valid with the replacement of the dimension d by the spectral dimension $\widetilde{d}$ [6].
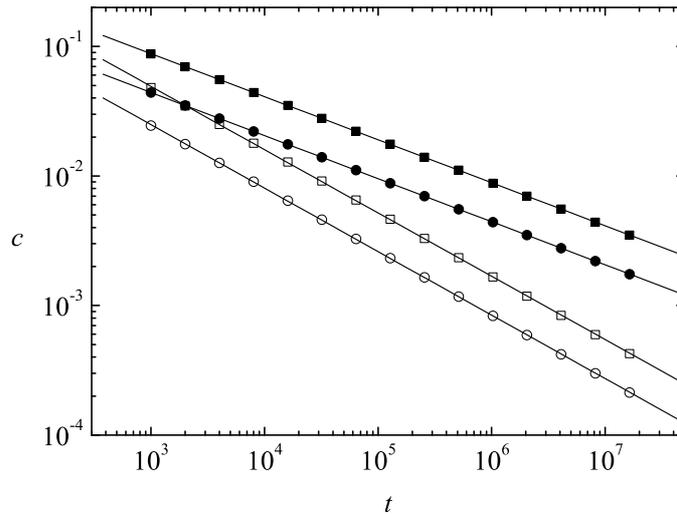

Fig. 1.4 Simulation results for the concentration $c(t)$ of subdiffusive particles in a one-dimensional (open symbols) and three-dimensional (filled symbols) quenched-disorder lattice with $\alpha = 1/2$ where they react by coalescence ($A + A \to A$, squares) and annihilation ($A + A \to 0$, circles). The fitted lines have a slope of 0.33 for $d = 1$ [0.49 for $d = 3$] in good agreement with the theoretical exponents $\gamma/2 = 1/3$ [$\gamma = 1/2$].

1.4.2
Annihilation of two species, $A + B \rightarrow 0$

Consider now the two-component annihilation reaction $A + B \rightarrow 0$ and let us assume that the initial concentration of both species of particles, arranged at random in a d-dimensional substrate, are equal, $c_A(0) = c_B(0)$. (Some two-species reactions with different initial concentrations will be studied in Section 1.6.) It is well known that when the particles are normally diffusive, the concentration of either species decays as [5,6,65,66]

$$c(t) \sim \begin{cases} 1/t^{d/4}, & d < 4, \\ 1/t, & d > 4, \end{cases} \tag{1.21}$$

where c stands for c_A or c_B. Thus, the law of mass action result $c(t) \sim t^{-1}$ obtained from the usual macroscopic rate law $dc/dt = -kc^2$ holds only above four dimensions (and with logarithmic corrections at the critical dimension $d = 4$). To understand the $d < 4$ behavior one notes that in an initially random distribution of reactants there are local density fluctuations which lead to a local surplus of one species over the other. In a region of volume r^d this surplus is of order $[c(0)r^d]^{1/2}$. The fluctuations decay by diffusion even while at the same time the concentrations of both species decay because of the reaction. For $d < 4$ the decay due to the occurrence of fluctuations and the attendant diffusion is slower than the rate equation decay. Thus, as time passes the particles inside this volume will diffuse and cover the entire volume in a time of order $t \sim r^2$ during which $A - B$ pairs will have annihilated. The concentration of the surviving majority species is then roughly the initial surplus divided by the volume r^d, that is, $c(t) \sim [c(0)r^d]^{1/2}/r^d = [c(0)/r^d]^{1/2} \sim t^{-d/4}$. This gives rise to increasing segregation of species, producing growing regions rich in one species or the other. The reaction occurs only at the interfaces and is hence slower than predicted by the macroscopic law of mass action rate equation. At the critical dimension $d = 4$ the rates of the two decay mechanisms coincide, and when $d > 4$ diffusion is able to mix the particles effectively and consequently the law of mass action applies.

For subdiffusive particles described by a CTRW the results in Equation (1.21) generalize to

$$c(t) \sim \begin{cases} 1/t^{\gamma d/4}, & d < 4, \\ 1/t^{\gamma}, & d > 4. \end{cases} \tag{1.22}$$

The $d < 4$ result, which follows from the subordination trick $t \rightarrow t^{\gamma}$, can be found in Reference [6] and can be obtained following the arguments laid out above generalized to the subdiffusive case (see References [1,5,65,66]). The initial surplus of one species over the other in a volume r^d is still $\sim [c(0)r^d]^{1/2}$. Now, however, the particles inside the volume will cover it in a time of order

$t \sim r^{2/\gamma}$, so that reactions inside the volume will leave the majority species with concentration $c(t) \sim [c(0)/r^d]^{1/2} \sim t^{-\gamma d/4}$. That the concentration above the critical dimension decays as $c(t) \sim t^{-\gamma}$, and that the critical dimension for the above behavior is still $d = 4$, has, to our knowledge, not been proven and must rely for now on the subordination argument, which we repeat in this context for the sake of clarity. In the law of mass action regime (or its analog for subdiffusive particles), the change Δc in the density $c(t)$ when particles make Δn jumps is proportional to the number of encounters between opposite species during these jumps. For $d > 4$ we assume that, as in the case of normal diffusion, the subdiffusive process mixes the particles effectively so that the number of encounters is proportional to c^2. Therefore $dc/dn \sim c^2$ and it follows that $c \sim 1/n$. For diffusive particles $n \sim t$, and consequently one recovers the classical result $c \sim 1/t$. For subdiffusive particles $n \sim t^\gamma$, and consequently $c \sim 1/t^\gamma$.

Finally, for fractal media the results in (1.21) and (1.22) for $d < 4$ are also valid with the replacement of d by the spectral dimension $\tilde{d}$ [6]. It would seem reasonable to conjecture, on the basis of the subordination procedure, that the results for $d > 4$ are also valid with this replacement.

1.5
Reactions with non-homogeneous distribution of reactants

In the preceding sections we focused on the global reaction kinetics of different reactive systems, our main objective being the estimation of the time dependence of the global concentration $c_i(t)$ of the reactants. However, in some cases, specifically for systems where the spatial arrangement of reactants is inhomogeneous, it might be more convenient or even necessary to consider a mesoscopic description, and to study how the concentrations of the species vary in space as well as time. In this case the quantities of interest will be the $c_i(\mathbf{r}, t)$.

Of course, as a first proviso this study requires knowledge of how the concentrations of species evolve in the absence of reactions. For normal diffusive particles, the evolution of $c_i(\mathbf{r}, t)$ is given by the diffusion equation. On the other hand, for the long-tailed CTRW model the concentration of particles evolves according to the fractional diffusion equation (1.8):

$$\frac{\partial c_i}{\partial t} = K_i \, _0D_t^{1-\gamma}\nabla^2 c_i(\mathbf{r}, t). \tag{1.23}$$

For N-component reactive systems with normal diffusive species, the reaction-diffusion equations for the local concentrations are

$$\frac{\partial c_i}{\partial t} = K_i\nabla^2 c_i(\mathbf{r}, t) + f_i(c_1, \cdots, c_N). \tag{1.24}$$

The reaction terms f_i are typically those corresponding to the law of mass action, $f_i = \pm \kappa_i \prod_{j=1}^{N} c_j^{n_j}$, where the n_j are the stoichiometric coefficients.

What are the analogous equations when the reactants are subdiffusive? In previous sections, specially in section 1.4, we have appealed to subordination arguments to obtain the reaction kinetics for subdiffusive systems from their diffusive counterparts by means of the change $t \to t^\gamma$. This might lead us to think that a similarly simple substitution could be true for reaction-diffusion equations. Looking at (1.8) and (1.24), one might be tempted to conjecture that the change equivalent to the subordination $t \to t^\gamma$ is perhaps $\nabla^2 \to {}_0D_t^{1-\gamma}\nabla^2$, so that the subdiffusion-limited reactions would be described by

$$\frac{\partial}{\partial t}c_i(\mathbf{r},t) = K_i \, {}_0D_t^{1-\gamma}\nabla^2 c_i(\mathbf{r},t) + f_i(c_1,\cdots,c_N). \tag{1.25}$$

Although this may seem natural, it is, in general, false!. For example, $\partial c/\partial t = K\partial^2 c/\partial x^2 - \kappa c(x,t)$ is a well-behaved equation describing the change in the concentration because the particles disappear with rate coefficient κ (we assume $\kappa > 0$) and also because of diffusion. However, the equation

$$\frac{\partial c}{\partial t} = K \, {}_0D_t^{1-\gamma}\frac{\partial^2 c}{\partial x^2} - \kappa c(x,t) \tag{1.26}$$

leads to the unphysical prediction of negative concentrations [13] (see Figure 1.5)! This example should serve as a strong indicator that the subject of subdiffusion-limited reactions is tricky and should be approached with caution.
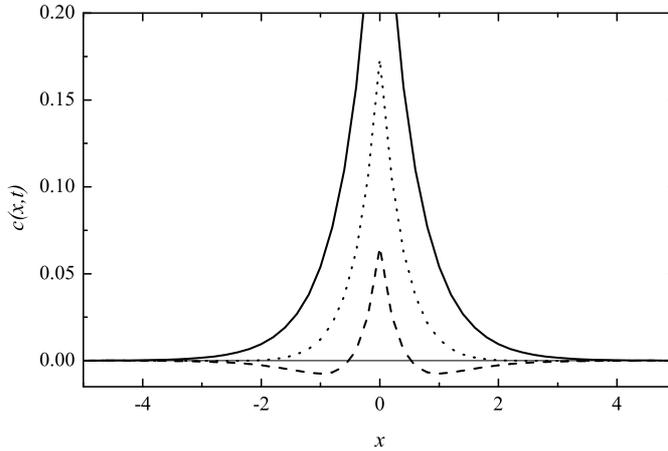

Fig. 1.5 Concentration $c(x,t)$ for $t = 0.2$ (solid line), $t = 0.4$ (dotted line) and $t = 1$ (dashed line) obtained by solving Equation (1.26) by means of the numerical methods for integrating fractional diffusion equations described in [67]. Here $\gamma = 1/2$, $K = 1$, $\kappa = 5$, the initial condition is $c(x,0) = \delta(x)$, and free boundary conditions are used.

1.5.1
Reaction-subdiffusion equations

The above example prompts a less naive, less ad hoc, more fundamental construction of the reaction-subdiffusion equations . Indeed, it calls for building reaction-subdiffusion equations (equations that are a mesoscopic description of the reactive system) from a microscopic approach. Some work along these lines has recently been published [12, 13, 32–35, 37, 68–72]. In Reference [32] Seki et al. consider geminate recombination (that is, recombination of particles produced from a common precursor) of subdiffusive particles. Their analysis is based on the CTRW scheme. In their model one particle migrates subdiffusively back toward the other, the reaction taking place when the particles are separated by a distance between R (the reaction radius) and $R + dr$. If the reaction occurs at a rate comparable with the transport kinetics, two types of waiting time distributions at the encounter distance are relevant: the waiting time distribution for making a jump to a neighboring lattice site, $\psi_{\text{out}}(t) = \psi(t) \exp(-t/\tau_{\text{rc}})$, and the waiting time distribution of reaction defined as the probability that the particle which is initially at a site within the encounter distance will undergo reaction without making a jump at time t, $\psi_{\text{rc}}(t) = \tau_{\text{rc}}^{-1} \exp(-t/\tau_{\text{rc}}) \int_0^\infty dt_1 \psi(t_1)$, τ_{rc}^{-1} being the reaction rate constant.[2] In Reference [32] it is shown that this model leads to the reaction-subdiffusion equation

$$\frac{\partial c}{\partial t} = {}_0D_t^{1-\gamma} \left[K\nabla^2 c(r,t) - \kappa\delta(r-R)c(r,t) \right], \tag{1.27}$$

where K and κ are constants. For $\gamma = 1$, the Riemann-Liouville derivative is the identity operator and the conventional equation is recovered. As discussed earlier, the substitution $\nabla^2 \rightarrow {}_0D_t^{1-\gamma}\nabla^2$ in the normal reaction-diffusion equation does not lead to the correct subdiffusive counterpart. Equation (1.27) is remarkable: it shows that the exit from the encounter distance described by a long-tailed waiting time distribution of jumps interferes with the reaction at the encounter distance. This leads to a memory in the reaction term like the one that describes subdiffusive motion [32].

Another interesting problem that leads to a reaction-subdiffusion equation where, as in Equation (1.27), a fractional (subdiffusive) operator affects both the diffusion and the reaction terms is that proposed by Henry et al. [13] (see also Reference [73]). In this problem a constant proportion of subdiffusive particles in a one-component system is removed instantaneously at the start

2) When the jump waiting time distribution $\psi(t)$ is long-tailed, we see
  that the reaction has memory in the sense that the probability of not
  reacting during a given time affects the probability of reaction after
  this time; this is not the case when the jump waiting time distribu-
  tion is exponential, that is, for normal diffusive particles.

(or end) of each jump. It turns out that this CTRW model leads to the reaction-subdiffusion equation [13]

$$\frac{\partial c}{\partial t} = \mathcal{D}_t^{1-\gamma} \left[K \frac{\partial^2 c}{\partial x^2} - \kappa c(x, t) \right], \tag{1.28}$$

where K and κ are constants, and where $\mathcal{D}_t^{1-\gamma}$ is an integro-differential operator (closely related to the Riemann-Liouville derivative[3]), defined by the relation $\mathcal{L}\mathcal{D}_t^{1-\gamma} y(t) = u^{1-\gamma} \widetilde{y}(u)$. Here $\mathcal{L}$ is the Laplace operator, u the Laplace variable, and $\widetilde{y}(u)$ the Laplace transform of $y(t)$. Once again the subdiffusive character of the reactants modifies the classical reaction term $-\kappa c(x, t)$ through the same fractional operator $\mathcal{D}_t^{1-\gamma}$ that modifies the classical diffusion term $K \partial^2 c / \partial x^2$.

In the models leading to Equations (1.27) and (1.28) the reactions at small scales are subdiffusion controlled, that is, in these models the (subdiffusive) movement of the particles leads to encounters among them which eventually lead to reactions. A different scenario occurs when the reaction at small scales is decoupled from the (subdiffusive) movement of the particles. Such models have also been proposed recently [12, 13, 33, 74]. For example, in References [12, 13, 33] a model in which the subdiffusive particles disappear at a constant rate independent of their position and movement is considered. In this case the reaction-subdiffusion equation is

$$\frac{\partial c}{\partial t} = Ke^{-\kappa t} \mathcal{D}_t^{1-\gamma} \left[e^{\kappa t} \frac{\partial^2 c}{\partial x^2} \right] - \kappa c(x, t). \tag{1.29}$$

Although in a form different from Equations (1.27) and (1.28), this equation again shows that the contributions of subdiffusion and reaction to the time evolution of the density are not separable.

The reaction-subdiffusion systems discussed in this section are monomolecular.[4] Some attempts to arrive at mesoscopic descriptions of multicomponent reaction-subdiffusion systems where the subdiffusion is described by the CTRW formalism and the reaction is modeled locally by means of the law of mass action have recently begun to appear in the literature [33, 34]. However, on the whole, a microscopic approach to multicomponent subdiffusion controlled systems such as that considered below in section 1.5.2, is still lacking, and the subdiffusion-reaction equations employed for these systems are for now mostly of an ad hoc nature.

---

3) In fact both operators $\mathcal{D}_t^{1-\gamma}$ and $_0 D_t^{1-\gamma}$ are the same when applied to sufficiently regular functions $f(t)$ as determined by the condition $\lim_{t \to 0} \int_0^t d\tau (t - \tau)^{\gamma-1} f(\tau) = 0$.

4) The geminate recombination reaction is analyzed by Seki et al. [32] as an effective monomolecular reaction where particles of a given species are absorbed at a boundary.

1.5.2
Reaction Fronts

In many reaction-diffusion and reaction-subdiffusion systems, either by design or by natural evolution of the system, the spatial distribution of reactants is spatially inhomogeneous. This occurs, for instance, when initially the reactants are separated by a physical boundary that is then removed, or when there are inhomogeneous sources of reactants that feed the system through its boundaries, or even in constrained geometries where random fluctuations of initially mixed reactants can grow in time as the local majority species overwhelms the minority. In these cases, the system may consist of essentially single-component domains so that the reactions between different components occur only (or mainly) at the interphases or boundaries of the domains.

The quintessential front problem is a d-dimensional systems where two reacting species, A and B, that form product C, are initially separated by a $(d-1)$-dimensional planar wall situated at $x = 0$. The concentrations of the species are denoted by a, b and c, and the problem is to determine a number of measures such as the concentration profiles $a(x,t)$ and $b(x,t)$ of the reactants, the rate of production of C particles $R(x,t) \equiv \partial c(x,t)/\partial t$ (often called the reaction profile), the global reaction rate $R(t) = \int_{-\infty}^{\infty} R(x,t)dx$, and the position of the front $x_f(t)$ defined as the position where $c(x,t)$ is maximum. This system, in contrast with those of section 1.5.1, is a truly multicomponent reaction problem. Reaction fronts involving diffusive particles have been extensively studied. The standard analytic starting point in this case is the set of mean-field reaction-diffusion equations

$$\frac{\partial}{\partial t}a(x,t) = D_A \frac{\partial^2 a(x,t)}{\partial x^2} - ka(x,t)b(x,t),$$
$$\frac{\partial}{\partial t}b(x,t) = D_B \frac{\partial^2 b(x,t)}{\partial x^2} - ka(x,t)b(x,t), \tag{1.30}$$

where the choice $R(x,t) = ka(x,t)b(x,t)$ corresponding to the law of mass action has been made. Initially the A particles are uniformly distributed with concentration a_0 in the region $x < 0$, and the B particles are uniformly distributed with concentration b_0 in the region $x > 0$. A variety of interesting analytic results are known for this system, obtained mainly from scaling approaches grounded on adiabatic time scale separation arguments [5, 75, 76]. For example, for $d \geq 2$ the mean-field description (1.30) is valid, and when $D_A = D_B$ the width w of the reaction front (the region where $R(x,t)$ is appreciable) scales as $t^{1/6}$, its height $h = R(x_f, t)$ as $t^{-2/3}$, the global reaction rate $R(t)$ as $t^{-1/2}$, and, provided that $a_0 \neq b_0$, the position of the front x_f as $t^{1/2}$ (if $a_0 = b_0$ then clearly $x_f = 0$ at all times). Note that for the critical dimension $d = 2$ for this behavior there are logarithmic corrections to these results [77, 78]. Another version of the problem deals with a steady-state situ-

ation, where A and B particles are injected at equal rates J at opposite boundaries. Again there are scaling arguments that lead to steady state predictions for a number of quantities [79, 80]. For example, for $d \geq 2$ the width of the reaction front scales as $w \sim (kJ/D^2)^{-1/3}$ when $D_A = D_B \equiv D$. Here, too, $d = 2$ is the critical dimension for this behavior. These results break down below the critical dimension, that is, for systems such as one-dimensional lattices or two-dimensional percolation clusters. When $d < 2$, microscopic density fluctuations become important and the mean field reaction-diffusion formalism is no longer valid (see [5, 23, 81] and references in [82]). The exponents in this case are entirely different. For instance, in one dimension in the time-dependent scenario the width of the reaction front grows as $t^{1/4}$ (with perhaps a logarithmic correction [80]) instead of $t^{1/6}$ [78, 83, 84].

How do these results change when the particles are subdiffusive? First, it is commonly agreed that the critical dimension for the importance or negligibility of microscopic fluctuations is in any case still $d = 2$. Beyond this, the answers have been sought in two contexts. In one [81], numerical simulations are carried out in a system with a form of quenched disorder in which the mean square displacement of the particles is sublinear in time, $\langle x^2 \rangle \sim t^\gamma$, as in Equation (1.4). Araujo in [81] found empirically that for $d > 2$, $w \sim t^\alpha$ and $h \sim t^\beta$ with $\alpha = \gamma/6$ and $\beta = 1 - \gamma/3$. These exponents are thus associated with mean field behavior. For $d < 2$ the empirical results $\alpha = \gamma/(2 + 2\gamma)$ and $\beta = 1 - \gamma/2 + \alpha$ differ from mean field behavior, presumably due to the importance of microscopic fluctuations. Hecht et al. [23] simulated the reaction on a two-dimensional percolation cluster, and found and exponent $\alpha \simeq 0.246$ very close to the one-dimensional normal-diffusive result $\alpha = 1/4$ and, again, $\beta = 1 - \gamma/2 + \alpha$.

The second context in which subdiffusive species in the quintessential front problem have been investigated is that of a regular lattice in which the particle motion is governed by a long-tailed CTRW model [82]. Computer simulations for $d = 2$ confirm the mean field exponents $\alpha = \gamma/6$, $\beta = 1 - \gamma/3$. The system was also studied analytically by postulating a set of fractional mean-field reaction-diffusion equations,

$$
\begin{aligned}
\frac{\partial}{\partial t} a(x,t) &= {_0}D_t^{1-\gamma} \left[K \frac{\partial^2 a(x,t)}{\partial x^2} - ka(x,t)b(x,t) \right], \\
\frac{\partial}{\partial t} b(x,t) &= {_0}D_t^{1-\gamma} \left[K \frac{\partial^2 b(x,t)}{\partial x^2} - ka(x,t)b(x,t) \right],
\end{aligned}
\tag{1.31}
$$

which was inspired by the work of Seki et al. [32, 69, 70] in the geminate recombination problem. Note that Equations (1.31), like Equations (1.27) and (1.28), involve a fractional diffusion operator working simultaneously on the classical normal diffusion and reaction terms. Also, an entirely similar set of equations has recently been used by Langlands et al. [72] in a study of Turing

patterns in subdiffusion-reaction systems. For simplicity the coefficients K in front of the second derivative terms have been set equal for the two species. While the validity of this form bears further discussion [33,34], the predictions that emerge from this model agree with those obtained from the CTRW simulations, including the behaviors $w \sim t^{\gamma/6}$, $h \sim t^{1-\gamma/3}$, and $R(t) \sim t^{\gamma/2}$. From Equations (1.31) it is not difficult to prove that the position of the front is given by $x_f = S_f \sqrt{Kt^\gamma}$, where S_f is determined by the equation

$$\frac{2q}{1+q} = H_{11}^{10} \left[S_f \; \middle| \; \begin{array}{c} (1, \frac{\gamma}{2}) \\ (0, 1) \end{array} \right],$$ (1.32)

with $q = b_0/a_0 \leq 1$ [82]. Here H_{11}^{10} is the Fox H-function [85]. An alternative analysis of Equations (1.31) that includes the case where one of the species is static is discussed in Reference [86].

Clearly, the problem of fronts involving reactions of subdiffusive species is a field in its infancy in which much work remains to be done.

1.6
Reactants with different (sub)diffusion exponents

The classic target and trapping problems discussed in section 1.3 are both subsumed under the reaction $A + B \rightarrow B$. In the target problem the particle A is stationary and the traps B move, while in the trapping problem the traps B are stationary and A moves. A more difficult $A + B \rightarrow B$ problem occurs when both A and B move, especially if their motion is characterized by different exponents (see a sketch of this problem in Fig. 1.2).

Even in the case of normally diffusive particles, the $A + B \rightarrow B$ problem is notoriously difficult and has only recently been fully solved asymptotically. The first rigorous results for this problem were actually derived from an analysis of the $A + B \rightarrow 0$ reaction. In Section 1.4.2 we reported results for this reaction when the initial concentrations $c_A(0)$ and $c_B(0)$ are equal. When the initial concentrations are not equal the decay laws are entirely different from the power laws reported in Equation (1.21). Instead, the decay law for the minority species, say A, take on an exponential form, shown by Bramson and Lebowitz [87] to be given by

$$c_A(t) \sim \begin{cases} \exp(-\lambda_d t^{d/2}), & d < 2, \\ \exp(-\lambda_2 \ln t/t), & d = 2, \\ \exp(-\lambda_d t), & d > 2. \end{cases}$$ (1.33)

The connection with the $A + B \rightarrow B$ problem arises because at the late times when these asymptotic laws apply one has a few isolated A particles diffusing in a background or sea of B particles whose density remains essentially

fixed. While these exponential forms were posited, contradicted, and argued by a number of authors preceding Bramson and Lebowitz, theirs was the first rigorous proof that this is indeed the asymptotic behavior [8]. Note that because the A particles move independently, the evaluation of c_A is equivalent to that of the survival probability $P(t)$ of a single A particle moving in a sea of B traps, $c_A(t) \propto P(t)$.

The dimension-dependent constants λ_d remained undetermined for almost 15 years, until Bray and Blythe [88] applied an ingenious bounding procedure leading to lower and upper bounds that converge asymptotically to yield the explicit constant for $1 \leq d \leq 2$. Some of these bounding results were extended by Oshanin et al. [52] to systems where the traps perform a compact exploration of the space, that is, where the random walk dimension d_w of the traps is greater than the dimension d of the space. The upper bound for the survival probability was based on the so-called Pascal principle, which states that the best strategy for survival is for an A particle surrounded by moving traps not to move. Thus, the upper bound is the target problem of Section 1.3.1. That this is an upper bound was assumed without proof by Bray and Blythe and later proved by Moreau [89] and by Bray et al. [90], although it had been proved earlier [91] in the context of incoherent exciton quenching. The lower bound for the survival probability of the A particle was found by calculating the probability that A is surrounded by a trap-free region of size $\mathcal{L}$ from which it does not move out as it diffuses and into which no B particle diffuses in. Optimization of this lower bound with respect to $\mathcal{L}$ leads to the same leading contribution as the upper bound, and this procedure thus led to explicit results for the λ_d. In one dimension they found the asymptotic survival probability (or, equivalently, the concentration of A particles)

$$c_A(t) \sim \exp[-4\rho(Dt/\pi)^{1/2}], \tag{1.34}$$

where ρ is the density of the sea of traps B [that is, $\rho \simeq c_B(0) - c_A(0)$] and D is the diffusion constant of the traps. Note that this is exactly the survival probability for a particle that remains still, but it is only the leading term of the lower bound and hence it is an asymptotic result. The asymptotic survival probability is thus independent of the diffusion coefficient of the particle A, which is consistent with the fact that the Pascal principle provides an upper bound that is ultimately hugged by the lower bound.

We now pose the question: What is the survival probability of a subdiffusive particle A in a sea of subdiffusive traps B? To add to the complexity, what happens when the subdiffusive exponents for the particle and the traps are different? In particular, if a subordination procedure were to hold, how might it involve such different exponents? This is not just a theoretical scenario, see for example [92].

An upper and lower bound that meet asymptotically can be calculated for subdiffusive particles and traps in one dimension following the procedures of Bray and Blythe [88], but not for arbitrary subdiffusive exponents [15,16]. The upper bound of the survival probability is found from the Pascal principle and can again be calculated exactly,

$$P_U(t) = \exp\left[-2\rho(Kt^\gamma)^{1/2}/\Gamma\left(1 + \frac{\gamma}{2}\right)\right], \tag{1.35}$$

where K and γ are the generalized diffusion coefficient and the subdiffusion exponent, respectively, for the traps. When $\gamma = 1$ this reduces to the result (1.34). The lower bound is again obtained by calculating the probability that A is surrounded by a trap-free region of size $\mathcal{L}$ from which it does not move out as it diffuses and into which no B particle diffuses in. Interestingly, when the particle A is subdiffusive, optimization of the lower bound leads to a time-independent size $\mathcal{L}$ whereas for a diffusive A the optimal size is time dependent (regardless of the way the traps move). In any case, these two bounds do not converge asymptotically for all values of the exponents γ (traps) and γ' (particle). In particular, the bounds do meet for diffusive or subdiffusive traps as long as the particle is subdiffusive, that is, for $0 < \gamma' < 1$ and $0 < \gamma \leq 1$:

$$c_A(t) \sim \exp\left[-2\rho(Kt^\gamma)^{1/2}/\Gamma\left(1 + \frac{\gamma}{2}\right)\right]. \tag{1.36}$$

Thus, comparing this result with Equation (1.34) we see that the subordination procedure works *as determined by the traps*, regardless of the particle's subdif-
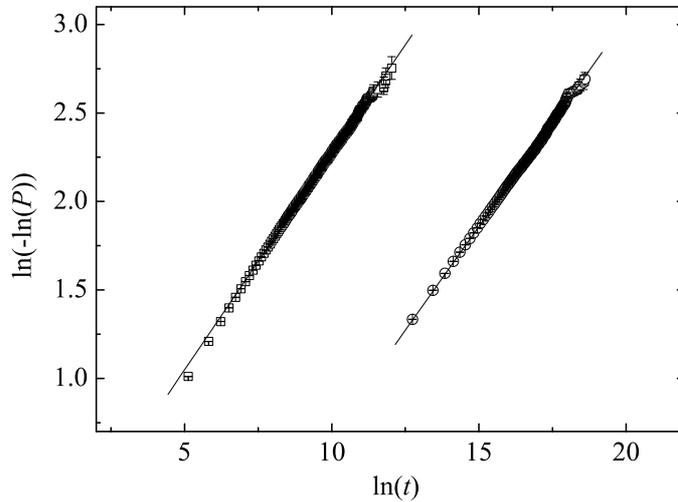

Fig. 1.6 Simulation results for the survival probability for $\gamma = \gamma' = 0.5$. The left set of data (squares) corresponds to a trap density of $\rho = 0.5$ and a slope of 0.24, the right set (circles) to $\rho = 0.1$ and a slope of 0.23. The asymptotic prediction for the slope is $\gamma/2 = 0.25$.

fusive exponent (provided that the particle is subdiffusive). This is again reasonable in view of the fact that the Pascal principle leads to an upper bound for the survival probability to which the lower bound eventually converges, so that it does not matter whether or not the particle moves at all. If the particle is diffusive, $\gamma' = 1$, then the result (1.36) is still asymptotically valid provided $2/3 < \gamma \leq 1$, that is, *provided the traps are not too slow*. Again, in this regime asymptotically it does not matter whether or not the particle moves.

The uncertainties about the survival probability remain when the particle is diffusive ($\gamma' = 1$) and the traps move too slowly ($0 < \gamma \leq 2/3$). The bounds now no longer converge [15]. We interpret this to mean that it is no longer unimportant that in fact the particle does move. In the marginal case $\gamma = 2/3$ the bounds provide sufficient information to determine that

$$c_A(t) \sim \exp\left(-\lambda t^{1/3}\right), \tag{1.37}$$

but not sufficient to determine the value of the constant λ. It is interesting to note that this particular time dependence is the same as the classic result for the survival probability of a diffusive particle in a sea of immobile traps, see Equation (1.18) with $\tilde{d} = 1$. For even slower traps, $0 < \gamma < 2/3$, this procedure does not even provide converging bounds for the time dependence. One might postulate that the form (1.37) holds in this regime, but proof of this conjecture is still under investigation [17].
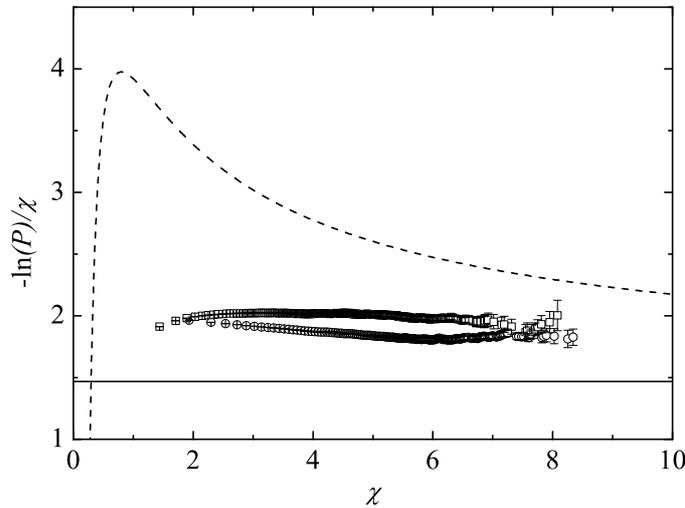

Fig. 1.7 Simulation results for the exponential prefactor $\widetilde{\lambda}$ in Equation (1.38) for $\gamma = \gamma' = 0.5$. Solid line at $1.4688\ldots$: upper bound; dashed curve: lower bound. Data points are for $\rho = 0.5$ (squares) and $\rho = 0.1$ (circles).

The asymptotic results obtained for subdiffusive particles and traps do not provide an estimate of the time of validity of these results, nor of the way in which the survival probability approaches the asymptotic regime. Extensive computer simulations show that in some parameter regimes the asymptotic theory describes the simulation results very well even for relatively short times, while in others it is not even possible to arrive at asymptotes within ordinary computational means [16]. In particular, when $\gamma \geq \gamma'$ the asymptotic behavior is reached rather quickly: when the survival probability is of $O(10^{-1}) - O(10^{-2})$ the agreement of simulations with the asymptotic results is already very good. On the other hand, when $\gamma < \gamma'$ the asymptotic behavior is reached much more slowly, especially as the difference between the exponents increases. In some cases, we have been unable to reach the asymptotic regime even when the survival probability is as small as 10^{-6}. Representative results for the exponent of t in Equation (1.36) are shown in Figure 1.6. Equation (1.36) can be rewritten in terms of the dimensionless quantities $\chi = \rho \langle x^2 \rangle^{1/2}$ and $\widetilde{\lambda} = [2\Gamma(1+\gamma)]^{1/2}/\Gamma(1+\gamma/2)$ as

$$P(t) \sim \exp(-\widetilde{\lambda}\chi). \tag{1.38}$$

In Figure 1.7 are shown simulation results for $-\ln P/\chi$ together with the upper bound (and long-time asymptotic prediction) $\widetilde{\lambda}$ and also the theoretical lower bound (cf. Equation (45) of Reference [15]). The agreement between simulation results and theoretical predictions in this stringent test is excellent. In both Figures 1.6 and 1.7 the anomalous diffusion exponents are $\gamma = \gamma' = 0.5$.

1.7
Finale

In this chapter we have presented an overview of the current state of the literature on reaction-subdiffusion problems. Reactions that have been discussed include $A \to 0$, $A + A \to A$, $A + A \to 0$, $A + B \to B$ and $A + B \to 0$. Depending on the spatial distribution of reactants (homogeneous, non-homogeneous) and on the way in which reactants move (diffusively, subdiffusively, or not at all), different methods have been brought to bear on this discussion, including scaling arguments and bounding arguments that lead to global concentrations $c(t)$, and reaction-subdiffusion equation approaches that provide information on local concentrations $c(\mathbf{r}, t)$. These theories are often asymptotic, and must be accompanied by extensive numerical simulations to ascertain when the asymptotic results are valid. While some results in the subdiffusion case follow from a subordination argument whereby one simply replaces t in the appropriate diffusion problem by t^γ, this is by no means always the case, nor

is it always obvious when the subordination procedure may apply and when it does not.

The concentration of species (global or local) is of course not the only interesting measure of a reaction-subdiffusion process, and a fuller understanding requires that one go beyond, at least to the level of pair correlation functions, to understand the spatial structure of these systems. While there is work in the literature at this deeper level which length constraints did not permit us to review here, results are few and far between and are based mostly on numerical simulations.

We have highlighted some of the areas that are way open for further investigation. Very little is known about the behavior of subdiffusive systems with reactants characterized by different subdiffusive exponents, the only exception being the $A + B \rightarrow B$ system when the concentration of A is much smaller than that of B, and even then only in some parameter regimes. There is very little known about how to even construct reaction-subdiffusion equations at the mesoscopic level involving local concentrations; existing ones are either ad hoc or peculiar to very particular conditions. Effects of aging associated with processes that have been ongoing before the start of the observation have essentially not been addressed in the context of reactions. The structure and time-dependence of two-particle (or higher) correlation functions is essentially unknown. This is a field that still requires the development of numerical simulation methods able to cover the long time scales and the presence of multiple time scales that arise in these problems. While such methods have been developed for reaction-diffusion problems, much work needs to be done to design and optimize numerical methods when the motion of reactants is subdiffusive. The list could go on, but we simply close by hoping to have aroused curiosity and engendered new ideas in our readership.

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