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Steady state of imperfect annihilation and coagulation reactions

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Abstract. We study the coagulation ($A+A \to A$) and annihilation ($A+A \to 0$) reactions with input probability ϵ and reaction probability p in a one-dimensional lattice. In the steady state we find two different behaviours for the density of nearest-neighbour occupied sites Γ against the density of particles ρ. These behaviours correspond to the diffusion-limited regime ($\rho \to 0$) and to the reaction-limited regime ($\rho \sim 1$). Using a scaling ansatz for Γ against ρ we derive an approximation for ρ as a function of ϵ and p that agrees well with Monte Carlo numerical results.

1. Introduction

In recent years much effort has been dedicated to the study of simple reactions [1, 2] (for a recent review, see, e.g., [3] and references cited therein) such as coagulation ($A+A \to A$), annihilation ($A+A \to 0$), annihilation of two species ($A+B \to 0$) and related models [4]. This is mainly due to the anomalous kinetics that arise when the particles diffuse over low-dimensional substrata. It has been shown [5] in systems without input that the influence of the probability of reaction may be negligible at very long times but is very important at short or intermediate times (the lower the probability of reaction, the longer the time during which the influence is important).

In the present work we analyse the influence of the probability of reaction p in the steady state of annihilation and coagulation reactions when there is an input of particles in a one-dimensional system [6].

In the works by Rácz [7] and ben-Avraham *et al* [8] the exact steady-state density ρ of annihilation and coagulation reactions for the case of $p = 1$ in a one-dimensional lattice were found. The diffusion process is represented by particles that move randomly to the nearest lattice site with a hopping rate $2D/(\Delta x)^2$, where D is the diffusion coefficient and Δx is the lattice spacing. The input process takes place when any empty site becomes occupied by a particle with a probability rate $R\,\Delta x$, where R is the average number of particles input per unit length per unit time. The coagulation or annihilation process takes place instantaneously, with probability $p = 1$, when two particles collide. For a coagulation reaction the steady-state density is

$$\rho^{\mathrm{coag}}(R, D) = \frac{|\mathrm{Ai}'(0)|}{\mathrm{Ai}(0)} \left(\frac{R}{2D}\right)^{1/3} = 0.729\ldots \left(\frac{R}{2D}\right)^{1/3} \qquad p = 1 \tag{1}$$

where Ai is the Airy function and, for an annihilation reaction

$$\rho^{\mathrm{ann}} = 2^{-2/3} \rho^{\mathrm{coag}} \qquad p = 1. \tag{2}$$

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In this work we try to extend these results to any value of the probability of reaction p. The results obtained are approximate, but we would like to remark on the importance of producing approximations because of the lack of exact results in problems where we have annihilation or coagulation reactions where particles react with a given probability, or there are interactions between them. Examples of approximate results in related problems can be found in [5, 8, 9].

Exact results in a closely related problem are given in [10] where the imperfect reaction $A+A \rightarrow B$ in one dimension is studied and the behaviour of the density is exactly obtained. In [11] the annihilation reaction in d-dimensional systems with an input of particles is studied. They consider immobile particles that react via transfer rates dependent on the interparticle distance and calculate exactly, in the form of bounds, the steady-state density.

The motivation for the present work is not to reproduce or predict any specific experiment but to analyse the general effects of the introduction of the probability of reaction which is present in almost all catalytic reactions. This probability of reaction accounts for the actual energy barrier that particles must overcome in order to get close enough to react. In order to understand the influence of this probability in a real low-dimensional substrate we study the simplest case of a one-dimensional lattice.

2. The model and the Monte Carlo simulation

In the model the particles perform a random walk between nearest-neighbour (NN) sites in a lattice of size $L = 10^5$ (lattice spacing $\Delta x = 1$). We use periodic boundary conditions in order to avoid edge effects. Each site of the lattice can either be occupied by only one particle or empty.

At each Monte Carlo step, one of the L sites of the system is randomly chosen. The following situations may appear.

(i) If the chosen site is empty, it is occupied with a particle with probability ϵ.

(ii) If the site is occupied, the particle tries to jump to any of the NN sites with equal probability 1/2. If the neighbour site is empty the jump is performed, otherwise, the particles react with probability p. If the reaction is performed the first particle is eliminated from the system (coagulation reaction) or both particles are eliminated (annihilation reaction); if not, nothing happens and the particles remain at their sites.

After each Monte Carlo step time is increased by $1/L$ so that, at a time interval equal to 1, every particle has, on average, a chance to jump and every empty site has a chance to be occupied by an input particle.

The reaction rate β is related to the reaction probability p. The first is defined as the inverse of the reaction time, i.e. the mean time that particles need to react when they are close to each other and which is equal to the average number of reaction trials $(1/p)$ multiplied by the average time interval between trials (Δt). Hence, $\beta = p/\Delta t$. In this model the diffusion coefficient is $D = 1/2$. The input probability ϵ is the probability that an empty site is occupied by an input particle in, on average, a time interval Δt. So, it is related to the input rate R by $\epsilon = R\Delta x \Delta t$. In our model we have $\beta = p$ and $\epsilon = R$ because of the length and time scales ($\Delta x = 1$ and $\Delta t = 1$, respectively) chosen. Then, for the case $p = 1$, we have that the steady-state density depends only on the input probability (see equations (1) and (2))

$$\begin{aligned} \rho^{\text{coag}}(\epsilon) &= 0.729\ldots\epsilon^{1/3} \qquad p = 1 \\ \rho^{\text{ann}}(\epsilon) &= 0.459\ldots\epsilon^{1/3} \qquad p = 1. \end{aligned} \tag{3}$$

3. The balance equation

Let us denote by P_- the probability that a reaction takes place in a Monte Carlo step and by P_+ the probability for an input in a Monte Carlo step. The average change of the density is

$$\frac{\mathrm{d}\rho(t)}{\mathrm{d}t} = \frac{\delta\rho_+}{\delta t}P_+ + \frac{\delta\rho_-}{\delta t}P_- \tag{4}$$

where $\delta\rho_-$ is the density change due to reaction, $\delta\rho_+$ is the density change due to input and $\delta t = 1/L$ is the time increment in a Monte Carlo step. We have $\delta\rho_+ = 1/L$ and $\delta\rho_- = -a/L$, where $a = 1$ for a coagulation reaction and $a = 2$ for an annihilation reaction.

Let us consider a given pair of NN occupied sites. The probability that one of these two particles is selected at random in a Monte Carlo step is $2/L$. The probability that the selected particle reacts with the other particle is $p/2$. Then, $P_- = (2/L)(p/2)n_1$, where n_1 is the number of NN pairs of particles present in the system at time t. We define $\Gamma(t) \equiv n_1/L$ as the number of pairs of NN occupied sites per lattice site. If we call s_i the occupation number of site i ($s_i = 1$ if site i is occupied and $s_i = 0$ if not), Γ can be defined as $\Gamma = \langle s_i s_{i+1}\rangle$, where the average is taken over every site of the lattice. Hence,

$$P_- = p\Gamma(t). \tag{5}$$

The probability of selecting an empty site in a Monte Carlo step is $1 - \rho(t)$ and the input probability is ϵ, then,

$$P_+ = \epsilon[1 - \rho(t)]. \tag{6}$$

Substituting into (4) we have

$$\frac{\mathrm{d}\rho(t)}{\mathrm{d}t} = -ap\Gamma(t) + \epsilon[1 - \rho(t)]. \tag{7}$$

Another way of obtaining this equation is presented in [12]. The first term of equation (7) represents the decrease of ρ due to reaction. The second term represents the input of particles: the input probability ϵ multiplied by the probability of finding an empty site. In the steady state there is a balance between input and reaction:

$$\epsilon(1 - \rho) = ap\Gamma \qquad \text{steady state.} \tag{8}$$

We call this the balance equation.

Let us now analyse two limiting cases: when $\rho \to 0$ and when $\rho \sim 1$.

The limit $\rho \to 0$ is obtained when $\epsilon \to 0$. In this case the particles are spread and they diffuse without interacting most of the time. The diffusion time (the mean time between collisions) is much greater that the reaction time (the mean time that particles need to react when they are close to each other). This is the so called diffusion-limited regime. We will assume in this case that the value of the steady-state density only depends on the value of ϵ and does not depend on p (in the same way, when we have no input, the density decay does not depend on p for long enough times [5]). This assumption will be confirmed by numerical simulations in figure 2. We have,

$$\rho(\epsilon) = b\epsilon^{1/3} \qquad \text{for all } p \text{ and } \rho \to 0. \tag{9}$$

The value of parameter b depends on whether we have an annihilation or coagulation reaction (see equation (3)). From equation (8) the behaviour of Γ is $\Gamma = (1 - \rho)\epsilon/ap$. Considering that $\rho \ll 1$ and using equation (9) we have

$$\Gamma = \frac{1}{ap}\left(\frac{\rho}{b}\right)^3 \qquad \text{for } \rho \to 0. \tag{10}$$

Let us analyse the case when $\rho \sim 1$. The reasons for having $\rho \sim 1$ could be a high input probability, $\epsilon \sim 1$, or a low reaction probability, $p \to 0$. Both factors contribute to having a random distribution of particles. With a high input rate any inhomogeneity in the particle distribution is erased. With a low reaction probability the particles have to collide many times in order to react, contributing in this way to randomizing the particle distribution. In this case the probability of having two particles at NN sites simply is ρ^2. Then,

$$\Gamma = \rho^2 \qquad \text{for } \rho \sim 1. \tag{11}$$

We have two different behaviours for Γ described by equations (10) and (11). The crossover density ρ_c between both behaviours is easily obtained from equations (10) and (11). We find,

$$\rho_c = ab^3 p. \tag{12}$$

4. The scaling function and an approximation for ρ

In order to analyse the universal (independent of p) behaviour of Γ as a function of ρ we propose the scaling ansatz

$$\Gamma = \rho_c^2 f(\rho/\rho_c) \tag{13}$$

where

$$f(x) = \begin{cases} x^2 & \text{if } x \gg 1 \\ x^3 & \text{if } x \ll 1. \end{cases} \tag{14}$$

In figure 1 we plot the Monte Carlo data of Γ/ρ_c^2 against ρ/ρ_c in $\log_{10}$–$\log_{10}$ scales for different values of p. Let us stress that the Monte Carlo results are in agreement with the asymptotic behaviour. The scaling function for an annihilation reaction is the same as that for a coagulation reaction, so both types of reaction are used in figure 1. The observed data collapse supports the scaling ansatz.

A simple function which fulfils the scaling form is

$$f(x) = \frac{x^3}{x+1}. \tag{15}$$

We will use equation (15) in order to find an approximate expression for the steady-state density ρ, ϵ and p. It is possible to use other forms for the scaling function f, but here we use equation (15) because of its simplicity and because the approximation obtained in this way is in good agreement with numerical results as we can see in figure 1.

From equations (13) and (15) we have

$$\Gamma = \frac{\rho^3}{\rho + \rho_c}. \tag{16}$$

Using equation (8),

$$\epsilon = \frac{ap\rho^3}{(1-\rho)(\rho+\rho_c)}. \tag{17}$$

In figure 2 we plot the steady-state density ρ against ϵ in $\log_{10}$–$\log_{10}$ scales for different values of p for the coagulation reaction A+A $\to$ A. The points are the Monte Carlo data and the curves represent the approximation of equation (17). The agreement between analytical and numerical results is reasonably good. A very similar plot is obtained with the data for

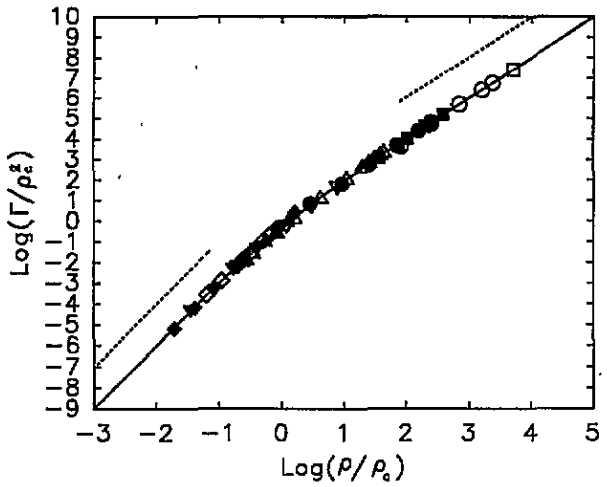

Figure 1. Scaling of $\log_{10}\Gamma/\rho_c^2$ against $\log_{10}\rho/\rho_c$. For an annihilation reaction, $p = 0.001$ (□), $p = 0.01$ (■), $p = 0.1$ (△), $p = 0.5$ (▲) and $p = 1$ (◇). For a coagulation reaction, $p = 0.001$ (○), $p = 0.01$ (●), $p = 0.1$ (▽), $p = 0.5$ (▼) and $p = 1$ (◆). The curve corresponds to the approximation of equation (16). The dashed lines are drawn as a guide and have slopes of two and three (see equation (14)).

the annihilation reaction $A + A \rightarrow 0$. For low enough values of ρ we can see in the figure a collapse of the curves for different values of p. This is a confirmation of the assumption made in section 3 with respect to the fact that, for $\rho \rightarrow 0$, the behaviour of the density is independent of p.

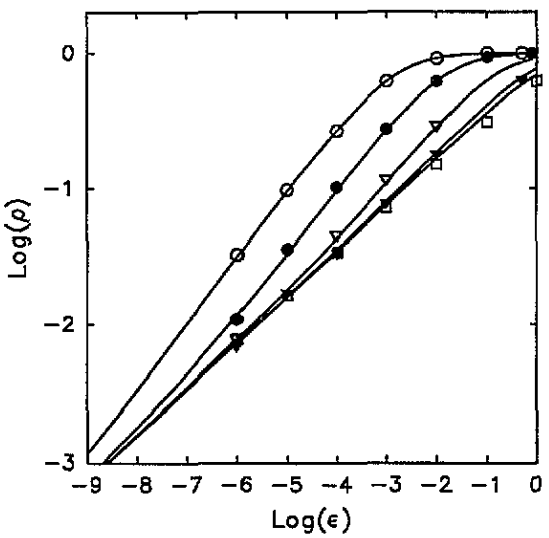

Figure 2. $\text{Log}_{10}\rho$ plotted against $\log_{10}\epsilon$ for the coagulation reaction. Each curve corresponds to different values of p. From top to bottom: $p = 0.001$ (○), $p = 0.01$ (●), $p = 0.1$ (▽), $p = 0.5$ (▼) and $p = 1$ (□). The points are numerical results and the curves are the approximation of equation (17).

5. Conclusions

We have constructed an analytical expression for the constant input probability, ϵ, which is necessary to obtain a steady-state density ρ when the particles react with probability p (included in the crossover density $\rho_c = ab^3p$), equation (17), for both annihilation and coagulation reactions in a one-dimensional lattice. Although the result is approximate, as we state in the introduction, we consider that it is interesting to present approximate results because of the difficulties that arise in exactly solving very simple reaction–diffusion systems which are slightly complicated with the introduction of the probabilities of reaction or interactions between particles.

An important conclusion is that we find two different behaviours for the density of NN occupied sites Γ when $\rho/\rho_c \ll 1$ and when $\rho/\rho_c \gg 1$. The first corresponds to the diffusion-limited regime where the steady-state density does not depend on the probability of reaction p. The second is the reaction-limited regime where we have a random distribution of particles. From the analysis of these two behaviours a scaling ansatz is proposed (equation (13)). Using the simple function (15) which fulfils the scaling form, we obtain the analytical approximation for the density of particles which we plot in figure 2. The expression obtained agrees well with numerical results.

For a given value of p, the maximum value of the density is $\rho(\epsilon = 1)$. In general, we expect that the collapse of the data of figure 1 improves when $\rho(\epsilon = 1)/\rho_c$ increases. For $p = 1$ we have that the condition $\rho(\epsilon = 1)/\rho_c \gg 1$ is not fulfilled and at this point a small separation of Γ from the data collapse curve appears. This separation is difficult to appreciate on the scale of figure 1 but can be appreciated in the curve for $p = 1$ in figure 2 for high values of ϵ. The deviations for $p \leqslant 0.5$ are between 2.5% and 4%.

In our approximation of the density we use a simple phenomenological interpolation between low and high density behaviours. In [9] a more elegant approximation is made directly in the kinetic equation of the model and a good agreement between Monte Carlo data and their approximation for $A + A \rightarrow A$ is obtained, with error values similar to ours. The advantage of our method is that the same scheme is used for both annihilation and coagulation reactions. Moreover, our procedure can be easily extended to the case of diffusion on a fractal substratum of spectral dimension d_s [13]. In this case, in the limit $\rho \rightarrow 0$ and for $d_s \leqslant 2$, we expect $\rho(\epsilon) = c\epsilon^{d_s/(d_s+2)}$ [14] independent of p. One can obtain the value of the constant c from Monte Carlo simulations. For $\rho \sim 1$ we have $\Gamma = \rho^2$. Making a phenomenological interpolation between these two regimes, an approximation for ρ can be obtained.

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