Diffusion-Limited Annihilation and the Reunion of Bounded Walkers

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We study the long time behavior of a one-species reaction-diffusion process $kA \to \ell A$ where k particles coalesce into ℓ particles. The asymptotic time behavior of the density of particles is derived by mapping the reaction-diffusion process into the problem of the reunion of k random walkers bounded to move in a limited region.

I Introduction

The study of reaction-diffusion processes has been the subject of much interest in the last two decades [1-40]. In a reaction-diffusion system the reactants are transported by diffusion. These systems have two characteristic time scales: the reaction time and the diffusion time. When the reaction time is much larger than the diffusion time the process is called reaction-limited. In this case most of the time the reactants are performing diffusion so that the whole process is limited by reaction. The kinetics is dominated by diffusion which implies that it is well described by the laws of mass-action or mean-field equations.

When the diffusion time is much larger than the reaction time the process is called diffusion-limited. In this case the reactions take place in a very short time so that the whole process is limited by diffusion. For low dimensions, the process is dominated by fluctuations and the kinetics is no longer described by mean-field equations.

Here we are interested in the limiting case of diffusion-limited processes in which the reactions take place instantaneously. Moreover, we will consider only the case of one-species annihilation and coalescence processes. More specifically, one considers a one-species process in which particles react only when a certain number k of them meet, $kA \to \ell A$, with $\ell < k$. The extinction of particles by reaction may be total ($\ell = 0$, annihilation) or partial ($\ell \neq 0$, coalescence). In any case, the density of particles $\rho(t)$ vanishes in the long-time limit. Such systems have been studied for the case of bimolecular reactions ($k = 2$) in one dimension [5,10,13,16-22,30,32,34-36] as well as in general dimension [3,8,11,12,14,23,25,28]. Some works concentrated on the case of multimolecular reactions in one dimension [24,26,27,29,33] as well as in general dimension [7,31].

The classical rate equation, or mean-field equation, for the density of particles is given by

$$\frac{d\rho}{dt} = -a\rho^k \tag{1}$$

where a a positive constant. From this equation it follows that the density of particles decreases asymptotically according to the power law

$$\rho \sim t^{-1/(k-1)} \tag{2}$$

This mean-field behavior is valid for dimensions d greater than a critical dimension d_c given by

$$d_c = \frac{2}{k-1} \tag{3}$$

For $d < d_c$ it is conjectured that

$$\rho \sim t^{-d/2} \tag{4}$$

For $d = d_c$ the mean-field result is expected to have logarithm corrections.

The results (3) and (4) have been conjectured by means of scaling arguments [7,8], exact results in one dimension [5,10,13,15-17,19,20,21,27], renormalization group calculations [12,23,25,28,31], and probabilistic approaches [3,16,17]. The main purpose of the present article is to derive the results (2), (3) and (4) by mapping the reaction-diffusion process, in its late stages, into the problem of finding the time it takes for a group of random walkers, confined in a limited space, to meet.

II Model and mean-field solution

In this section we consider a mean-field approach to the diffusion-limited annihilation of particles in a lattice. We will see that, although the approach does not provide us with equation (1), it gives other rate equations from which one derives the expected asymptotic time behavior of the density given by equation (2).

Consider a d-dimensional hypercubic lattice in which particles diffuse over the sites. To each site one associates a variable η_i that takes the values 0, 1, 2, ..., $k-1$ according whether the site is empty, occupied by just one particle, two particles, ..., $k-1$ particles. At each time step, a pair of nearest-neighbor sites is chosen at random and their state changes according to the following rules:

a) diffusion

$$(\eta_i, \eta_j) \rightarrow (\eta_i - 1, \eta_j + 1) \qquad \eta_i \neq 0 \qquad \eta_j \neq k-1 \quad (5)$$

$$(\eta_i, \eta_j) \rightarrow (\eta_i + 1, \eta_j - 1) \qquad \eta_j \neq 0 \qquad \eta_i \neq k-1 \quad (6)$$

b) extinction of particles

$$(\eta_i, k-1) \rightarrow (\eta_i - 1, \ell) \qquad \eta_i \neq 0 \quad (7)$$

$$(k-1, \eta_j) \rightarrow (\ell, \eta_j - 1) \qquad \eta_j \neq 0 \quad (8)$$

When a site is occupied by k particles, $k-\ell$ of them disappear instantaneously and the site becomes occupied by just ℓ particles. In the following we will set up and solve the mean-field equations. For convenience we will consider only the annihilation case, $\ell = 0$.

Let us define $P_n(t)$ as the probability that a given site has n particles at time t. According to the rules above we find the following time evolution for this probability

$$\frac{d}{dt} P_0 = \alpha \{ \sum_{m=1}^{k-1} P_{k-1,m} + \sum_{m=0}^{k-1} P_{1,m} - \sum_{m=1}^{k-1} P_{0,m} \} \quad (9)$$

and

$$\frac{d}{dt} P_n = \alpha \{ \sum_{m=1}^{k-1} P_{n-1,m} + \sum_{m=0}^{k-1} P_{n+1,m} - \sum_{m=1}^{k-1} P_{n,m} - \sum_{m=0}^{k-1} P_{n,m} \} \quad (10)$$

for $0 < n \leq k-1$, with the condition $P_{k,m} = 0$, where $P_{nm}(t)$ is the probability that a nearest neighbor pair of sites have n and m particles at time t, and α is a constant. These equations can be written in the form

$$\frac{d}{\alpha dt} P_0 = (P_{k-1} - P_{k-1,0}) + P_1 - (P_0 - P_{00}) \quad (11)$$

and

$$\frac{d}{\alpha dt} P_n = (P_{n-1} - P_{n-1,0}) + P_{n+1} - (P_n - P_{n,0}) - P_n \quad (12)$$

for $0 < n \leq k-1$, with the condition $P_{k,m} = 0$.

These equations are exact but cannot be solved by themselves since we need the time evolution equation for the two body correlation P_{nm}. To solve them we use a truncation scheme which consists in using the approximation $P_{n,m} = P_n P_m$ on the right had site of (11) and (12). The equations then become closed in the variables P_n

$$\frac{d}{\alpha dt} P_0 = (P_{k-1} - P_0)(1 - P_0) + P_1 \quad (13)$$

and

$$\frac{d}{\alpha dt} P_n = (P_{n-1} - P_n)(1 - P_0) + P_{n+1} - P_n \quad (14)$$

for $0 < n \leq k-1$, with the condition $P_k = 0$. These equations can be solved in the long time regime with the solution

$$P_n = (\alpha t)^{-n/(k-1)} \quad (15)$$

for $n = 1, 2, ..., k-1$. In expression (15), only the dominant term is presented. Terms of order smaller than the dominant are neglected.

The density of particles ρ is given by

$$\rho = \sum_{n=1}^{k-1} n P_n \quad (16)$$

and has the asymptotic behavior

$$\rho = (\alpha t)^{-1/(k-1)} \quad (17)$$

as expected.

III The reunion of bounded walkers

It is convenient to define two useful quantities. The first is the average time interval between two consecutive reactions, denoted by τ. Since just after a reaction the number of particles is reduced by an amount $k-\ell$, it follows that τ is related to the decreasing rate of the density ρ by

$$-\frac{d}{dt}\rho=(k-\ell)\frac{1}{\tau} \tag{18}$$

The other quantity, denoted by L, is related to the mean distance between particles, or more precisely, it is the size of a hypercubic cell containing k particles, on the average. If the lattice is partitioned into hypercubic cells of linear size L with k particles each, on the average, it follows that L is related to the density of particles ρ by

$$\rho=k\frac{1}{L^d} \tag{19}$$

If a relation between τ and L is found then this relation together with equations (18) and (19) will allow us to obtain the density ρ as a function of time.

The relation between τ and L can be obtained as follows. Consider a typical hypercubic cell of linear size L in the d-dimensional space where the particles, or random walkers, are diffusing according to the rules (5), (6), (7), and (8). This typical cell will have k walkers which are assumed to be bounded to move inside this cell. An estimate of the quantity τ will be the time it will take for these k walkers to meet, starting, for instance, far away from each other.

Consider k random walkers confined on a region of linear size L of a d-dimensional lattice. The walkers perform independent Brownian motion and eventually meet. Assuming translational invariance it suffices to consider the movement of the walkers relative to one of the walkers which we place at the origin. The problem then becomes equivalent to finding the time τ^* it takes for the other $k-1$ walkers to meet at the origin. The relation between τ and τ^* is $\tau=\tau^*L^d$.

Since the walkers move independently of each other the kinetics can be reduced to just one random walker diffusing in a hypercubic space of dimension $D=d(k-1)$ which we may think as the direct product of $k-1$ subspaces of dimension d. The projection of the solitary walker trajectory over each of the subspaces gives the trajectory of each of the $k-1$ walkers. The problem is then reduced to finding the time it takes for this solitary walker to reach the origin.

We will consider next a random walk on a hypercubic lattice of dimension D with periodic boundary conditions and $N=L^D$ distinct lattice points. The walker starts from a given point $x_0\neq 0$ and at each time step the walker jumps to one of the $2D$ nearest neighbor sites with equal probability. To calculate the average time to reach the origin we let the origin be an absorbing point. Let $P(x,t)$ be the probability that the walker be at site x at time t. Its time evolution obeys the equation

$$\frac{d}{dt}P(x,t)=\sum_\delta\{w(x+\delta)P(x+\delta,t)-w(x)P(x,t)\} \tag{20}$$

where $w(x)$ is the rate of jumping to a neighboring site and the summation is over the $2D$ nearest neighbor sites of site x. The rate $w(x)=\alpha$, a nonzero constant, for $x\neq 0$ and $w(0)=0$ since the origin is an absorbing site.

The probability that the walker be at the origin (and remain forever there) at time t is $P(0,t)$. For a finite lattice, in any dimension, $P(0,t)\to 1$ as $t\to\infty$ since $x=0$ is an absorbing state. In this case, the average time τ^* to reach the origin will be finite and is given by

$$\tau^*=\int_0^\infty t\frac{d}{dt}P(0,t)dt \tag{21}$$

This formula can be understood observing that the probability that the walker reach the origin between t and $t+\Delta t$ is $P(t+\Delta t)-P(t)\approx(dP/dt)\Delta t$.

Using the Laplace transform

$$\widehat{P}(x,z)=\int_0^\infty P(x,t)e^{-zt}dt \tag{22}$$

equation (20) becomes

$$z\widehat{P}(x,z)-P(x,0)=\sum_\delta\{w(x+\delta)\widehat{P}(x+\delta,z)-w(x)\widehat{P}(x,z)\} \tag{23}$$

where $P(x,0) = \delta(x, x_0)$ since at time $t = 0$ the walker is at position $x = x_0$.

We define next the Fourier transform of $\widehat{P}(x, z)$ given by

$$\widetilde{P}(q, z) = \sum_x \widehat{P}(x, z) e^{iq\cdot x} \qquad (24)$$

where the summation is over the sites of the hypercubic lattice, and q is a vector belonging to the first Brillouin zone. From equation (23) it follows that

$$\widetilde{P}(q, z) = \frac{e^{iq\cdot x_0}}{z + \lambda(q)} + \frac{\lambda(q)}{z + \lambda(q)} \widehat{P}(0, z) \qquad (25)$$

where

$$\lambda(q) = 2\alpha \sum_{i=1}^{D} (1 - \cos q_i) \qquad (26)$$

Summing the right and left hand sides of equation (25) over q and taking into account that

$$\widehat{P}(x, z) = \frac{1}{N} \sum_q \widetilde{P}(q, z) e^{iq\cdot x} \qquad (27)$$

where the summation in q is over the first Brillouin zone, we get

$$\widehat{P}(0, z) = \frac{G(x_0, z)}{zG(0, z)} \qquad (28)$$

where

$$G(x, z) = \frac{1}{N} \sum_q \frac{e^{iq\cdot x}}{z + \lambda(q)} \qquad (29)$$

is the lattice Green function.

From the Laplace transform $\widehat{P}(0, z)$ we can obtain the probability $P(0, t)$ and from it the average time τ^*. However, it is possible to calculate τ^* directly from $\widehat{P}(0, z)$. Indeed, from (21) it follows that

$$\tau^* = \lim_{z\to 0} \{-\frac{d}{dz}[z\widehat{P}(0, z)]\} \qquad (30)$$

For small values of z, the Green function (29) behaves as

$$G(x, z) = \frac{1}{Nz}\{1 + z \sum_{q(\neq 0)} \frac{e^{iq\cdot x}}{\lambda(q)}\} \qquad (31)$$

as long as N is finite. Owing to equation (28), we get finally the following result for the first-passage time [41]

$$\tau^* = \sum_{q(\neq 0)} \frac{1 - e^{iq\cdot x_0}}{\lambda(q)} \qquad (32)$$

This equation allows us to calculate the τ^* for large values of L in any dimension D. We need τ for the case in which x_0 is proportional to L. We will set $x_0 = (L/2, L/2, ..., L/2)$. The asymptotic results, valid for large values of L, are

$$\tau^* = \frac{\alpha}{2} L^2 \qquad D < 2 \qquad (33)$$

$$\tau^* = \frac{2}{\pi} L^2 \ln L \qquad D = 2 \qquad (34)$$

$$\tau^* = C_D L^D \qquad D > 2 \qquad (35)$$

where the constant C_D is given by

$$C_D = \frac{1}{(2\pi)^D} \int \frac{1}{\lambda(q)} d^D q \qquad (36)$$

For $D \geq 2$, the dominant contribution comes from small q.

Using these results with $D = d(k-1)$ and equations (18) and (19), and recalling that $\tau = \tau^* L^d$, we obtain the following asymptotic behavior for the density

$$\rho \sim t^{1/(k-1)} \qquad d > \frac{2}{k-1} \qquad (37)$$

$$\rho \sim (\frac{\ln t}{t})^{d/2} \qquad d = \frac{1}{k-1} \qquad (38)$$

$$\rho \sim t^{-d/2} \qquad d < \frac{2}{k-1} \qquad (39)$$

IV Conclusion

We have studied the long time behavior of a one-species reaction-diffusion process in a hypercubic lattice where a specified number of particles coalesce into a smaller number of particles. The asymptotic behavior of the density of particle was obtained by mapping the process into the problem of the reunion of random walkers that are confined to move in a limited region.

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