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Diffusion-limited coalescence with finite reaction rates in one dimension

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Abstract. We study the diffusion-limited process $A + A \rightarrow A$ in one dimension, with finite reaction rates. We develop an approximation scheme based on the method of inter-particle distribution functions (IPDF), which was used formerly for the exact solution of the same process with an infinite reaction rate. The approximation becomes exact in the very early time regime (or the reaction-controlled limit) and in the long-time (diffusion-controlled) asymptotic limit. For the intermediate time regime, we obtain a simple interpolative behaviour between these two limits. We also study the coalescence process (with finite reaction rates) with the back reaction $A \rightarrow A + A$, and in the presence of particle input. In each of these cases the system reaches a non-trivial steady state with a finite concentration of particles. Theoretical predictions for the concentration time dependence and for the IPDF are compared with computer simulations.

1. Introduction

In recent years much effort has been dedicated to diffusion-limited reactions in low dimensions [1–10]. Most research has focused on the bi-molecular reaction $A + B \rightarrow \text{inert}$ [2], and on one-component coalescence, $A + A \rightarrow A$ [3–8], and annihilation, $A + A \rightarrow 0$ [9, 10]. The last two systems were solved exactly in one dimension and are especially useful in elucidating the anomalous kinetics of diffusion-limited reaction processes. Naturally, simple generalizations and extensions of these basic processes are of much interest, because of the possibility that they may also be solved exactly. Indeed, the coalescence process, $A + A \rightarrow A$, has also been solved together with the back reaction, $A \rightarrow A + A$, and under an input of A particles [5], as well as for systems of finite size [7] and with inhomogeneous initial conditions [8].

In the diffusion-limited coalescence process reactions occur at an infinite rate, taking place immediately upon the encounter of any two particles. An obvious generalization would be to make the reaction rate finite. This more physical process would also exhibit an interesting crossover from a classical reaction-limited behaviour, at early times, to a diffusion-limited regime, in the long-time asymptotic limit. Surprisingly, this simple-minded generalization makes it difficult (perhaps even impossible) to solve the model exactly.

Simulations have been performed, both on the one-component annihilation process and on the coalescence process in one dimension, with a finite reaction rate [11–13]. The simulations show three different regimes: (i) an early time regime where the particles merely diffuse with a negligible change in the initial concentration; (ii) an intermediate regime, in

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which the concentration of particles decays faster than the diffusion-limited case, $c \sim 1/\sqrt{t}$, but not quite as fast as the classical limit, $c \sim 1/t$ and (iii) a long-time diffusion-limited regime, where the system behaves exactly as if the reaction rate were infinite. Based on these simulation results, the intriguing possibility that in the intermediate regime the concentration decays anomalously in time, with a power dependent on the reaction rate, was raised [11]. Subsequent theoretical work by Privman *et al* [13] and Hoyuelos and Martín [12] has suggested that the kinetics in the intermediate regime can be explained as an interpolation between the classical and the diffusion-controlled limits.

The analysis of Privman *et al* [13] is based on the concept of inter-particle distribution functions (IPDF), which had been introduced earlier for the exact solution of the coalescence process with infinite reaction rate [5]. In the IPDF method a diffusion equation is derived for the probability that the two nearest particles are a distance x apart (the IPDF), and the reaction is represented by absorbing boundary conditions at the origin. Privman *et al* have replaced this boundary condition with a radiative one, in order to approximate the finite reaction rate. Their approach yields an elegant, *qualitative* understanding of the three regimes discussed above. Hoyuelos and Martín [12] have found an interpolation formula for the challenging intermediate regime, which fits the simulation data reasonably well. However, the derivation is largely phenomenological and it requires a scaling ansatz which we find physically obscure.

In this paper, we study the one-dimensional coalescence process, $A+A \rightarrow A$, with finite reaction rate. Our approach is based on the IPDF method but differs from that of Privman *et al* in important details. In particular, it allows us to derive a closed analytic expression for the concentration decay at all times. For the intermediate regime, an interpolative formula between the classical and diffusion-controlled limits emerges as a natural consequence of the approximation. We also study the coalescence process with back reactions, $A \rightarrow A+A$, and with particle input, $0 \rightarrow A$. In each of these cases the system arrives at a non-trivial steady state where the concentration is finite. Finally, we study the IPDFs themselves, which show different characteristics at different time regimes and in the stationary cases. Our theoretical results compare quite well with computer simulations.

The rest of the paper is organized as follows. Our model and a physical approximation based on the method of IPDFs are introduced in section 2. In section 3, we perform a mathematical approximation which enables us to solve the equations derived in section 2 in a closed form. In the same section, we compare simulations and analytic results. The two cases of non-trivial steady state are explored in section 4, both through our analytic approach and through computer simulations. We conclude with a discussion, in section 5.

2. The reaction model and the IPDF method

Our model is defined on a one-dimensional lattice with lattice spacing Δx . Each site can be either empty (\circ) or occupied (\bullet) by one particle. The particles move randomly, independently of each other, to a nearest-neighbour site with a hopping rate $D/(\Delta x)^2$ (to each side). On long length and time-scales this yields normal diffusion with diffusion coefficient D . When a particle hops onto a site which is occupied, coalescence takes place with probability k , while with probability $(1-k)$ the particle is reflected back to its original position and no reaction takes place. Thus, the probability k controls the rate of the reaction



When $k = 0$ the reaction rate is zero. The particles merely diffuse, bouncing off each other and no reactions take place. In the other extreme, when $k = 1$, reactions are immediate, i.e. the reaction rate is infinite. This is the purely diffusion-limited case. When k is very small but finite, one expects to find a regime which is dominated by the slow reaction rate. This is the classical reaction-limited case.

To solve the system, we follow the IPDF method, used previously for the exact solution of this model in the case of $k = 1$ [5]. We define, as usual, $E_n(t)$, the probability that a randomly chosen segment of n consecutive sites is empty, i.e. it contains no particles. The probability that a site is occupied is $1 - E_1 \equiv C$, and the density of occupied sites is

$$c(t) = (1 - E_1(t))/\Delta x = C(t)/\Delta x. \quad (2)$$

E_n gives the probability that, say, sites 1 through n are empty, while E_{n+1} gives the probability that sites 1 through n are empty and also site $n + 1$ is empty. Thus, the probability that a segment of n sites is empty, but that the adjacent $(n + 1)$ th site is occupied, is $\text{Prob}(\circ \circ \dots \circ \bullet) = E_n - E_{n+1}$. It can also be shown [5] that

$$E_{n-1} - 2E_n + E_{n+1} = Cp_n \quad (3)$$

where p_n is the probability that nearest-neighbour particles are exactly n sites apart (this is the IPDF, from which the method derives its name [6]). In particular, the probability of finding two adjacent occupied sites is given exactly by $\text{Prob}(\bullet\bullet) = 1 - 2E_1 + E_2$.

When the reaction probability $k = 1$, one can write down an exact equation for the evolution of E_n [5]:

$$\partial_t E_n = \frac{2D}{(\Delta x)^2} \{ (E_{n-1} - E_n) - (E_n - E_{n+1}) \}. \quad (4)$$

The first term on the RHS describes the creation of an empty n -sites interval, when a particle at the inner edge of the interval hops out. The second term describes annihilation of an empty interval, when a particle at the outer edge of the interval hops in.

When the reaction probability $k < 1$, hopping out of the interval is not always possible. The target site may be occupied, in which case hopping (and coalescence) will be disallowed, with probability $1 - k$. To account for this effect, we require the probability of finding intervals of $n - 1$ consecutive empty sites, followed by two occupied sites. Since this probability cannot be expressed exactly in terms of E_n , we use the approximation [14]

$$\text{Prob}(\overbrace{\circ \circ \dots \circ}^{n-1} \bullet\bullet) \approx \frac{\text{Prob}(\overbrace{\circ \circ \dots \circ}^{n-1} \bullet) \text{Prob}(\bullet\bullet)}{\text{Prob}(\bullet)} = \frac{(1 - 2E_1 + E_2)(E_{n-1} - E_n)}{1 - E_1}. \quad (5)$$

With this approximation, the evolution equation for arbitrary k is

$$\partial_t E_n = \frac{2D}{(\Delta x)^2} (E_{n-1} - 2E_n + E_{n+1}) - \frac{2D}{(\Delta x)^2} (1 - k) \frac{1 - 2E_1 + E_2}{1 - E_1} (E_{n-1} - E_n) \quad (6)$$

where the correction due to failed coalescence attempts is represented by the last term. Notice that when $k = 1$ this reduces properly to (4).

Equation (6) is valid for $n > 1$. For $n = 1$ we have the exact equation

$$\partial_t E_1 = \frac{2D}{(\Delta x)^2} k(1 - 2E_1 + E_2) \quad (7)$$

which simply states that sites become empty at the same rate as particles coalesce. Comparing (6) and (7) we see that they may be combined, by requiring the boundary condition

$$E_0(t) = 1. \quad (8)$$

Equation (6) may thus be extended to the case of $n = 1$. A second boundary condition is

$$E_n(t) = 0 \quad \text{as } n \rightarrow \infty \quad (9)$$

since an infinitely long segment will always contain particles, as long as the concentration is finite.

The only approximation made here is in (5), where some correlations between the probable state of consecutive intervals are neglected, which is known to be valid in the limit of small densities, $c(t)$ [14]. We argue, however, that (6) is asymptotically correct both in the early and long time regimes, and hence it may provide a reasonable interpolation for the intermediate time regime. If the starting configuration of the system is random, as assumed in this work, then $E_n = E_1^n$ and the state of consecutive intervals are uncorrelated, regardless of how large $c(0)$ may be. This situation will persist, and (5) will hold, until the concentration drop is noticeable (i.e. the end of the early time regime) for it is only reactions which induce correlations (in fact, diffusion randomizes the system). On the other hand, after very long times the concentration of particles becomes very small. As a result, adjacent occupied sites become extremely rare and the correction term in (6) eventually becomes negligible. Equation (6) then degenerates to the case of an infinite reaction rate and it no longer matters how imprecise the correction term is.

3. Integration of the evolution equation

There exist various techniques for solving (6), with the boundary conditions of (8) and (9). Perhaps the most straightforward method is numerical integration, which requires discretization of the time variable in (6). A second approach, which worked well for the case of $k = 1$, is passing to the continuum limit [5]. This is achieved by defining the spatial coordinate $x = n \Delta x$. The probabilities $E_n(t)$ are replaced by the function $E(x, t)$. Letting $\Delta x \rightarrow 0$, (6) is replaced by

$$\partial_t E = 2D \partial_x^2 E - 2D(1-k) \frac{\partial_x^2 E|_{x=0}}{\partial_x E|_{x=0}} \partial_x E \quad (10)$$

and the boundary conditions of (8) and (9) become

$$E(0, t) = 1 \quad \text{and} \quad E(x \rightarrow \infty, t) = 0. \quad (11)$$

We see that the finite reaction rate gives rise to a non-local, nonlinear term in (10). However, notice that $\partial_x^2 E|_{x=0}/\partial_x E|_{x=0} \equiv \omega(t)$ is a function of time only. Thus, in principle, one can proceed by Laplace transforming (10) with respect to the spatial variable x , and then determine $\omega(t)$ in some self-consistent way. Unfortunately, this procedure leads to complicated expressions and one is forced to resort to series expansions, limiting the solution to a few asymptotic results.

Here we propose an alternative approach, based on an approximation of (6). We emphasize that this approximation is merely a *mathematical* convenience, designed to enable us to obtain a solution to (6) in closed form. The *physical* approximation made in (5) is the real focus of this paper. Indeed, (6) can be solved to any degree of accuracy employing numerical methods.

We first sum (6) over the index n , from 1 to ∞ , to yield

$$\partial_t \sum_{n=1}^{\infty} E_n = \frac{2D}{(\Delta x)^2} (1 - E_1) - \frac{2D}{(\Delta x)^2} (1 - k) \frac{1 - 2E_1 + E_2}{1 - E_1} \quad (12)$$

where we have used the boundary conditions of (8) and (9). The RHS. can be made a function of E_1 only with the help of (7). For the LHS we make the approximation $\sum E_n \approx A/(1 - E_1)$, where A is a constant. The motivation for this is that in the long-time asymptotic limit $E_n \approx 1$ for all n up to a characteristic $\langle n \rangle = 1/(1 - E_1)$, and falls sharply to zero for $n > \langle n \rangle$. More precisely, in the long-time asymptotic limit the reaction proceeds as if k is effectively 1, in which case we know that $A = 2/\pi$, exactly [5]. The approximation lies in the fact that we assume A to be constant *at all times*. Indeed, the variation in A is quite small; at the beginning of the process, when the distribution is random, $A = 1$. Let us then assume that $A = 2/\pi$ (to match the exact long-time asymptotic solution) holds true throughout the process. Equation (12) then becomes

$$\frac{d}{d\tau} \frac{2}{\pi C} = C + \frac{1 - k}{kC} \frac{dC}{d\tau} \quad (13)$$

where $\tau \equiv (2D/(\Delta x)^2)t$ is a dimensionless time variable, and we have used $1 - E_1 = C$ (2). The solution to (13) is

$$C = \frac{1 - k + \sqrt{\left(\frac{2k}{\pi C_0} + 1 - k\right)^2 + \frac{4k^2}{\pi} \tau}}{2\left(\frac{k}{\pi C_0^2} + \frac{1-k}{C_0} + k\tau\right)} \quad (14)$$

where $C_0 \equiv C(t = 0)$.

In figure 1, we plot the concentration decay as computed from a numerical integration of (6), from the analytical expression of (14), and from computer simulations, for the same choice of parameters (D and C_0) and for various choices of k . The agreement between (14) and the numerical integration is excellent—little is lost in the ‘mathematical’ approximation. More importantly, there is good agreement between theory and simulations: the early and late time regimes match almost perfectly, and in spite of differences of up to 9% in the intermediate regime, the slope of the curves and the crossover times are almost identical.

From (14), we see that the intermediate time regime is merely an interpolation between a classical decay, $C \sim 1/t$, and a diffusion-limited decay, $C \sim 1/\sqrt{t}$. We can use our result to estimate the crossover times. We first expand $C(\tau)$ in powers of t :

$$C(\tau) = C_0 - \frac{\pi k C_0^3}{2k + \pi(1 - k)C_0} \tau + \mathcal{O}(\tau^2). \quad (15)$$

We obtain the crossover time between the early time regime and the intermediate regime, τ_1 , by requiring that the term linear in τ be a finite fraction, ϵ , of C_0 :

$$\tau_1 = \epsilon \left(\frac{2}{\pi C_0^2} + \frac{1 - k}{k C_0} \right). \quad (16)$$

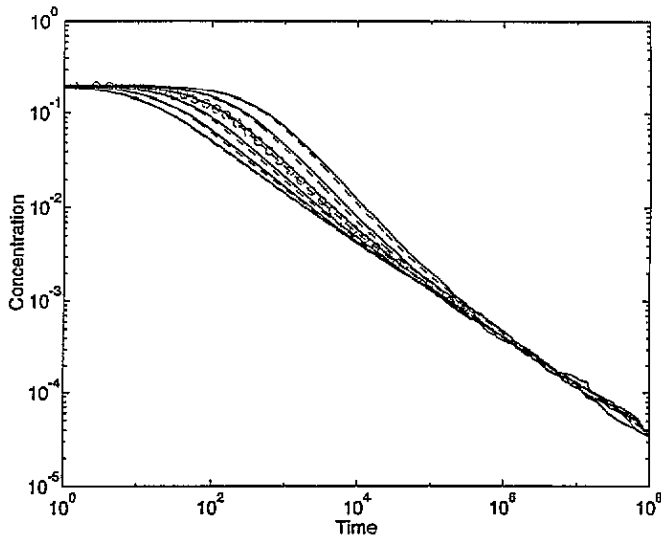


Figure 1. Concentration decay as a function of time for the coalescence process as obtained from computer simulations (full curve), and from (14) (broken curve). The different curves represent different values of the reaction probability; $k = 0.005, 0.01, 0.02, 0.04, 0.08$ and 0.16 (from top to bottom). Also shown are results from numerical integration of (6) for $k = 0.02$ (circles).

Even in the diffusion-limited case, when $k \approx 1$, there is an early time regime where reactions go unnoticed. Since coalescence is immediate, the crossover time equals the typical time that two nearest particles will take to reach each other. The average distance between particles is $1/c_0$, and since the particles diffuse, $t_1 \approx 1/Dc_0^2$ [15], in agreement with the estimate above. The second term on the RHS predicts that the crossover time τ_1 will increase proportionally to $1/kc_0$, which is characteristic of the classical limit (classically, $dc/dt = -kc^2$ and $c = c_0/(1 + kc_0t)$).

Next, we expand (14) in powers of $1/\sqrt{\tau}$:

$$C(\tau) = \frac{1}{\sqrt{\pi\tau}} + \frac{1-k}{2k\tau} + \mathcal{O}\left(\frac{1}{\tau^{3/2}}\right). \quad (17)$$

Notice that the leading term corresponds to the long-time asymptotic limit, where the concentration decays as $c = 1/\sqrt{2\pi Dt}$ (as in the exact solution for $k = 1$). Interestingly, the second term also does not retain any memory of the initial density, C_0 , but has some k -dependence. Comparing the leading term to the first correction we get an estimate for τ_2 , the crossover time between the intermediate regime and the long time regime:

$$\tau_2 = \frac{\pi(1-k)^2}{4k^2}. \quad (18)$$

This can be explained heuristically, as follows. The long-time asymptotic regime occurs because the reaction probability k effectively renormalizes to 1: if the density of particles is C , the number of sites between neighbouring particles is on average $1/C$. Because the particles diffuse, it takes them of the order of $1/C^2$ steps to meet each other. During this time, each of the $1/C$ sites is visited of the order of $(1/C^2)/(1/C) = 1/C$ times. In particular, two neighbouring particles will collide about $1/C$ times before wandering off

from each other to interact with other particles. This means that two neighbouring particles will almost surely react before meeting other partners if $(1/C)k \approx 1$, i.e. the crossover will occur when $C \approx k$, or, since in the long-time asymptotic regime $C = 1/\sqrt{\pi\tau}$, $\tau_2 \approx 1/\pi k^2$, in agreement with (18).

To obtain the IPDF, we integrate (6) numerically and then use (3). At time $t = 0$, we start with a random distribution of particles, so that $p_n(0) = (1 - C_0)^n / C_0$. In the continuum approximation, this can be written in the scaling form $p(\xi) = \exp(-\xi)$, where $\xi \equiv c(t)x$. As the reaction proceeds, the likelihood of finding nearby particles decreases, due to the coalescence process. Thus, coalescence gives rise to an effective repulsion. In the long-time asymptotic limit, when k effectively renormalizes to 1, the IPDF arrives at the stationary scaling form $p(\xi) = (\pi\xi/2) \exp(-\pi\xi^2/4)$ [5]. During the intermediate time regime, the IPDF makes a smooth transition between these two limits. In figure 2, we plot $p(\xi)$ as obtained from numerical integration and compare with computer simulations at various stages of the process. As might be expected, the agreement is worst in the intermediate time regime.

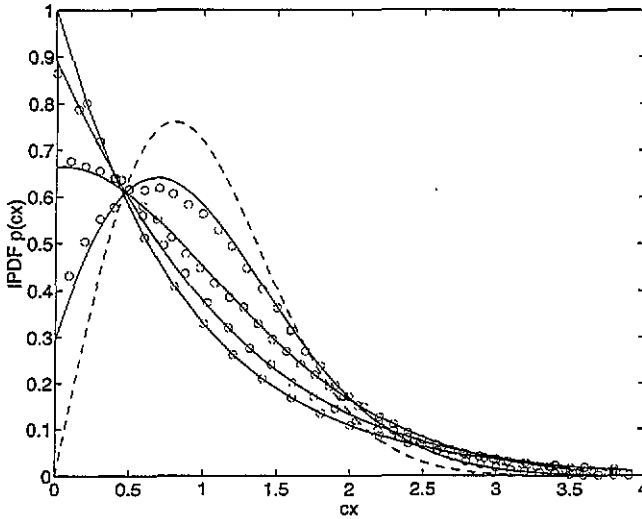


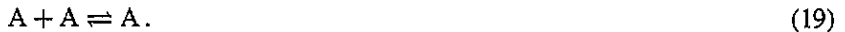
Figure 2. The scaled IPDF, $p(cx)$, for the coalescence process for $k = 0.02$, as obtained from computer simulations (circles) and from numerical integration of (6) (full curve). Results are shown for $t = 0, 100, 1000$ and 10000 ($p(0)$ decreases with time). The crossover times for this particular process are roughly at $t_1 = 15$ and $t_2 = 4000$. Also shown is the IPDF in the long-time asymptotic limit (broken curve).

4. Coalescence with non-trivial steady states

Until now, we have treated the case where in the long-time asymptotic limit the concentration drops to zero. We now want to discuss situations with a non-trivial steady state. It is important to examine such situations because they impose a stricter test on the validity of our approximation.

Back reactions

We consider first the case where the reaction (1) is reversible [5]:



In the reverse process, $A \rightarrow A + A$, a particle gives birth to another at an adjacent site, at rate $v/\Delta x$ (this means rate $v/2\Delta x$ on either side of the original particle). The corresponding evolution equation is

$$\begin{aligned} \partial_t E_n = & \frac{2D}{(\Delta x)^2} (E_{n-1} - 2E_n - E_{n+1}) - \frac{2D}{(\Delta x)^2} (1-k) \frac{1-2E_1+E_2}{1-E_1} (E_{n-1} - E_n) \\ & - \frac{v}{\Delta x} (E_n - E_{n+1}) \end{aligned} \quad (20)$$

where the last term describes the annihilation of an n -sites empty interval due to a birth event from a particle at its outer edge.

In the steady state, the LHS is equal to zero and (20) becomes a recursion relation for E_n . The solution can be found by assuming a steady state of maximum entropy: since the process is reversible, the steady state is an *equilibrium* state and hence the IPDF is a Poisson distribution, $E_n = E_1^n$. Taking into account the boundary conditions of (8) and (9), we find

$$E_n = \left(\frac{2Dk}{2Dk + v\Delta x} \right)^n \quad (21)$$

and

$$c_s = \frac{1 - E_1}{\Delta x} = \frac{v}{2Dk + v\Delta x}. \quad (22)$$

Notice that although (20) contains an approximation, the corresponding steady-state equation is exact: when the IPDF is completely random the approximation of (5) becomes exact. Thus, the result of (21) and (22) is exact. This is well confirmed by simulations.

Particles input

Consider now the case of a random, steady input of particles. At each time step empty sites become occupied with probability $R\Delta x$. That is, R is the increase in concentration per unit time, due to input [5]. The evolution equation is

$$\begin{aligned} \partial_t E_n = & \frac{2D}{(\Delta x)^2} (E_{n-1} - 2E_n - E_{n+1}) - \frac{2D}{(\Delta x)^2} (1-k) \frac{1-2E_1+E_2}{1-E_1} (E_{n-1} - E_n) \\ & - Rn\Delta x E_n \end{aligned} \quad (23)$$

where the last term represents the annihilation of an n -sites empty interval due to input.

Here the steady-state limit is less simple than for back reactions. Although the input sustains a steady concentration of particles at the long-time asymptotic limit, this stationary state is not a true equilibrium state (the input process is *not* the reverse of coalescence) and the particles are more ordered than in a Poisson distribution. Nevertheless, (23) with $\partial_t E_n = 0$ still yields an approximate recursion relation for the stationary E_n . This can be

solved exactly, but the solution is rather cumbersome. Instead, it is more enlightening to consider the continuum limit of the steady state equation

$$0 = 2D\partial_x^2 E - 2D(1-k)\omega\partial_x E - xRE \quad (24)$$

where $\omega = \partial_x^2 E|_{x=0}/\partial_x E|_{x=0} = -\partial_x^2 E|_{x=0}/c_s$ is now a constant. To determine ω , let us look at the discrete steady-state equation for $n = 1$

$$0 = \frac{2D}{(\Delta x)^2}k(1 - 2E_1 + E_2) - \Delta x RE_1. \quad (25)$$

It simply equates the rates of input events and coalescence events in the steady state. The continuum limit of (25) is too drastic in that it yields zero for each of these rates (and also $\omega = 0$).

A somewhat inelegant, but effective way around this is to retain $\Delta x R$ finite, so that $\omega = -R\Delta x/2Dkc_s \neq 0$. Then, the solution to (25) with the boundary conditions of (11) is

$$E(x) = \exp\left(-\frac{x}{\kappa c_s}\right) \frac{\text{Ai}\left[r^{1/3}x + r^{-2/3}/(\kappa c_s)^2\right]}{\text{Ai}\left[r^{-2/3}/(\kappa c_s)^2\right]} \quad (26)$$

where $\kappa = 4Dk/(1-k)R\Delta x$ and $r = R/2D$. From the relation $c_s = -\partial_x E|_{x=0}$, we then obtain a transcendental equation for the steady-state concentration, c_s :

$$c_s = \frac{1}{\kappa c_s} - r^{1/3} \frac{\text{Ai}'\left[r^{-2/3}/(\kappa c_s)^2\right]}{\text{Ai}\left[r^{-2/3}/(\kappa c_s)^2\right]}. \quad (27)$$

In figure 3, we plot c_s as a function of the reaction probability k , for fixed r ($r^{1/3} = 0.04$), as obtained from computer simulations and from numerical integration of the discrete steady-state equation. The agreement between simulations and theory is quite good. Also, for the range shown, the agreement between (27) and the numerical integration is better than 4%.

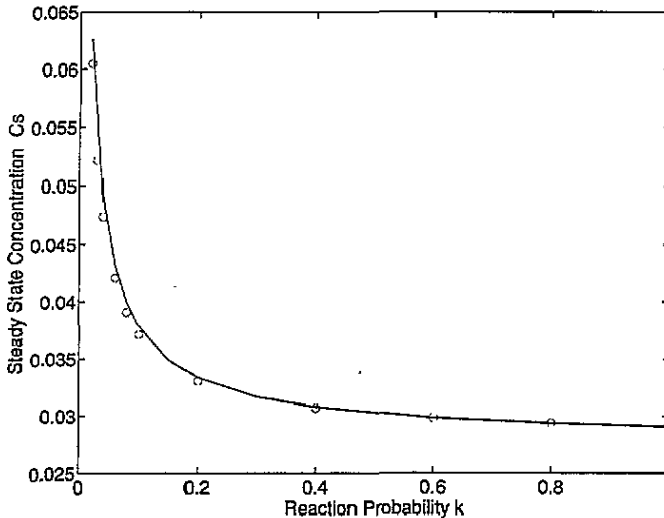


Figure 3. The stationary concentration, c_s , as a function of the reaction probability, k for coalescence with input of particles, with $r = (0.04)^3$. Numerical integration of (23) (circles) is compared with computer simulation results (full curve).

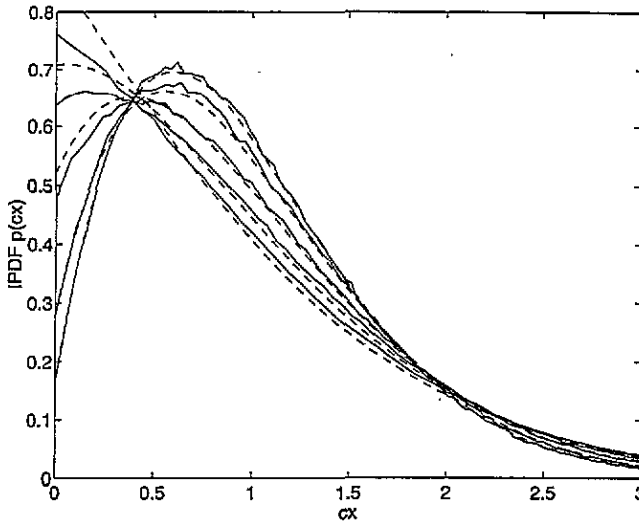


Figure 4. The scaled IPDF, $p(cx)$ for the same process as in figure 3 for $k = 0.02, 0.04, 0.08, 0.20$ and 0.40 ($p(0)$ is smaller for larger k), as computed from the second derivative of (26) (broken curve) and compared with computer simulations (full curve).

For small concentrations, (27) itself may be simplified. If $c \ll r^{1/3}/\kappa$, then $\text{Ai}'[r^{-2/3}/(\kappa c_s)^2]/\text{Ai}[r^{-2/3}/(\kappa c_s)^2] \approx \text{Ai}'(0)/\text{Ai}(0) = 0.72901\dots$ and the equation reduces to a simple quadratic, with the solution

$$c_s = \frac{1}{2} \left(\bar{c}_s + \sqrt{\bar{c}_s^2 + \frac{2(1-k)\Delta x}{k} r} \right) \quad \bar{c}_s = -\frac{\text{Ai}'(0)}{\text{Ai}(0)} r^{1/3}. \quad (28)$$

Here \bar{c}_s is the steady-state concentration when $k = 1$, and is exact [5]. In the range shown in figure 3, equation (28) agrees with the c_s obtained from numerical integration of (23) to within 10%. We emphasize, again, that the mathematical approximations made here are not essential to our method, but are merely done to obtain simple final expressions, to better understand the consequences of the physical approximation made in writing (23).

Finally, the IPDF itself is obtained from $p(x) = (1/c_s)\partial^2 E/\partial x^2$, and using (26) with the c_s found from numerical integration (or any of the approximation formulae). In figure 4, we compare the IPDFs obtained in this way and from computer simulations for $r^{1/3} = 0.04$ fixed, and various values of k . The tail of $p(x)$ falls off as $\exp(-x^{3/2})$ and for moderately large k $p(x)$ shows a maximum. Thus, the system is more ordered than in the case of back reactions, but less ordered than in the case of pure coalescence, where the tail of the IPDF decays as $\exp(-x^2)$. The agreement between theory and simulations is best for large k . From figures 3 and 4 one can see that the IPDF is a much more sensitive test for approximations than the concentration alone.

An interesting result is that $p(x = 0)$ is zero only when $k = 1$. This is in contrast with the case of pure coalescence, where in the long-time asymptotic limit $p(0) = 0$, regardless of the value of k . Recall that in the latter case k effectively renormalizes to 1 when the concentration decreases. This cannot happen in the case of back reactions, when c approaches a stationary *finite* value. Then, if the reaction rate is small enough it can overcome the strong effective repulsion between nearest particles.

5. Summary and discussion

We have introduced an approximation, based on the IPDF method, which allows us to draw analytically simple descriptions of the coalescence process $A + A \rightarrow A$ in one dimension, with finite reaction rates. The intermediate time regime is convincingly shown to be a crossover behaviour between the classical, reaction-controlled limit, in which the concentration decays as $c \sim 1/t$, and the diffusion-controlled limit, where $c \sim 1/\sqrt{t}$. This result, summarized in (14), is similar to that of Hoyuelos and Martín [12]. It requires no fitting parameters and no approximations other than the standard approximation of (5).

The approximation yields exact results for the equilibrium state, reached in the presence of the reverse reaction $A \rightarrow A + A$. This is because in the equilibrium state the fundamental approximation of (5) becomes exact. Surprisingly, we obtain rather accurate results for the stationary state of the process with input, in spite of the strong spatial correlations that do evolve.

The present approach is similar to that of Privman *et al* [13]. Their equation for the IPDF

$$\partial_t p(x, t) = 2D \partial_x^2 p(x, t) + 2D(1 - k)p(0, t) \partial p(x, t) \quad (29)$$

is closely related to our (10), through $p(x, t) = \partial_x^2 E(x, t)/c(t)$. The difference is that $\text{Prob}(\circ \circ \dots \circ \bullet \bullet) \approx \text{Prob}(\circ \circ \dots \circ \bullet) \text{Prob}(\bullet)$ is used, instead of our (5). Although (5) is a bit more sensitive to short-range correlations, we believe that this difference is trivial. The advantage of our approach is more likely in that in writing an evolution equation for $E(x, t)$, we are able to use the exact boundary condition $E(0, t) = 1$. In contrast, there is no such constraint on $p(x = 0, t)$ of (29).

Regarding reverse reactions and input of particles, here we have discussed only the stationary limits and have not addressed the time-dependent relaxation to the steady state. A straightforward separation of variables and decomposition into eigenvalue equations is not possible, because of the nonlinear nature of the correction term arising from the finite reaction rate. In the case of back reactions and infinite reaction rate, there is a dynamical phase transition in the characteristic relaxation time [5]. It will be interesting to see how this transition is affected by finite reaction rates. Is there a range of reaction rates for which the transition disappears? The approximation method used here has been employed successfully, with slight modifications, for the study of the diffusion-limited processes $3A \rightarrow 2A$ and $3A \rightarrow A$ [16], and for the contact process in one dimension [17]. It may be worthwhile to further explore its potential. For example, (5) can be systematically improved, by writing a hierarchy of evolution equations for the state probabilities of finite size intervals and introducing a truncation scheme at a later stage. These intriguing questions are left for future work.

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