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1997 J. Phys. A: Math. Gen. 30 6587

(http://iopscience.iop.org/0305-4470/30/19/003)

J. Phys. A: Math. Gen. **30** (1997) 6587–6599. Printed in the UK PII: S0305-4470(97)84217-5

Fractal-time approach to dispersive transport in single-species reaction-diffusion

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Received 16 May 1997

Abstract. The effect of dispersive transport in the single-species reaction-diffusion models of coagulation ($A+A \to A$) and annihilation ($A+A \to 0$) is considered. This transport is modelled through a fractal-time random walk, in which the stepping-times of the walker (a typical particle) follows a renewal process characterized by a pausing time distribution proportional to a stable law at long times, $\psi(t) \sim t^{-1-\gamma}$, with $0 < \gamma < 1$ (the fractal dimension of the time). This leads to a sublinear mean squared displacement for the particles: $\langle \boldsymbol{r}^2(t) \rangle \sim t^{\gamma}$. The decay of the concentration of particles, $A(t)$, is obtained for all space dimensions d, and for the whole course of the reactions. The obtained results are exact for short and long times, with the long time asymptotics $A(t) \sim t^{-\gamma/2}$ for $d = 1$, $A(t) \sim \ln(t) t^{-\gamma/2}$ for $d = 2$ and $A(t) \sim t^{-\gamma}$ for $d \geqslant 3$. The effect of highly non-homogeneous space distributions of particles is also considered. It is found that a fractal segregation of dimension α (with $0 < \alpha < d$) in the initial distribution of particles in the space leads to $A(t) \sim t^{-\gamma\alpha/2}$ for $d = 1$, $A(t) \sim \ln(t) t^{-\gamma\alpha/2}$ for $d = 2$ and $A(t) \sim t^{-\gamma+\gamma(d-\alpha)/2}$ for $d \geqslant 3$, $d-2 < \alpha < d$ and $A(t) \sim cte > 0$ for $0 < \alpha < d-2$. This shows a subordination phenomenon in the combination of space- and time-fractal distributions.

1. Introduction

Despite the extensive literature that exists on the coagulation ($A + A \to A$) and annihilation ($A + A \to 0$) reaction-diffusion models, many aspects of these reactions still deserve closer scrutiny. One of these aspects is the effect which subdiffusive transport may have on the evolution of the particle concentration, $A(t)$. While most previous work has been concerned with a pure diffusive behaviour, here we address the case of a *sublinear* evolution of the mean squared displacement of the particles: $\langle \boldsymbol{r}^2(t) \rangle \sim t^{\gamma}$ characterized by an exponent $0 < \gamma < 1$.

The *annihilation* reaction under such particle motion was addressed for the first time by Blumen, Klafter and Zumofen (BKZ), see [1] and references therein. They modelled the reactions as a continuous-time random walk (CTRW) with waiting-time distributions (WTD) displaying long-time tails

$$\psi(t) \sim ct^{-1-\gamma}. \tag{1}$$

The WTD $\psi(t)$ is the probability density for the elapsed time between the consecutive steps of a given particle. If $0 < \gamma < 1$, this distribution does not have integer moments (with the exception of the normalization or zero-moment)

$$\langle t^m \rangle = \int_0^{\infty} \mathrm{d}t\, t^m \psi(t) \to \infty \qquad \text{for } 0 < \gamma < 1 \text{ and } m = 1, 2, \ldots. \tag{2}$$

0305-4470/97/196587+13$19.50

In this case $\psi(t)$ originates a time renewal process in which the mean number of events (particle steps) grows as $\langle s(t)\rangle \sim t^{\gamma}$. If the variance of the single-step displacement, σ^2, is finite, then the mean squared displacement is $\langle \boldsymbol{r}^2(t)\rangle = \sigma^2\langle s(t)\rangle$. Therefore, for $0 < \gamma < 1$ subdiffusive transport occurs.

The expression 'fractal-time' (of dimension γ) was coined for this model of subdiffusion [2, 3]. In fact, a renewal process with such a WTD suffers very sporadic behaviour; long intervals may exist, followed by bursts of events. The most probable pauses between events are short but occasionally very long pauses exist. Given a long pause, there is still a smaller but finite probability that an even longer one will occur. The resulting pattern of events, as pictured as a point process along the time axis, is a cluster structure and one would not be able to measure a mean pausing time between points by examining this pattern. The relation of power law (1) to a fractal set of event times can be viewed by constructing a dilatationally symmetric WTD, by taking into account events occurring on all time scales. For example, starting with the exponential distribution characteristic of a Poisson process (however, any other process will lead to the same conclusion)

$$\psi^{(\text{Poisson})}(t) = \lambda \exp(-\lambda t) \tag{3}$$

one constructs a new distribution in the following way:

$$\psi(t) = \frac{1-a}{a} \sum_{j=1}^{\infty} (ab)^j \exp(-b^j t) \tag{4}$$

where $0 < b$ and $0 < a < 1$ in order to ensure normalization. This WTD satisfies

$$\psi(bt) = \psi(t)/(ab) - (1-a)b \tag{5}$$

and thus at long times $\psi(bt) \sim \psi(t)/(ab)$, which has a solution of the form (1) when $\gamma = \ln(a)/\ln(b)$.

Let us recall that (1) follows from the distribution of carrier release times from low-lying traps to the conduction band [4]. This distribution is fundamental to the multiple trapping formalism. For activated processes the rates depend exponentially on the energy, so that an equidistant level spacing $E_j = j\Delta$ leads to rates proportional to $\exp(E_j/kT) = b^j$, with $b = \exp(-\Delta/kT)$. Furthermore, the density of states in the energy tail is often itself exponential in energy, $\exp(-E_j/kT)$ (where one introduces an effective temperature T_0) so that the density of states follows a^j with $a = \exp(-\Delta/kT_0)$. Thus, in this example $\gamma = \ln(a)/\ln(b) = T/T_0$ for $T < T_0$ and one has dispersive transport below T_0.

In [1, 5] BKZ reported an Smoluchowski-type approximation for the particle population decay in bimolecular reactions. This consists in approximating $A(t) \sim \Phi(t)$ by the relaxation function, $\Phi(t)$, of an alternative trapping problem. Here $\Phi(t)$ is the survival probability of a particle in the presence of randomly distributed *static* traps. To obtain $\Phi(t)$, the Rosenstock approximation was used as well as some criteria for approximating the mean number of distinct sites visited by a particle under dispersive motion up to time t, $S(t)$. They found

$$\Phi(t) \sim 1/S(t) \sim \begin{cases} t^{-\gamma d_s/2} & \text{for } d_s < 2,\ \gamma < 1 \\ t^{-\gamma} & \text{for } d_s > 2,\ \gamma < 1 \end{cases} \tag{6}$$

where d_s is the spectral dimension. Simulation results for the annihilation reaction reported in [1] seemed to be in agreement with this ansatz.

In [6] the temperature-programmed reaction $A + A \rightarrow$ *products* with such anomalous diffusion was studied by simulations. In [7] the two-species reaction $A + B \rightarrow$ *products* with reacting particles with non-diffusional motion at short times was approached by means

of a generalized diffusion equation. On the other hand, the anomalous relaxation pattern which occurs for the fractal-time random-walk model was study in [8].

In this work we offer a complete solution for both models: $A+A \to (2-\epsilon)A$ coagulation ($\epsilon \equiv 1$) and annihilation ($\epsilon \equiv 2$), under such a dispersive transport. Following the ideas in [1], we will model the motion of the particles as a CTRW on lattices of integer dimension d (for which is $d_s = d$).

This paper is organized as follows. In the next section we briefly explain the stochastic motion of the particles and obtain the function of main interest in our solution: the probability density for the first-meeting time of two particles under fractal-time. In section 3 we obtain a solution for these reactions on the one-dimensional lattice in explicit terms of the initial particle distribution. In section 4 we solve the reaction problem for lattice dimensionality $d \geqslant 2$. In section 5 we consider the additional effect of fractal segregation of the particles in the space.

2. The first-meeting rate of a pair of particles

Let $\rho(\boldsymbol{r})$ be the single-step-transition probability distribution of the random walker (a typical particle). Let $P_s(\boldsymbol{r})$ be the probability that the random walker be at site $\boldsymbol{r}$ after s steps, starting from $\boldsymbol{r} = \boldsymbol{0}$. Then we have $P_s(\boldsymbol{r}) = \sum_{\boldsymbol{r}'} \rho(\boldsymbol{r}-\boldsymbol{r}')P_{s-1}(\boldsymbol{r}')$. In the Fourier representation $P_s(\boldsymbol{k}) \equiv \sum_{\boldsymbol{r}} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} = \rho(\boldsymbol{k})P_{s-1}(\boldsymbol{k}) = \rho(\boldsymbol{k})^s$. We will consider that particles perform nearest-neighbour transitions on sc-lattices of unit spacing (this fixes the length scale). Then the structure function of the random walk is

$$\rho(\boldsymbol{k}) = [\cos(k_1) + \cdots + \cos(k_d)]/d. \tag{7}$$

First we require the probability $F_s(\boldsymbol{r})$ that a *single* random walker, starting at $\boldsymbol{r} = \boldsymbol{0}$, reaches site $\boldsymbol{r}$ for the first time in the sth step. As shown by Montroll and Weiss [3, 9], for any lattice with translational invariance its generating function $F(\boldsymbol{r}, z) \equiv \sum_{s=0}^{\infty} z^s F_s(\boldsymbol{r})$ can be obtained as [10, 11]

$$F(\boldsymbol{r}, z) \equiv \sum_{s=0}^{\infty} z^s F_s(\boldsymbol{r}) = \frac{G_d(\boldsymbol{r}, z)}{G_d(\boldsymbol{0}, z)} \qquad \text{for } \boldsymbol{r} \neq \boldsymbol{0} \tag{8}$$

where $G_d(\boldsymbol{r}, z) \equiv \sum_{s=0}^{\infty} z^s P_s(\boldsymbol{r})$ is the generating function of $P_s(\boldsymbol{r})$. In its Fourier representation this is given by

$$\sum_{\boldsymbol{r}} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} G_d(\boldsymbol{r}, z) = \frac{1}{1 - z\rho(\boldsymbol{k})}. \tag{9}$$

By means of an inverse Fourier transform one obtains

$$G_d(\boldsymbol{r}, z) = \frac{1}{(2\pi)^d} \int_{-\pi}^{\pi} \mathrm{d}^d\boldsymbol{k}\, \frac{\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}}{1 - z\rho(\boldsymbol{k})}. \tag{10}$$

- For $d = 1$ this is

$$G_1(\boldsymbol{r}, z) = \frac{1}{\pi} \int_0^{\pi} \mathrm{d}k\, \frac{\cos(rk)}{1 - z\cos(k)} = \int_0^{\infty} \mathrm{d}x\, \mathrm{e}^{-x} I_r(xz) = \frac{1}{\sqrt{1-z^2}} \left(\frac{z}{1 + \sqrt{1-z^2}} \right)^r \tag{11}$$

with $r = |\boldsymbol{r}|$, and then (8) is

$$F(\boldsymbol{r}, z) = \left(\frac{z}{1 + \sqrt{1-z^2}} \right)^r. \tag{12}$$

For higher dimensions there are no simple expressions for $G_d(\boldsymbol{r}, z)$. This function can only be obtained from recurrence relations based on $G_d(\mathbf{0}, z)$. This last function is

- For $d = 2$ [11–13],

$$G_2(\mathbf{0}, z) = \frac{1}{\pi^2}\int_0^\pi \mathrm{d}k_1 \int_0^\pi \mathrm{d}k_2 \, \frac{1}{1 - \frac{z}{2}[\cos(k_1) + \cos(k_2)]} = \frac{2}{\pi}\, K(z) \qquad (13)$$

where $K(\,)$ is the complete elliptic integral of the first kind.

- For $d \geqslant 3$ [14],

$$G_d(\mathbf{0}, z) = \frac{1}{\pi^d}\int_0^\pi \mathrm{d}k_1 \ldots \int_0^\pi \mathrm{d}k_d \, \frac{1}{1 - \frac{z}{d}[\cos(k_1) + \cdots + \cos(k_d)]} \qquad (14)$$

$$= \int_0^\infty \mathrm{d}x \, \mathrm{e}^{-x}[I_0(xz/d)]^d = \sum_{n=0}^\infty \frac{1}{n! d^{2n}} \left(\frac{1}{2}\right)_n H_n^{(d)} z^{2n} \qquad (15)$$

where

$$H_n^{(d)} = \sum_{m_1=0}^{n} \sum_{m_2=0}^{m_1} \cdots \sum_{m_{d-1}=0}^{m_{d-2}} \binom{n}{m_1}^2 \cdots \binom{m_{d-3}}{m_{d-2}}^2 \binom{m_{d-2}}{m_{d-1}}^2 .$$

The study of the long-time asymptotics of our results will require the expansion of (14) for $z \to 1$. This was derived by Joyce [15], Montroll and Weiss [9] and improved by Blumen and Zumofen [16].

We now turn back to the continuous time picture. Here the time elapsed between steps has a distribution given by the WTD $\psi(t)$. Correspondingly, the probability density $F(\boldsymbol{r}, t)$ for the time t in which a *single* random walker, which started at the origin, reaches the site $\boldsymbol{r}$ for the first time, follows as the sum over all possible step-numbers of the s-fold convolution of $\psi(t)$ times $F_s(\boldsymbol{r})$. This can be summed more easily in the Laplace representation:

$$F(\boldsymbol{r}, u) \equiv \int_0^\infty \mathrm{d}t \, \mathrm{e}^{-ut} F(\boldsymbol{r}, t) = \sum_{s=0}^\infty \psi(u)^s F_s(\boldsymbol{r}) = F(\boldsymbol{r}, z = \psi(u)). \qquad (16)$$

Now, let $F^{(\mathrm{rel})}(\boldsymbol{r}, t)$ be the probability density of the first-meeting time of two particles, initially a distance $\boldsymbol{r}$ apart. This can be viewed as the function $F(\boldsymbol{r}, t)$ corresponding to a new random walker whose motion mimics the relative motion of these two particles, i.e. with the same structure function and with twice the hopping rate. Strictly speaking, this is exact only for the case in which each particle follows a Poisson renewal process for its stepping times, characterized by an exponential WTD, equation (3), i.e. for the case of pure diffusive motion $\langle r^2(t)\rangle = \lambda t$, with $\lambda = 2dDt$. This is so because the relative motion follows a point process in the time obtained as the *pooling* (superposition) of two renewal processes. The difficulty is that this pooling process is a renewal process in turn only if the component processes are Poisson [17–20]. Only in this case, can the relative motion be handled exactly as the CTRW of a single walker with the WTD $\psi^{(\mathrm{rel})}(t) = 2\lambda \exp(-2\lambda t)$, in terms of which $F^{(\mathrm{rel})}(\boldsymbol{r}, t)$ is obtained in the Laplace representation as $F^{(\mathrm{rel})}(\boldsymbol{r}, u) = F(\boldsymbol{r}, z = \psi^{(\mathrm{rel})}(u))$. However, a detailed study [21–23] reveals that in the general case, for long times (i.e. small u) this pooling process is very well approximated as a renewal process with a WTD $\psi^{(\mathrm{rel})}(t)$ given by $\psi^{(\mathrm{rel})}(t) \cong 2\psi(2t)$, that is,

$$\psi^{(\mathrm{rel})}(u) \cong \psi(u/2) \qquad \text{as } u \to 0. \qquad (17)$$

Equation (17) is of course exact for the exponential WTD. Then, in this long-time approximation, from (16) we have

$$F^{(\mathrm{rel})}(\boldsymbol{r}, u) = F(\boldsymbol{r}, z = \psi^{(\mathrm{rel})}(u)) \cong F(\boldsymbol{r}, z = \psi(u/2)). \qquad (18)$$

3. Solution for one-dimensional reactions

The exact solution methods known for $d = 1$ assume that particles cannot pass over each other without reaction and that they perform a pure diffusive motion. Under these conditions Spouge [24] showed that the general solution is given as a suitable average of the survival probability of two particles

$$A(t)/A(0) = \langle U^{(\mathrm{rel})}(t)\rangle. \tag{19}$$

Here $U^{(\mathrm{rel})}(t)$ is the survival probability of a pair of particles, initially a distance r apart, averaged over the distribution $\beta(r)$ defined as

$$\beta(r) = \begin{cases} p_1(r) & \text{for coagulation} \\ 2\displaystyle\sum_{n=1}^{\infty}(-1)^{n+1}p_n(r) & \text{for annihilation.} \end{cases} \tag{20}$$

Here $p_n(r)$ is the probability distribution of the distance of a typical particle to its nth neighbour at $t = 0$ (the initial distribution is assumed to be translationally invariant). In particular, $p_1(r)$ is the inter-particle distribution function (IPDF) [25], whose first moment equals the inverse initial mean concentration on the line

$$\sum_{r=1}^{\infty} r p_1(r) = 1/A(0). \tag{21}$$

Moreover, as only one particle per site can be present, we define $p_1(r = 0) = 0$. We will rewrite the result (19), (20) as a closed expression in explicit terms of the initial distribution. Assuming an initial distribution generated as a renewal process on the lattice, we have

$$p_n(r) = \sum_{r'=0}^{r} p_1(r - r')p_{n-1}(r'). \tag{22}$$

With a ζ-transformation [26] of this renewal equation we obtain

$$p_n(\zeta) \equiv \sum_{r=0}^{\infty} \zeta^r \; p_n(r) = [p_1(\zeta)]^n. \tag{23}$$

With a similar ζ-transform for $\beta(r)$ we obtain

$$\beta(\zeta) \equiv \sum_{r=0}^{\infty} \zeta^r \beta(r) = \begin{cases} p_1(\zeta) & \text{for coagulation} \\ 2p_1(\zeta)/[1 + p_1(\zeta)] & \text{for annihilation.} \end{cases} \tag{24}$$

In terms of $F^{(\mathrm{rel})}(r, t)$, equation (19) is

$$\begin{aligned} \frac{A(t)}{A(0)} &= 1 - \int_0^t \mathrm{d}t' \, \langle F^{(\mathrm{rel})}(t)\rangle \\ &= 1 - \int_0^t \mathrm{d}t' \sum_r \beta(r) F^{(\mathrm{rel})}(r, t) \\ &= \mathcal{L}^{-1}\left\{\frac{1}{u}\,[1 - \langle F^{(\mathrm{rel})}(u)\rangle]\right\} \end{aligned} \tag{25}$$

with $\mathcal{L}^{-1}$ the inverse Laplace operator (transforming from $u \to t$), and $\langle F^{(\mathrm{rel})}(u)\rangle = \sum_r \beta(r) F^{(\mathrm{rel})}(r, u)$. Using (12), (18) we obtain $F^{(\mathrm{rel})}(r, u) = \xi(u)^r$ with

$$\xi(u) = \frac{\psi(u/2)}{1 + \sqrt{1 - \psi(u/2)^2}}. \tag{26}$$

Therefore $\langle F^{(\mathrm{rel})}(u)\rangle = \beta(\zeta = \xi(u))$ and our final expression for the one-dimensional solution is

$$\frac{A(t)}{A(0)} = \begin{cases} \mathcal{L}^{-1}\left\{\dfrac{1}{u}[1 - p_1(\zeta = \xi(u))]\right\} & \text{for } A + A \to A \\ \mathcal{L}^{-1}\left\{\dfrac{1}{u}\dfrac{1 - p_1(\zeta = \xi(u))}{1 + p_1(\zeta = \xi(u))}\right\} & \text{for } A + A \to 0 \end{cases} \tag{27}$$

in terms of the ζ-transform of the initial IPDF, $p_1(r, t = 0)$. In the pure diffusive case exponential WTD (3) is $\psi(u) = \lambda/(\lambda + u)$, therefore (26) is

$$\xi(u) = \left(1 + \frac{u}{2\lambda}\right) + \sqrt{\left(1 + \frac{u}{2\lambda}\right)^2 - 1}$$

and the solutions (27) are exact, with the known long-time decay

$$A(t) \cong \frac{1}{\epsilon}(\pi\lambda t)^{-1/2}. \tag{28}$$

On the other hand, for the fractal-time case (1) is

$$\psi(u) \sim 1 - \alpha u^{\gamma} \qquad \text{with } \alpha = \frac{c\Gamma(1-\gamma)}{\gamma}. \tag{29}$$

Now the small u-expansion of (26) is $\xi(u) = 1 - \sqrt{2\alpha}u^{\gamma/2} + \cdots$, which, from Tauberian theorems [27], leads to the result

$$A(t) \sim \frac{1}{\epsilon}\frac{\sqrt{2c\Gamma(1-\gamma)/\gamma}}{\Gamma(1-\gamma/2)}(2t)^{-\gamma/2} + \cdots. \tag{30}$$

In figure 1(a) we show simulation results for coagulation on the one-dimensional lattice under subdiffusive transport, modelled by the following long-time tailed WTD

$$\psi(t) = \gamma(1 + t)^{-1-\gamma} \tag{31}$$

for which $c = \gamma$. The lower broken curve shows, as a comparison, the simulation with a pure diffusive motion, using (3) with $\lambda = 1$. The straight line shows the known asymptotics (28). The upper broken curve corresponds to the simulation in fractal-time, using WTD (31), with $\gamma = 0.8$. The heavy full curve is our analytical result (27). The full line displays its asymptotes (equation (30)). Note that apparently the theoretical asymptotes are shifted with respect to the curves corresponding to the simulations. However, this is only a transient effect, while the pure asymptotes (30) establish at times which cannot be reached by simulations. In order to display this fact, let us define the relative difference $\Delta(t) = [A_{\mathrm{simul}}(t) - A(t)]/A(t)$, where $A(t)$ is our analytical result (27). In figure 1(b) we show that in fact this difference tends to vanish as slow as $\Delta(t) \sim t^{-0.02}$.

4. Solution for higher dimensions

In this section we will consider these reactions under anomalous diffusion in $d \geqslant 2$. The method used in the previous section cannot be extended to higher dimensions, so we will introduce an approximated method of solution which yields closed expressions for the particle number evolution in satisfactory agreement with simulations. These solutions are exact for very short and long times. With this aim, we define $P(N, t)$ to be the probability of having N particles at time t. Here we are assuming a finite lattice with L^d sites and $N(0)$ randomly distributed particles at the beginning of the reaction, i.e. with an initial particle

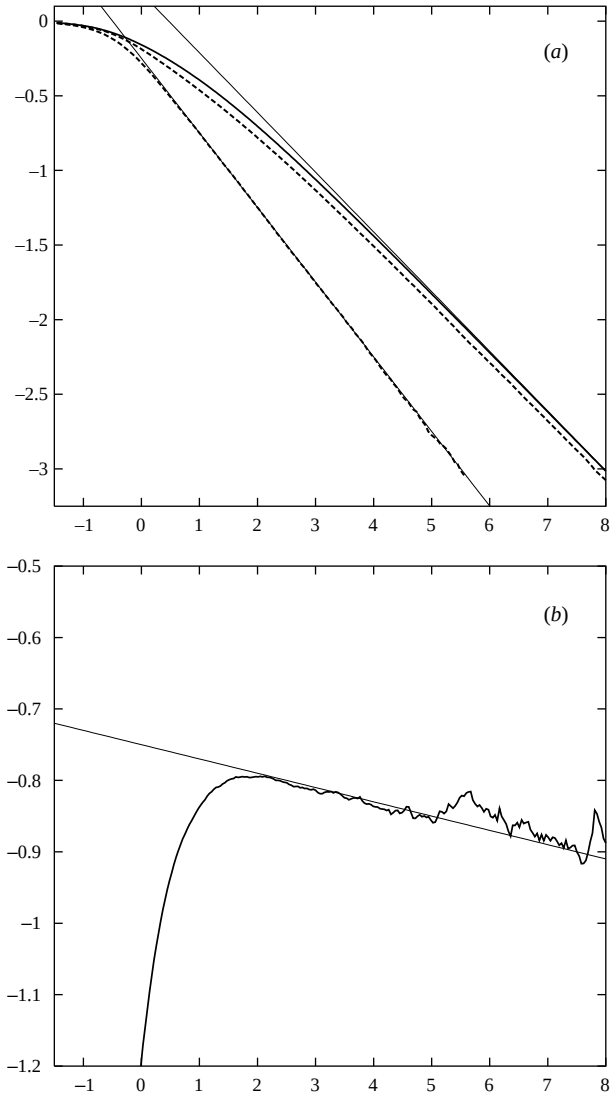

Figure 1. (*a*) Simulation (broken curves) of the coagulation on the one-dimensional lattice. $\mathrm{Log}_{10}A(t)/A(0)$ versus $\log_{10}(t)$ is shown. The lattice size is $L = 200\,000$ and initially there is one particle per site, i.e. $A(0) = 1$, averaged over five realizations. See explanation in the main text. (*b*) The approach of the predicted asymptotics in the fractal-time simulation shown in (*a*): the vertical axis is the logarithm of the relative difference between simulation and theory: $\log_{10}\Delta(t)$; the horizontal axis as in (*a*). The full line has slope -0.02.

concentration $A(0) = N(0)/L^d$. Later, the limit of an infinite lattice will be considered. We write the following evolution equation for this probability

$$\partial_t P(N,t) = \omega(N+\epsilon,t)P(N+\epsilon,t) - \omega(N,t)P(N,t). \tag{32}$$

Here $\omega(N,t)\,\mathrm{d}t$ is the probability that a reaction occurs in $[t, t+\mathrm{d}t]$ given that there are N particles at this time. Because at each particle meeting the reaction takes place with probability one, the frequency $\omega(N,t)$ can be split in terms of an overall meeting rate,

$\mathcal{F}(t)$, and a probability $\Lambda(N,t)$

$$\omega(N,t) = \mathcal{F}(t)\Lambda(N,t). \tag{33}$$

The meaning is as follows. First we consider that particles move independently of each other, without interaction or reactions. For this case $\mathcal{F}(t)$ is the rate of first encounters of pairs of particles. On the other hand, $\Lambda(N,t)$ is the probability that two particles, which meet for the first time at time t, have not reacted in the actual problem with reaction. In a decoupled approximated scheme, the transition frequency $\omega(N,t)$ follows as the product of these functions. Whereas $\mathcal{F}(t)$ can be computed exactly taking advantage of CTRW techniques (which will be given later), $\Lambda(N,t)$ cannot be obtained exactly. However, as we will see *a posteriori*, a mean-field-like approximation of the form

$$\Lambda(N,t) \cong \left[\frac{N(t)}{N(0)}\right]^2 \tag{34}$$

yields a good approximation for the entire course of the reaction. Indeed, this approximation becomes exact as $t \to 0$ or $t \to \infty$ and, in general, it improves for increasing lattice dimension d.

Let $\kappa(t)$ be the time-dependent reaction rate per particle

$$\kappa(t) \equiv \epsilon\mathcal{F}(t)/N(0). \tag{35}$$

If each site is initially occupied independently and with probability $A(0)$, from the definition of $\mathcal{F}(t)$ and taking the limit of an infinite lattice, we have

$$\kappa(t) = \frac{\epsilon}{2}A(0)\sum_{\boldsymbol{r}\neq\boldsymbol{0}} F^{(\mathrm{rel})}(\boldsymbol{r},t). \tag{36}$$

Here the sum runs over all the lattice sites, except the origin. In terms of the relative mean number of particles in the limit of large L, $n(t) \equiv \langle N(t)\rangle/\langle N(0)\rangle = A(t)/A(0)$, from equations (32), (33) is

$$\partial_t n(t) = -\kappa(t)n(t)^2 \tag{37}$$

that is

$$n(t) = \frac{1}{1+\int_0^t \mathrm{d}t'\,\kappa(t')}. \tag{38}$$

Noting that $\sum_{\boldsymbol{r}} G_d(\boldsymbol{r},z) = G_d(\boldsymbol{k}=\boldsymbol{0},z) = 1/(1-z)$ (see equation (10)), and using the approximation (18) (let us remember that this is exact for an exponential WTD) the solution (37) reads

$$n(t) \cong \left[1 - \frac{\epsilon}{2}A(0) + \frac{\epsilon}{2}A(0)\mathcal{L}^{-1}\left\{\frac{1}{u[1-\psi(u/2)]G_d(\boldsymbol{0},z=\psi(u/2)}\right\}\right]^{-1}. \tag{39}$$

From Tauberian theorems [27], and particularizing for sc-lattices of unit lattice-spacing, we obtain:

- for $d = 2$:

$$n(t) \sim \frac{4c}{\epsilon A(0)}\frac{(2t)^{-\gamma}}{\sin(\gamma\pi)}K\left(\frac{(2t)^{\gamma}}{\alpha+(2t)^{\gamma}}\right) \sim \frac{2c}{\epsilon A(0)}\frac{(2t)^{-\gamma}}{\sin(\gamma\pi)}\ln\left[\frac{8\gamma}{c\Gamma(1-\gamma)}(2t)^{\gamma}\right] \tag{40}$$

- for $d \geqslant 3$:

$$n(t) \sim \left[1 - \frac{\epsilon A(0)}{2} + \frac{\epsilon A(0)}{2}\,\frac{(2t)^{\gamma}/\alpha}{\Gamma(1+\gamma)G_d(\boldsymbol{0},1)}\right]^{-1} \sim \frac{4c}{\epsilon A(0)}\frac{G_d(\boldsymbol{0},1)}{\sin(\gamma\pi)}\,(2t)^{-\gamma}. \tag{41}$$

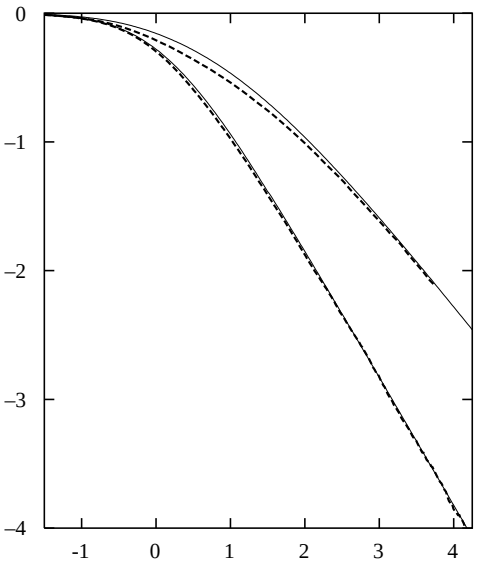

Figure 2. Plot of $\log_{10} A(t)/A(0)$ versus $\log_{10}(t)$ for the coagulation reaction on the square lattice, of 200^2 sites, under subdiffusion modelled by means of the same WTD as in figure 1, with $\gamma = 0.8$ (upper curves, 50 realizations). Initially $A(0) = 1$, with $N(0) = 40\,000$. The bottom curves show, as a comparison, the pure diffusive case, for which $\psi(t) = \psi^{(\mathrm{Poisson})}(t)$, equation (3), with $\lambda = 1$.

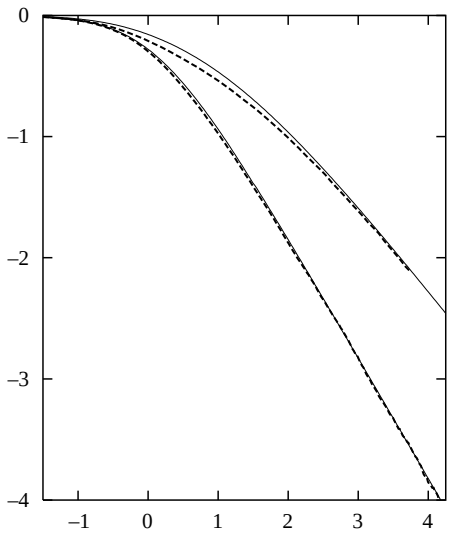

Figure 3. The same as figure 2, for the $d = 3$ *sc*-lattice, with $N(0) = 50^3 = 125\,000$, three realizations. In all cases the simulations considered periodic boundary conditions.

In figures 2 and 3 we show our general result (39) in comparison with Monte Carlo simulations on the square and three-dimensional *sc*-lattice, respectively. For the last one, the exact value of the integral (14) for $z \to 1^-$ is known [28]†: $G_3(\mathbf{0}, 1) = \frac{\sqrt{6}}{32\pi^3}\Gamma(1/24)\Gamma(5/24)\Gamma(7/24)\Gamma(11/24) = 1.516\ldots$. As for the one-dimensional case, the simulations were performed using the WTD (31). In all cases the simulations started with one particle per site ($A(0) = 1$) and particles performed transitions to nearest-neighbour sites. For the coagulation reaction, each time a particle lands on an already occupied site, one of the two meeting particles, selected at random, was removed.

5. Fractal initial distributions

Next let us consider highly inhomogeneous initial distribution of particles, modelled as fractal distributions of (Hausdorff) dimension α ($0 < \alpha < d$). There are some experimental situations in which this initial distribution of particles is relevant. As is well known, the diffusion–annihilation reaction is formally related to the Ising model by identifying domain walls with particles [25, 29]. Here the distribution of domain sizes can be of fractal type for ferro-magnetic (-electric) configurations. Therefore, it could be of interest in the study of the relaxation to the equilibrium of some substances like potassium dihydrogen phosphate, KH_2PO_4, for which a ferroelectric structure with fractal aspects of the pentad Cantor set of

† This is the exact expression of $G_3(\mathbf{0}, 1)$, as obtained in [12, 13] but an unfortunate printing mistake in this original paper is being reproduced in many other works [3, 10, 11].

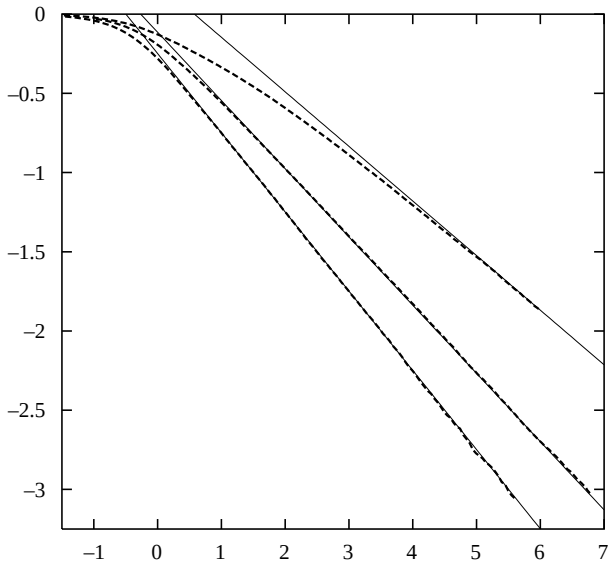

Figure 4. Coagulation reaction (axis as in previous figures) under fractal-time ($\gamma = 0.8$) and fractal initial distribution on the lattice, constructed as a Cantor set of base 5 ($\alpha = \ln(4)/\ln(5) = 0.861\ldots$): upper curve. The full line corresponds to our result (42). The middle broken curve shows a comparison, the same initial distribution but with pure diffusive motion (exponential-WTD). Here the full line shows the decay $\sim t^{-\alpha/2}$. The bottom curve gives as a comparison, an initial distribution of a particle per site, and reaction with pure diffusive motion. Here the full line shows the known result (28).

Hausdorff dimension $\alpha \cong 0.756$ was recently reported [30, 31].

Another situation of interest is that of particles building up percolation clusters by being adsorbed on surfaces, after which they perform recombination reactions. Recently, in order to obtain information about the adsorption energy distribution on a catalytic surface, the measurement of the particle number decay along the entire course of the reaction was proposed [32]. It was found that the kinetics of the reaction $A + A \rightarrow 0$ is strongly influenced by energy correlations in the adsorptive field.

• For the one-dimensional case a fractal pattern is readily constructed as a renewal process along the lattice with an IPDF $p_1(r) \sim r^{-1-\alpha}$. Such a distribution in our result (27) yields

$$A(t)/A(0) \sim t^{-\gamma\alpha/2}. \tag{42}$$

In figure 4 we show a test of this result against simulations for an initial distribution corresponding to a deterministic fractal, namely a Cantor set of base 5 [33], for which $\alpha = \ln(4)/\ln(5) = 0.861\ldots$, and fractal time with $\gamma = 0.8$ (see upper curves).

For higher dimensions, considering isotropic initial fractal distributions, we define $\wp(r) \sim r^{\alpha-1}$ to be the density of particles at a distance $r = \sqrt{r_1^2 + \cdots + r_d^2}$ of a typical particle when the reaction starts, i.e. now the initial concentration $A(0) \sim \Omega_d \int_0^L \wp(r)\,\mathrm{d}r \sim L^\alpha$, depends parametrically on the typical system size L. Here Ω_d is the solid angle in d-dimensions. In terms of this density, in place of equation (36) we have

$$\kappa(t) \sim \frac{\epsilon}{2}\Omega_d \int_0^\infty \mathrm{d}r\, \wp(r) F^{(\mathrm{rel})}(r, t). \tag{43}$$

Proceeding as in the previous section, we readily obtain the asymptotics:

- For $d = 2$:

$$A(t)/A(0) \sim t^{-\gamma\alpha/2} \ln(b' t^{\gamma}) \tag{44}$$

where the factor b' depends on the particular form of the long-tailed WTD and on the particular fractal structure of the initial particle distribution. We see that the logarithmic factor, which is typical for $d = 2$, remains unaffected by the fractal initial distribution.

- For $d = 3$:

$$A(t)/A(0) \sim t^{-\gamma + (\frac{d-\alpha}{2})\gamma}. \tag{45}$$

The case $\alpha = d - 2$ is marginal, for which $A(t) \sim 1/\ln(b' t^{\gamma})$, whereas for $\alpha < d - 2$ the relative particle concentration goes asymptotically to a non-vanishing time-independent value: $A(t)/A(0) \to cte$, $0 < cte < 1$. This surprising decay, namely to an asymptotic state in which the reaction seems to have died out, was advanced in [34] for the diffusive case.

6. Conclusions

In this work we have studied the single-species reaction models of bimolecular coagulation and annihilation controlled by anomalous *sub*diffusion. While in [35] the same reactions under anomalous *super*diffusion were examined, the *sub*diffusive case was still an open problem; mainly due to the difficulty in dealing with the non-trivial problem of the relative motion of two subdiffusive particles (while in the *super*diffusive case this problem is trivial). Using the method worked out in this paper we have found closed expressions for the particles number decay along the whole course of the reactions in very satisfactory agreement with Monte Carlo simulations. The obtained solutions are exact in the short- and long-time asymptotics. While in the diffusive case the concentration of particles in the coagulation and annihilation reaction models behaves as

$$A(t) \approx \begin{cases} t^{-1/2} & \text{for } d = 1 \\ \ln(t)/t & \text{for } d = 2 \\ t^{-1} & \text{for } d \geqslant 3 \end{cases} \tag{46}$$

for the same reactions under dispersive (or *sub*diffusive) transport we have established the following decay laws:

$$\left.\begin{array}{l} \langle \boldsymbol{r}^2(t) \rangle \sim t^{\gamma} \\ (0 < \gamma < 1) \end{array}\right\} \Rightarrow A(t) \sim \frac{\epsilon}{2} \begin{cases} a_1 t^{-\gamma/2} & \text{for } d = 1 \\ a_2 \ln(b t^{\gamma}) t^{-\gamma} & \text{for } d = 2 \\ a_3 t^{-\gamma} & \text{for } d \geqslant 3 \end{cases} \tag{47}$$

with the coefficients a_1, a_2, a_3, b entering in these expressions obtained exactly in (30), (40), (41). Moreover, as tested against simulations, the whole course of the reactions is well described by our general solutions: equation (27) for $d = 1$ and equation (39) for $d \geqslant 2$. For the diffusive case (46), above the critical dimension $d = 2$ the chemical-kinetic decay $A(t) \sim t^{-1}$ applies

$$\frac{\mathrm{d}}{\mathrm{d}t} A(t) = -\epsilon k A(t)^2. \tag{48}$$

On the other hand, equation (47) does not seem to have an equivalent upper critical dimension. However, in [36] it was shown that the diffusion equation with fractional

time-derivative of order γ just corresponds to a fractal-time CTRW with $\psi(t) \sim t^{-1-\gamma}$ if $0 < \gamma < 1$. Therefore, if we generalize the chemical-kinetic equation properly, namely

$$\frac{\mathrm{d}^\gamma}{\mathrm{d}t^\gamma} A(t) = -\epsilon k A(t)^2 \tag{49}$$

we get a generalized chemical-kinetics equation with solution $\sim t^{-\gamma}$. Then we see that for the *sub*diffusive case $d = 2$ is still the dimension beyond which the solution of equation (49) applies. In this generalized sense $d = 2$ remains the upper critical dimension for coagulation and annihilation under dispersive transport.

Moreover, we have analysed the combined effect of fractal-time and fractal initial distributions characterized by the fractal dimension $0 < \alpha < d$, and we have obtained the following asymptotics:

$$\left.\begin{array}{ll} \langle \boldsymbol{r}^2(t)\rangle \sim t^\gamma & (0<\gamma<1) \\ A(0) \sim L^\alpha & (0<\alpha<d) \end{array}\right\} \Rightarrow \frac{A(t)}{A(0)}$$
$$\sim \frac{\epsilon}{2} \begin{cases} (t^{-\gamma})^{\alpha/2} & \text{for } d = 1,\ 0 < \alpha < 1 \\ \ln(b' t^\gamma)\ (t^{-\gamma})^{\alpha/2} & \text{for } d = 2,\ 0 < \alpha < 2 \\ (t^{-\gamma})^{1-\frac{d-\alpha}{2}} & \text{for } d \geqslant 3,\ d-2 < \alpha < d \\ cte > 0 & \text{for } d \geqslant 3,\ 0 < \alpha < d-2 \end{cases} \tag{50}$$

which display a subordinative phenomenon: both fractal effects merge in a multiplicative way.

Our simulations support these results, as shown from the figures. Note that the simulation programmes of reactions with fractal-time are much more cumbersome than for pure diffusion. In this last case, it is not necessary to programme in continuous time, as at each stage of the reaction the next particle to move can be chosen randomly. In contrast, in the continuous-time simulations we have to remember the stepping-times of each surviving particle (each renewal processes has to be generated according to the WTD); because at a given time t the next particle to move is the one whose next stepping-time is the closest to the current time t. Both strategies are equivalent only for the exponential WTD, $\psi^{(\mathrm{Poisson})}(t)$. Technically, this means each time we want to move a particle we have to find the minimum of the $N(t)$ values, and this makes the simulations considerably slower than for the diffusive case.

Before closing this article we want to mention an interesting effect in the simulation of the coagulation reaction. For pure diffusive motion it does not matter which particle is removed when a meeting (reaction) occurs. This seems to be rather obvious, but in a deeper consideration one can understand this fact as a consequence of the waiting-time paradox [21, 37] characteristic of the exponential WTD. In contrast, when introducing another WTD, the particles are distinguishable according to whether the incoming particle is removed or survives. In our simulations this decision was taken at random. In the more pathological case of WTD with the two first moments infinite, as used here for modelling the fractal-time, the breakdown of the symmetry under coagulated particle is more marked. A detailed study of this effect lies beyond the scope of this paper, being the matter of a forthcoming article [38].

Acknowledgments

The author gratefully acknowledges helpful discussions with A Blumen, G Zumofen, D ben-Avraham, M O Cáceres, H Wio and D H Zanette. He also expresses his gratitude to

M L Glasser for sharing useful results on lattice integrals. The work was partially supported by the Deutsche Sonderforschungsgemeinschaft (SFB 60).

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