

The Pair Approach Applied to Kinetics in Restricted Geometries: Strengths and Weaknesses of the Method

Z. Konkoli,^{*,†} A. Karlsson,[‡] and O. Orwar[§]

Department of Applied Physics, Chalmers University of Technology and Göteborg University, SE-412 96 Göteborg, Sweden, Department of Chemistry, Göteborg University, SE-412 96 Göteborg, Sweden, Department of Physical Chemistry and Microtechnology Centre at Chalmers, Chalmers University of Technology, SE-412 96 Göteborg, Sweden

Received: March 15, 2003; In Final Form: August 14, 2003

In the rapidly emerging field of nanotechnology, as well as in biology, where chemical reaction phenomena take place in systems with characteristic length scales ranging from micrometer to the nanometer range, understanding of chemical kinetics in restricted geometries is of increasing interest. In particular, there is a need to develop more accurate theoretical methods. We used a many-particle-density-function formalism (originally developed to study infinite systems) in its simplest form (pair approach) to study a two-species $A + B \rightarrow 0$ reaction–diffusion model in a finite volume. For simplicity reasons, it is assumed that the geometry of the system is one-dimensional (1d) and closed into a ring to avoid boundary effects. The two types of initial conditions are studied with (i) equal initial number of A and B particles, $N_{0,A} = N_{0,B}$, and (ii) initial number of particles equal on average, $\langle N_{0,A} \rangle = \langle N_{0,B} \rangle$. In both cases, it was assumed that the particles are well mixed in the initial state. It is found that the particle concentration decays exponentially for both types of initial conditions. In the case of the type ii initial condition, the results of the pair-like analytical model agrees qualitatively with computer experiments (Monte Carlo simulation), while less agreement was obtained for the type i initial condition, and the reasons for such behavior are discussed.

I. Introduction

Classically, biochemical reaction kinetics is extrapolated from measurements in dilute solutions and fitted into the cellular reaction environment. However, several flaws in this approach have been pointed out.¹ The main motivation of our work is to improve the understanding of diffusion-controlled reactions in topologically complex nanoscale environments represented in biological cells. In this study, an attempt is made to develop theoretical methods that could describe diffusion-controlled reactions with boundaries. To achieve this goal, the many-particle-density-function (MPDF) approach^{2–5} is modified to account for presence of boundaries.

The theoretical findings of this study are relevant for experimental work done in refs 6–8. Even if we focus on biochemical reaction kinetics, the results should have an equal bearing on nanotechnological applications such as nanofluidics⁹ or molecular electronics.¹⁰ Both are likely to be strongly dependent on reaction–diffusion behaviors of molecules (nanofluidics) or electrons and holes (molecular electronics) in restricted nanoscale geometries.

Most of the studies on diffusion-controlled reactions have been performed for infinite systems without boundaries, and a variety of theoretical methods have been developed to assist in the study of such systems. The methods range from mean field treatments toward more exact approaches, which employ quantum spin-chains,¹¹ field theory,^{12,13} or MPDF formalism.^{2–5}

References 3 and 14 are excellent reviews on the subject. The opposite case when reactions take place in restricted geometries with reactants confined into finite size and eventually squeezed into very small volumes is less understood. There is, however, some pioneering work in this area.^{15–18} Here, we focus on testing the performance of a MPDF approach on diffusion-controlled reactions in finite volumes.

Infinite diffusion-controlled systems possess quite remarkable properties. When the dimensionality of the system, d , is lower than some critical dimension, d_c , a new nontrivial sort of kinetics sets in. For example, for $A + A$ reaction, $d_c = 2$, and for $A + B$, $d_c = 4$. One possible way of calculating critical dimension d_c for $A + A$ and $A + B$ reactions is described in refs 19 and 20, respectively.

The role played by critical dimension is best understood on an example, and in the following, the $A + B \rightarrow 0$ reaction will be discussed. The classical chemical kinetic rate equation for this reaction, with initial densities equal and homogeneous, is given by $\dot{n}(t) = -\lambda n(t)^2$, where the dot-over symbol denotes time derivative. For long times t , this equation would predict density decay in the form of a power law, $n(t) \approx \mathcal{A}t^{-\alpha}$. The amplitude of decay $\mathcal{A} = 1/\lambda$, and the decay exponent is given by $\alpha = 1$. In reality, $\alpha = 1$ holds only for a sufficiently high dimensionality of the system when $d > 4$, while for $d < 4$, one has $\alpha = d/4$ and $\mathcal{A} = \text{const} \sqrt{n_0} D^{-d/4}$, where const is just a numerical factor. Please note that for $d < 4$ the decay amplitude \mathcal{A} does not depend on the reaction rate λ and exhibits lack of dependence on chemical details (universality).

The kinetics of the type described above is commonly referred to as *anomalous* or *fluctuation-dominated*. The term “anomalous” points to the fact that the mean field (or classical rate) equations fail to describe such systems. The phrase “fluctuation-

* Corresponding author. E-mail: zorank@fy.chalmers.se.

[†] Department of Applied Physics, Chalmers University of Technology and Göteborg University.

[‡] Department of Chemistry, Göteborg University.

[§] Department of Physical Chemistry and Microtechnology Centre at Chalmers, Chalmers University of Technology.

dominated” emphasizes the importance of fluctuations in particle densities. Once the reaction creates a hole in the particle concentration, diffusion is very slow in restoring the homogeneous particle density. This has to do with recurrence of random walks. For $d \leq 2$, the probability that the random walker will return to the same site after an arbitrary number of steps is equal to one. Random walkers tend to wander around their initial position, and particles do not mix that well. The rule of thumb is that for lower dimensions the kinetics gets more anomalous. The role of dimensionality is well understood for both integer and fractal (noninteger) dimensions.²¹ On the other hand, much less is known about the consequences of shrinking the system size, which is studied here.

To progress the understanding of reactions taking place in a restricted geometry, we analyze the performance of a MPDF approach and modify it to account for a finite reaction volume. To test such method of calculation, the $A + B$ model is used as a study case. The $A + B$ model is a natural choice for such a task. This model has been intensively studied for infinite system sizes.^{4,20,22–29} It was found that the $A + B$ reaction has the remarkable property that domains rich in A or B particles are formed as time goes on. Once domains are formed, the reactions happen only at domain boundaries, which leads to the already mentioned decay exponent $\alpha = d/4$. It is interesting to study in what way the dynamics of the system (kinetics) changes as one reduces the volume available for the reaction, in particular whether domain-like structure survives. For simplicity reasons, the one-dimensional (1d) case is studied. In the calculation that follows, there is nothing special about the 1d model, and the present analysis can easily be extended to the two- or three-dimensional cases.

The $A + B$ model in a restricted geometry has been studied before with the assumption that one type of reactant is attached at the center of a small volume, and it was further assumed that one type of particle is in large excess.^{15–17} The more realistic problem in which all particles are allowed to move is much harder to solve, and the goal of our study is to describe such a situation. Also, here, the focus is on the case when the initial number of reactants is the same or roughly the same. Naturally, the shape of the reaction container might be important, but this issue is not addressed at the moment. To avoid boundaries completely, our 1d system will be closed into a ring.

The paper is organized as follows. In section 2, the model is developed, that is, detailed account is given of how particles move and react. The lattice model is used because of its conceptual simplicity. In section 3, equations of motion are derived using MPDF formalism in its simplest form (pair approach). In section 4, equations of motion are solved analytically and it is shown how multiexponential decay emerges. The results of computer experiments (Monte Carlo simulations) are given in section 5, followed by a comparison between theory and Monte Carlo simulations in section 6. We conclude by analysis of strengths and weaknesses of the pair approach applied to reactions in a restricted geometry in section 7. In Appendix A, explicit form of the master equation is given. Appendix B explains calculation of the effective reaction rate, $k(t)$, which determines density decay. In Appendix C, the algorithm used in the Monte Carlo simulations is discussed.

II. The Lattice Model

To test any theory, one inevitably needs a model, which serves as a study case. The model used here is defined as follows. Two species, A and B , move on a 1d lattice performing random jumps with rates (diffusion constants) D_A and D_B , respectively.

It is assumed that $D_A = D_B$. Position of lattice sites is given by $x_i = ih$ with $i = 0, 1, 2, 3, \dots, M$ and h denotes lattice spacing. Sometimes, x and y will be used instead of x_i . Periodic boundary conditions are assumed and sites $i = 0$ and $i = M$ are defined to be equivalent. There are M lattice sites in total and $L = Mh$. By using periodic boundary conditions, it is possible to work with a system of finite size and keep the spatial translational invariance. This greatly facilitates the analytical treatment of the problem.

It is assumed that the reaction probability (per unit time) for particle A at x and B at y is given by $\sigma(x - y)$. For $\sigma(x - y)$ the simplest possible form is used

$$\sigma(x - y) = \sigma_0 \theta(a - |x - y|) \quad (1)$$

where $\theta(x) = 0$ for $x < 0$ and $\theta(x) = 1$ for $x \geq 0$. In this way, two important aspects of chemical reactions are embedded; a corresponds to the effective range of reaction, and σ_0 is its strength. One could also say that each particle carries a ring of radius $a/2$ and when two rings overlap the particles can react. In this sense, $a/2$ could be thought of as the size (radius) of particles. For simplicity reasons, it is assumed that the reaction products influence neither reactants nor the $A + B$ reaction. Also, exclusion or steric effects are not taken into account, that is, particles are allowed to “enter” into each other (please see Figure 1) and react with the same probability independent of the direction from which they approach each other.

The model has the useful property that if a is thought of as the size of reactants, then by varying a several interesting situations can be studied. For example, when a is on the order of the system size L , one can think of situations of extreme crowding. On the other hand, when $a \ll L$, reactants appear as pointlike objects. In Figure 1, we offer a schematic way to think about these situations. The model presented above is solved analytically and numerically by a Monte Carlo simulation as described in the following sections.

III. Equations of Motion in Pair Approximation

To solve the $A + B$ reaction–diffusion model in a restricted geometry, we use a many-particle-density-function formalism (MPDF) because it has already been used to describe asymptotics of the same reaction in an infinite volume.^{2–5} We modify the formalism and apply it to the case of a restricted geometry. In the following, the formulation presented in ref 2 will be closely followed. On the way, the changes made to the original formalism will be discussed.

The dynamics of the system, as defined in the previous section, is stochastic and governed by the master equation, which describes time evolution of configurational probabilities of the system $P(c, t)$,

$$\dot{P}(c, t) = \sum_{c'} [W_{c' \rightarrow c} P(c', t) - W_{c \rightarrow c'} P(c, t)] \quad (2)$$

where c is short notation for occupancy of lattice sites and $W_{c \rightarrow c'}$ are transition probabilities, which can easily be deduced from the previous description of the model. (Explicit form of the eq 2 can be found in Appendix A). Here and throughout the paper, the dot-over symbol denotes time derivative.

The quantities of interest are particle densities, $\rho_A(x, t)$ and $\rho_B(x, t)$, and they can be calculated from $P(c, t)$ (at least in principle). Because the system is closed into a ring, translational invariance holds and concentrations cease to be position-dependent, which leads to $\rho_A(x, t) = n_A(t)$ and $\rho_B(x, t) = n_B(t)$. Following the recipe in ref 2 gives the following equations for

n_A and n_B :

$$\dot{n}_A(t) = -n_A(t)n_B(t) \int_{-L/2}^{L/2} dx \sigma(x)Y(x,t) \quad (3)$$

$$\dot{n}_B(t) = -n_A(t)n_B(t) \int_{-L/2}^{L/2} dx \sigma(x)Y(x,t) \quad (4)$$

In the process of deriving equations for densities, one has to employ a continuum limit, $h \rightarrow 0$, $M \rightarrow \infty$ with $L = Mh$ fixed (please see the original work in refs 2–5 for details). The $Y(x,t)$ denotes a correlation function for AB pairs. Absence of correlations is signaled by $Y(x,t) = 1$. Please note that in this work system size is finite, which enters through finite integration domain in the integrals above (it might appear as a minor technical detail, but this fact is very important). Also, it is assumed that reversal symmetry holds, that is, $Y(x,t) = Y(-x,t)$.

Again, following ref 2, one can derive an equation for $Y(x,t)$, which is given by

$$\begin{aligned} \dot{Y}(x,t) = & (D_A + D_B)Y''(x,t) - \sigma(x)Y(x,t) - \\ & n_B Y(x,t) \int_{-L/2}^{L/2} dy \sigma(y)Y(y,t)[X_B(x-y,t) - 1] - \\ & n_A Y(x,t) \int_{-L/2}^{L/2} dy \sigma(y)Y(y,t)[X_A(x-y,t) - 1] \end{aligned} \quad (5)$$

where prime denotes spatial derivative and $X_A(x,t)$ and $X_B(x,t)$ are correlation functions for AA and BB pairs, respectively. $X_A(x,t)$ and $X_B(x,t)$ obey similar equations, which are not given here to save the space.

Equations 3–5 are derived under the assumption of a Kirkwood superposition approximation, which is a technical way of saying that dynamics is governed by pair effects. For example, eq 5 shows that dynamics of correlation function for AB pairs is influenced by AA and BB correlations. The correlations of triples AAA, AAB, ABB, and BBB do not appear, though they should. Naturally, the assumption of the dominance of pairs effects is an approximation. It might or might not work, and the goal of the present study is to test this.

To make an analytic treatment possible, eq 5 will be simplified further by setting $X_A(x,t)$ and $X_B(x,t)$ equal to one. This amounts to ignoring correlations among AA and BB pairs and reduces dynamics to the one of a single AB pair. In such case, the dynamics of A–B distance x is governed by effective diffusion constant $D_A + D_B$, which is an indication of the fact that only relative motion of the particles in the pair is important.

In ref 2, it was shown that for infinite reaction volume the single-pair approximation considered here is too severe, leading to an incorrect decay exponent, $\alpha = d/2$. To obtain the proper density decay exponent, $\alpha = d/4$, correlations of AA and BB pairs have to be included in the description. Nevertheless, here we consider single-pair simplification. The validity of such an approximation, together with the fact that we are using a Kirkwood approximation, is tested via computer experiments later on.

The form of the boundary conditions for $Y(x,t)$ differs from the one used in ref 2. In the case of an infinite system, one takes

$$Y(x,t) \rightarrow 1, \quad x \rightarrow \infty \quad (6)$$

while for a finite system with periodic boundary conditions, another form has to be used

$$Y(x+L,t) = Y(x,t) \quad (7)$$

It will be shown later that the change from eq 6 to eq 7 leads

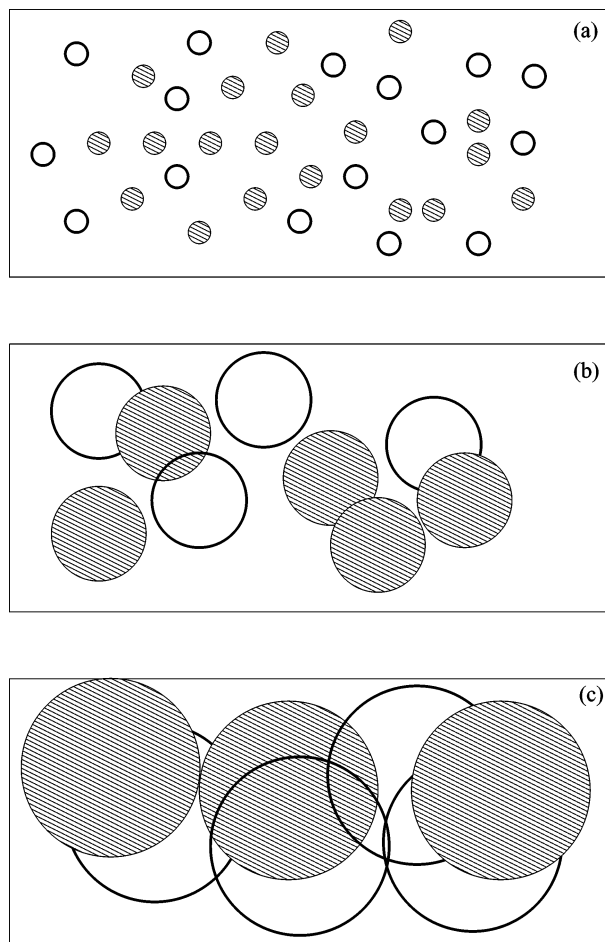


Figure 1. Various situations that are simulated. The three figures schematically depict various types of initial conditions from which simulation is started. Panel a shows a situation in which particles react when nearest-neighbors only. The reaction range is very short and particles come rarely in contact. Panel c shows a situation of dense packing with a large reaction range. It corresponds to situation of high packing, which occurs in a cell environment. It is unrealistic that particles can penetrate into each other, but we consider this case nevertheless because it is simpler to model. Panel b is midway between two extremes.

to a qualitative change from power law to (multi)exponential behavior for correlation dynamics. The rest of the boundary conditions are standard and are taken as in the case of an infinite system size,

$$n_A(0) = n_0 \quad (8)$$

$$n_B(0) = n_0 \quad (9)$$

$$Y(x,0) = 1 \quad (10)$$

Also, taking $L \rightarrow \infty$ should reproduce the findings of ref 2 within the set of approximations employed here.

IV. Emergence of Multiexponential Density Decay

With the assumptions $X_A = X_B = 1$, eq 5 reduces to

$$\dot{Y}(x,t) = (D_A + D_B)Y''(x,t) - \sigma(x)Y(x,t) \quad (11)$$

Equation 11 is solved by using a Laplace transform as shown in Appendix B. To simplify the algebra, it is assumed that σ_0 is arbitrarily large. The exponential behavior emerges because the spectrum of eq 11 is discrete because of the particular nature

of the boundary conditions. The final expression for $k(t)$ reads

$$k(t) = k_{\text{reg}}(t) + 2a\delta(t) \quad (12)$$

and the details of calculation are given in Appendix B. The regular part of $k(t)$ is given by

$$k_{\text{reg}}(t) = \frac{8D}{L - 2a_{m=1}} \sum_{m=1}^{\infty} e^{-\kappa_m D t} \quad (13)$$

and κ_m are constants of multiexponential decay (eigenvalues),

$$\kappa_m = \pi^2 \left(\frac{2m-1}{L-2a} \right)^2 \quad (14)$$

The δ -function term in eq 12 arises from the second term on the right-hand side of eq 27 when $\sigma_0 \rightarrow \infty$ (please see Appendix B).

Once $k(t)$ is available, one can calculate $n(t)$ as

$$n(t) = \frac{n_0}{1 + I(t)n_0 + 2an_0} \quad (15)$$

where

$$I(t) = \int_0^t dt' k_{\text{reg}}(t')$$

and

$$I(t) = \frac{8}{L - 2a_{m=1}\kappa_m} \sum_{m=1}^{\infty} \frac{1}{\kappa_m} (1 - e^{-\kappa_m D t}) \quad (16)$$

The $2an_0$ term in the denominator of eq 15 comes from the $\delta(t)$ term in eq 12. It describes the immediate annihilation of particles that are within reaction range. When $\sigma_0 \rightarrow \infty$, this happens instantaneously. Thus there is a sudden jump in particle concentration. For finite σ_0 , this jump becomes a smooth transition (exponential decay with decay exponent proportional to a large number σ_0). Also, another artifact of taking $\sigma_0 \rightarrow \infty$ is appearance of singularity $a = L/2$ in eq 16. When $a = L/2$, reaction range spreads throughout the whole system. Particles cannot hide away, and reactions proceed extremely rapidly.

For the infinite system size, the particle density decays through power law. For finite system size, decay is exponential. Can these two regimes be related by continuously increasing system size L ? This question is interesting from a theoretical point of view. The series in eq 15 can be rewritten by using a Poisson resummation formula. For $L \rightarrow \infty$, one can employ the fact that $Dt/(L/2 - a)^2$ is a very small quantity. This results in a series with a leading term given by $I(t) \approx t^{1/2}$, which is the power law sought for. However, this finding bears a more important message than just showing that it is possible to obtain power law decay from multiexponential decay.

The decay exponent obtained through a Poisson resummation procedure, $\alpha = 1/2$, is the same as the one that would result from a Smoluchowskii treatment (with correlations of AA and BB pairs ignored). We just reconfirm the well-known fact that for infinite systems the pair approach predicts too fast decay of particles (the true decay exponent is somewhat slower with $\alpha = 1/4$). It is interesting to note that for a finite system size one can have the reverse situation. For certain types of initial conditions, the decay obtained from the pair approach can be slower than the true decay. In that sense, the transition from

finite to infinite system size is not trivial at all. This point will be discussed in the following paragraphs.

Here, we consider two types of initial conditions. (i) When initially there is an equal number of A and B particles, one has $n \rightarrow 0$ as $t \rightarrow \infty$, and at the end, all particles have to annihilate. (ii) One can look at an ensemble of similar systems with equal number of A and B particles at $t = 0$ on average, $\langle N_{0,A} \rangle = \langle N_{0,B} \rangle$. In such a case, one has different asymptotics, $\langle N(t) \rangle \rightarrow N(\infty)$ as $t \rightarrow \infty$.

The theoretical prediction is that, as time goes to infinity, the particle density exponentially approaches the value $n_{\text{th}}(\infty)$,

$$n_{\text{th}}(\infty) = \frac{n_0}{1 + n_0 L} \quad (17)$$

The value for $n_{\text{th}}(\infty)$ above can be obtained by sending $t \rightarrow \infty$ in eqs 15 and 16. From eq 17, one sees that asymptotically the number of particles is given by

$$N_{\text{th}}(\infty) = N_0/(1 + N_0) \quad (18)$$

where $N_{\text{th}}(\infty) = L n_{\text{th}}(\infty)$. Please note that $N_{\text{th}}(\infty)$ never approaches zero and settles at a number between zero and one. In the case of type i initial conditions, all particles annihilate and $N(\infty) = 0$. This is clearly in contradiction with eq 17. However, the situation is not that hopeless, as will be discussed later. For the type ii initial condition, for each member in the ensemble there is a chance that more than one particle will be left because one starts the dynamics with (random) excess of A or B particles at $t = 0$. Thus, in average, $\langle N(\infty) \rangle$ will be larger than 0. Clearly, the pair approach has a better chance to describe this situation correctly.

In summary, we find an exponential decay in the long time limit, which is a pure artifact of the finites of the system. There is a clear indication that the quality of prediction depends on the type of initial conditions used in experiment. Also, the approximations made in deriving eq 15 are rather severe, and to check the applicability of such a pair approach, Monte Carlo simulation is used.

V. Results of Monte Carlo Simulations of A + B Reaction in Restricted Geometry

Figures 2–4 summarize the results of the Monte Carlo simulations in $d = 1$. The Monte Carlo algorithm is described in detail in Appendix C. Figure 2 shows a simulation for a system with a large initial number of particles with a varying reaction range from a nearest-neighbor interaction with $a/L = 0.0001$ toward a longer range with $a/L = 0.02$. Figure 3 shows the case when there are initially very few (exactly 10 = 5A + 5B) particles present in the reaction volume, also with varying reaction ranges from $a/L = 0.001$ to $a/L = 0.2$. Thus Figures 2 and 3 give simulation results for type i initial condition. Figure 4 deals with type ii initial condition, when the initial number of particles in an ensemble varies with the constraint that the sum of A and B particles equals 10. (For example, one run could be done with 7A and 3B, another run with 5A and 5B, and a third run with 4A and 6B particles, etc.) Figure 1 is a sketch of how to think of various situations when a changes from small to large values.

From Figure 2, it can be seen that in the case of the nearest neighbor reaction range ($a = 1$) four distinct regimes appear and the log–log plot is used to reveal them: (a) mean field decay, (b) a plateau region, (c) power law decay, and (d) exponential decay at the end. These regimes disappear as the

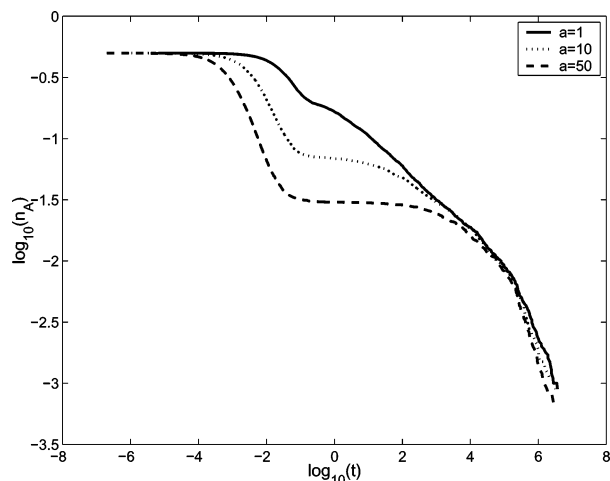


Figure 2. Result of Monte Carlo simulations in 1d for type i initial condition. A very large system is simulated on a lattice with $L = 10^4$ sites. Also, the initial number of particles $N_{0,A} = N_{0,B} = 5000$ is very large. Simulation starts from the largest possible density, $n_{\text{tot}}(0) = 1$ particle/site. A and B particles have the same diffusion constant $D_A = D_B = 1 \text{ s}^{-1}$. Asymptotically, the number of particles approaches zero. There are three distinct regimes present: (a) that of the mean field decay ($-\infty < \log(t) < -2$); (b) plateau where particle concentration does not change much ($-2 < \log(t) < 2$); (c) power law decay ($2 < \log(t) < 5$); (d) exponential decay at the end, $5 < \log(t) < \infty$. The indicated ranges are given roughly just to guide the eye. They also depend on which a is used in simulation.

reaction range is increased, and eventually, for very large a , one only has the exponential regime.

The mean field regime corresponds to annihilation of particles with all reactants being well mixed. This leads to depletion of lattice to concentration of the order $n \approx 1/a$, thus one particle per reaction range. Then diffusion starts to operate and mixes particles. What is interesting is that for very large values of a , the plateau region starts earlier and lasts longer. Apparently, it takes some time before the particles find each other by diffusion and start reacting again.

The power law decay starts after the plateau region. There is universality in the power law regime because all curves with different values of a merge into one. This is somewhat surprising because a larger a should mean faster annihilation, which indeed happens in the mean field regime, yet in the power law stage, all curves share the same power law behavior. We speculate that this has to do with self-organization and build up of correlation.

The exponential regime is entered after the power law regime, when the number of particles in the system becomes small. With the present computer hardware, it was not possible to resolve this exponential regime better. This is indeed done in Figure 3 with a smaller lattice size and lower particle number.

To illuminate this exponential decay at later stages of annihilation, we performed simulations with a smaller number of particles ($10 = 5A + 5B$) on a smaller lattice with 10^3 sites. Thus, we used type i initial condition. To obtain each curve, we followed 1000–3000 realizations of dynamics and averaged over such an ensemble. The result is shown in Figure 3. The upper figure is in $\log t$ scale to resolve the small and large t regions. The lower figure is in normal t scale, and we use it to detect exponential decay (where a straight line indicates exponential decay).

The crossover from mean field to plateaulike dynamics can be seen in the upper graph where all curves drop down to a plateau value, which is a -dependent. The theoretical prediction for this plateau is $n(0^+) = n_0/(1 + 2an_0)$. The initial drop in

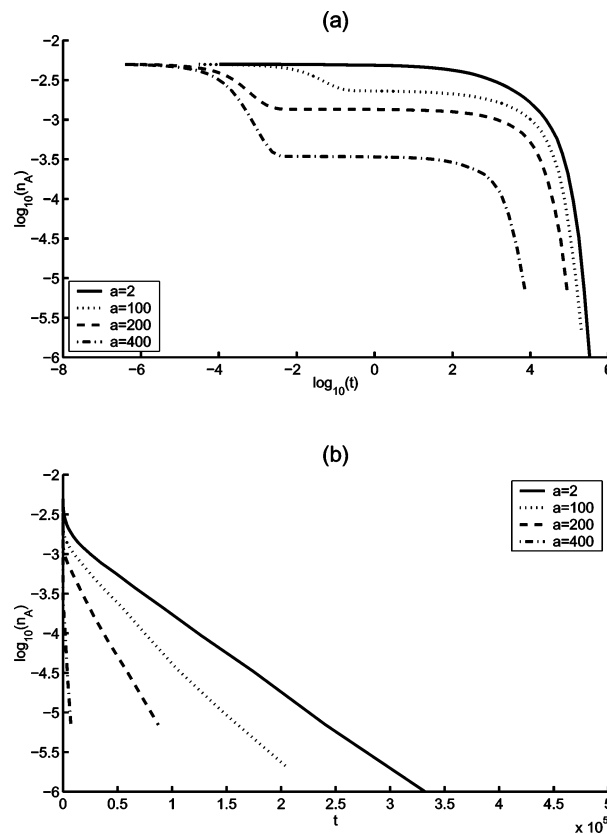


Figure 3. Study of the exponential regime where small number of particles is present on the lattice for type i initial condition with $N_{0,A} = N_{0,B} = 5$. The number of lattice sites is $L = 1000$. All other parameters are same as those in Figure 1. Each curve is obtained as average over 1000–3000 runs. Asymptotically, the number of particles approaches zero. Panel a shows $\log n$ versus $\log t$ plot to trace down power law decay (should appear as a straight line). There is no power law decay. Also, small and large t region are resolved better. Panel b shows $\log n$ versus t plot to indicate exponential decay (corresponds to straight lines). The particle density vanishes exponentially $n \approx -\kappa t$, where κ depends on a because the slopes for all curves are different. There is a value $a = L/2$ when κ becomes infinite (particles cannot escape each other).

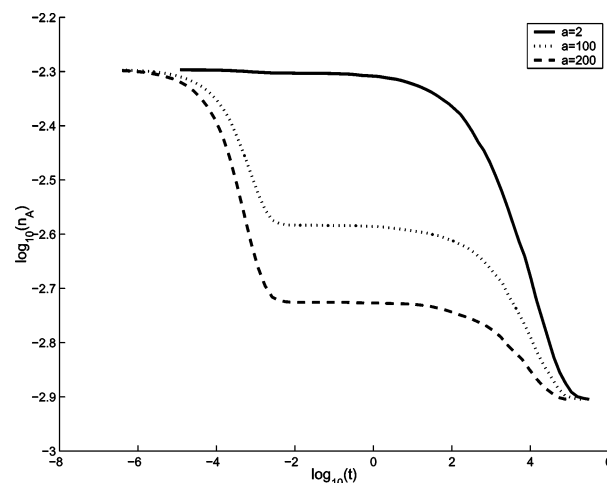


Figure 4. Simulation for type ii initial condition. All parameters are the same as those in Figure 2. The only difference from Figure 2 is in the initial condition. $N_{0,A}$ and $N_{0,B}$ vary randomly with the constraint that $N_{0,A} + N_{0,B}$ is fixed and equals 10. Asymptotically, the number of particles does not approach zero.

concentration is large for large a values. In the upper figure, it is hard to say when the plateau behavior turns into exponential decay.

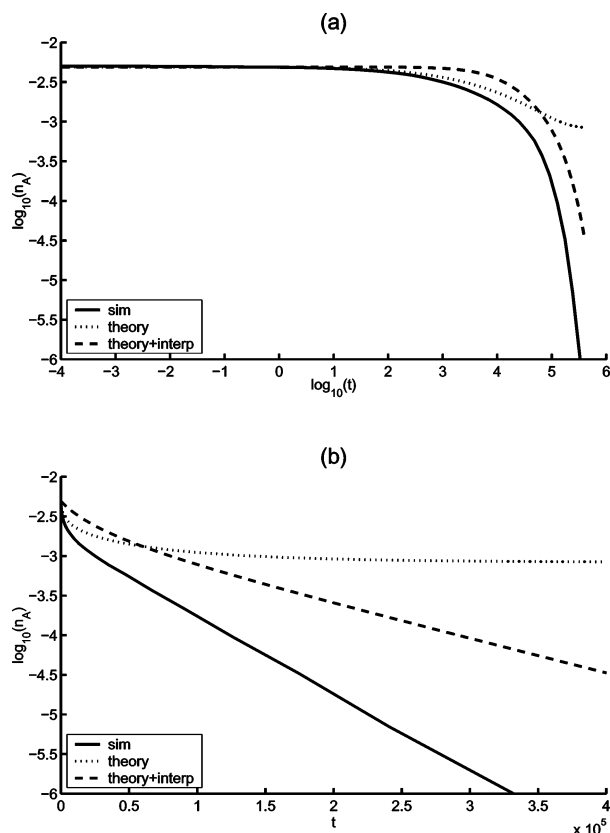


Figure 5. Comparison of theory and experiment (Monte Carlo simulation) for type i initial condition. Simulation data are taken from Figure 2. In panel a, theory (dotted line, eq 15) predicts $\lim_{t \rightarrow \infty} n(t) \neq 0$, while in reality $n(t \rightarrow \infty) = 0$. Reasons for this discrepancy are given in the text. In panel b, by using interpolation formula (eq 19), one obtains the dashed curve. Agreement with simulation gets better.

The lower graph shows that decay is indeed exponential because density curves at late times are straight lines in the $\log(n)-t$ plot. Thus, at the late times, $n \approx \exp(-\kappa_1 t)$. Also, the decay constant κ_1 is a -dependent because slopes are different for various values of a , and κ_1 becomes larger with larger a . Also, it appears that there is an upper limit for a at which decay becomes infinitely fast. Naturally, this happens when $a = L/2$ because none of the particles can escape from each other. The qualitative dependence of κ_1 on a just discussed is in agreement with the theoretical prediction given by eq 14 with $m = 1$.

Figure 4 is obtained in a similar way as Figure 2. The only difference is that Figure 4 deals with the type ii initial condition. For the particular run, when $N_{0,A} \neq N_{0,B}$, the final number of particles in the system is not zero. For example, when starting from 7A and 3B particles, the system will end up in the state of 4A particles. This comes from that fact that the $A + B$ reaction conserves the particle difference, $N_A(t) - N_B(t) = \text{const}$. Curves for different values of a saturate at one single value, which is independent of a . Clearly, the value of the plateau is solely controlled by the excess of particles at $t = 0$ and can be calculated from theory if needed, but the result of the Monte Carlo simulation is equally informative.

VI. Comparison of Computer Experiment and Theory

Figure 5 shows a comparison of the analytical treatment with computer experiment (simulation parameters as in Figure 3). It can be seen that the pair (Smoluchowskii) approach does not predict that the number of particles in the system should approach zero. The reasons for this are discussed later but have

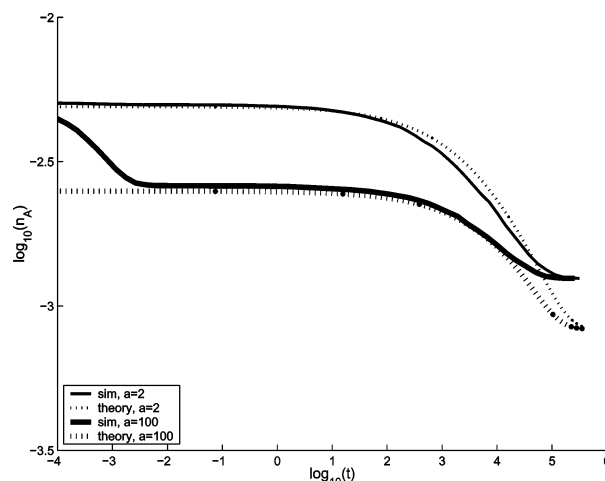


Figure 6. Comparison of theory and experiment (Monte Carlo simulation) for type ii initial condition. Both theory and simulation give $n(\infty) \neq 0$. Theory (dotted line, calculated with eq 15) predicts faster annihilation of particles.

to do with the fact that we are looking at a highly symmetric situation with equal number of A and B particles all the time. To enforce such zero asymptotics by hand, we use interpolation formula

$$n_{\text{int}}(t) = n(t) - n(\infty)(1 - e^{-\kappa_1 t}) \quad (19)$$

where κ_1 is the first dominant large time exponent in the expression for $k(t)$ (see eqs 15 and 16). It can be easily seen that the equation above holds exactly for $t = 0$ and $t = \infty$. If eq 19 is used instead of eq 15, the agreement with simulation improves in the sense that the decay is exponential and the qualitatively theoretical exponent is roughly the same as the one obtained from simulations. More work is in progress to develop improved interpolation formulas.

Figure 6 deals with the same type of comparison but with a simulation setup as in Figure 4 when the initial number of particles is not fixed but just the total number (type ii initial condition). One can see that the agreement between theory and simulation is much better. Clearly, Smoluchowskii theory deals better with the type ii initial condition represented by Figure 4 than with the type i represented by Figure 3. Also, in Figure 6, one can see that theory predicts too fast particle annihilation. This is no surprise because this is what one would expect from such a pair approach, which does not take into account formation of domains. (In that respect there is similarity with infinite systems, but only for the type ii initial condition).

VII. Discussion

The goal of the present work was to impact some understanding of diffusion-controlled reactions in restricted geometries with the aim to describe some aspects of chemical reactions in biological cells. Two issues have been dealt with: (1) The particular way of doing calculation was tested, the MPDF formalism developed by Kuzovkov and Kotomin (see ref 2 for details). To be able to solve equations analytically the hierarchy of many-particle densities was truncated at the level of three-particle density using a shortened Kirkwood superposition approximation. This approximation amounts to assuming that pair effects dominate correlations, and the present calculation can be viewed as variant of the pair approach. (2) A two species reaction-diffusion model $A + B \rightarrow 0$ in a restricted geometry was taken as a study case. Two types of initial conditions were

considered, type i in which the initial number of A and B particles is strictly equal and type ii in which the initial number of particles is equal only approximatively.

Thus the paper is best viewed as a method paper because the main goal is to test the strengths and weaknesses of the pair approach. To test the quality of approximations involved, all results have been compared with the results of computer experiments (Monte Carlo simulation).

From a theoretical point of view, it seems that the pair method, being widely used in calculation of bulk properties, works with mixed success for the restricted reaction diffusion systems, at least the one studied here. The agreement between theoretical calculation and computer experiment is qualitative in the case of type ii initial conditions. In the case of type i initial conditions, there is less agreement; however, the situation is not that hopeless.

In the case of type i initial conditions, the pair approach makes an error of the order of one particle (please see eq 18) because it predicts that, in the average, after very long time, there will be between zero and one particle in the system (though all particles should vanish). When the initial number of particles is relatively large, the pair approach can describe evolution of a system for rather long time, before the regime is reached in which only one particle is left in the reaction volume. However, in the case of small initial number of particles, there is no such time interval, and the mismatch between pair approach and simulation has to be addressed more seriously.

The weakness of the pair approach in dealing with type i initial condition rests on the fact that the truncated set of equations for many-particle densities does not recognize any effects that go beyond pair correlations. For example, in the present case, all information related to the fact that initially there were 5A and 5B particles in the system and that all particles have to vanish eventually is missing. Work is in progress to pass such type of information from higher-order particle-density functions to lower-order ones. For example, we already have a better interpolation scheme than the one given in eq 19 for the case when there are initially three particles in the system, but we are trying to understand how to extend such analysis to higher numbers.

Interestingly enough, it seems that, contrary to the systems with infinite sizes, setting $X_A(x,t) = X_B(x,t) = 1$ is a reasonable approximation for a finite system, but we have to perform more tests. This could have to do with the fact that if the system is too small, there will be no time to develop clusters of A and B particles and setting $X_A(x,t) = 1$ and $X_B(x,t) = 1$ might turn out to be a good approximation after all. Thus, one does not have to turn to more complicated methods of calculation if qualitative results are needed. Nevertheless, it is highly desirable to see what happens as one includes correlations among AA and BB pairs.

To be able to solve equations analytically, we had to simplify the MPDF method considerably, down to the level of a pairlike approach, and various calculation schemes contain the pair approach as a possible approximation. Perhaps the most common form of the pair approach is the one suggested by Smoluchowskii (e.g., see ref 3 for interesting review). The Smoluchowskii approach boils down to solution of a Poisson equation with different boundary conditions.

However, one has to keep in mind that the pair approach is an approximation, and it has to be tested to see whether it works. (For example, the pair approach cannot describe the A + B reaction-diffusion model when the system size is very large. This has been discussed in ref 4.) The advantage of the pair

approach, in the form used here, is that it is possible to go beyond it in a systematic way.

Also, from the particular way in which we have approached the pair problem, one can see that the difficulties associated with eq 18 are likely to be much deeper than just the fact that we are using the pair approach. (This problem clearly vanishes when the system size is infinite because $n_{th}(\infty)$ goes to zero.) Any scheme that focuses on low-rank particle-density functions will suffer in a similar way, in the case of the highly symmetric, for example, type i, initial conditions. One really has to find a way to incorporate information of higher-order correlation functions into lower-order ones without calculating higher-order correlations functions explicitly. This is a pressing issue.

We offer few words about the model used. The goal of the present work is to develop calculation methods rather than to describe specific chemical systems. We used the model that we could solve within a reasonable level of approximation. Nevertheless, the question of whether the present model has any relevance for real biological and chemical systems needs to be addressed.

The reaction-diffusion model studied here appears to be too simple for two reasons. First, it does not account for chemical details, which enter only through two parameters, namely, the diffusion constant D and the reaction rate λ . For example, the exclusion effects and steric effects are not contained in it. Also, the influence of product molecules is completely ignored. Second, the 1d character of the model might be too restrictive.

Despite its simplicity, the model used here contains basic characteristics of diffusion-controlled reactions (reaction times t_R are much smaller than the corresponding diffusion times t_D); particles are moving on the lattice and react when within reaction range with no memory of initial velocity. Previous research reviewed in refs 2 and 3 has shown that diffusion-controlled models, similar to the one used here, can be used to describe real chemical reactions. In particular, the A + B model has been used to study two reactions in capillary tube quite successfully, bromine + cyclohexene \rightarrow adduct and Cu^{2+} + disodium ethyl bis(5-tetrazolylazo)acetate trihydrate \rightarrow 1:1 complex in water.³⁰ Also, please note that these systems are quasi-one-dimensional because the radius of the tube is finite. Nevertheless, to a very good approximation, they can be described as one-dimensional systems.

Why can one be sloppy and ignore chemical details to some extent? The reason for this is universality. Most often, predictions of the reaction-diffusion models (on lattice) are insensitive to the details of the chemistry involved. (For example, the decay amplitude for A + B reaction does not depend on the reaction rate λ .) This statement is valid provided one deals with very large system sizes. Naturally, this view is not the only one. There are other ways to approach diffusion-controlled reactions. For a more chemical or biological approach to diffusion-controlled reactions, see refs 14, 31, and 32.

The simplicity of the model is not necessarily such a big handicap, until one reaches extremely small sizes. For small system sizes, density decay will start depending on details. However, there is a large window in system sizes between extremely large and extremely small where such kind of universality could survive. Here, we push the model over its borders by studying a situation of extreme crowding without accounting for exclusion effects.

Furthermore, we would like to notify the reader that we do refer to the model here as a "toy" model, and it is relatively simple to formulate it. However, this does not mean that the model is easy to solve, quite the contrary. In the case of an

infinite system size, it has taken much research effort to clarify that the decay exponent indeed is $d/4$. This issue was finally settled in ref 27, which provides a strict mathematical proof.

The model has a potential to describe experiments in refs 6–8 where, for example, the average diameter of the reaction container (liposome) is $L \approx 1\text{--}25\ \mu\text{m}$. The reactants A (enzyme) and B (substrate) are of the size of $a_E, a_S \approx 1\ \text{nm}$, and the typical number of reactants inserted is on the order of $N \approx 1000$. Thus, $a \ll L$ holds to a very good approximation. In these experiments, reactants appear as pointlike objects, and there is no need to give structure to reactants. Also, the problems associated with eq 18 will likely not cause any damage due to large number of particles at $t = 0$.

From the data above, the concentration of particles $n_{A,B} \approx N/L^3$ is easily estimated to be $n \approx 1\ \mu\text{m}^{-3}$, and the typical distance between particles is $d_{AB} \approx 1/c^{1/3} \approx L/N^{1/3} \approx 0.1\ \mu\text{m}$. Thus, in average, $a_{S,E} \ll d_{AB}$, and particles are very well separated. Therefore, it is reasonable to assume that pair effects are the dominant ones. This in turn simplifies the theoretical description considerably. Clearly, there are other scales in the problem, and the criteria on applicability of the pair approach are more subtle in reality.^{3,4}

To summarize, it would be extremely interesting to have a general method of calculation that could describe diffusion-controlled reactions in finite volumes, perhaps something on the level of the pair approach. The pair approach is attractive because inclusion of chemical details such as exclusion or steric effects is possible (e.g., see work in ref 33), which certainly opens a new route toward more quantitative results. However, the pair approach is an approximation, and before burdening the pair approach with increasing amount of chemical details, one has to test its ultimate reach. The present work is an attempt in this direction.

Appendix A: Details of the Master Equation

The occupancy of lattice sites c in eq 2 is specified as

$$c = (v_1, \dots, v_i, \dots, v_M) \quad (\text{A1})$$

and each site can be occupied by either A or B particle, or it may be empty. This gives three choices for v_i at each site $i = 1, 2, 3, \dots, M$ (sites $i = 0$ and $i = M$ being equivalent): $v_i = \text{A, B, or } 0$. Double occupancy of a site is not allowed. Also, the following notation will prove useful

$$|\Phi_i| = (v_1, \dots, v_{i-1}, \Phi_i, v_{i+1}, \dots, v_M) \quad (\text{A2})$$

where site i is emphasized having content Φ and Φ can be 0, A, or B.

Using notation A1 and A2, we can write the master equation (eq 2) as

$$\begin{aligned} \dot{P}(c, t) = & D_A \sum_{i,e} P(|A_i 0_e|) \Delta_{v_i,0} \Delta_{v_e,A} + \\ & D_B \sum_{i,e} P(|B_i 0_e|) \Delta_{v_i,0} \Delta_{v_e,B} - \\ & P(c, t) \sum_{i,e} [D_A \Delta_{v_i,A} + D_B \Delta_{v_i,B}] \Delta_{v_e,0} + \\ & \sum_{i,j} P(|A_i B_j|, t) \sigma(x_i - x_j) \Delta_{v_i,0} \Delta_{v_j,0} - \\ & P(c, t) \sum_{i,j} \sigma(x_i - x_j) \Delta_{v_i,A} \Delta_{v_j,B} \end{aligned} \quad (\text{A3})$$

where $\Delta_{\Phi,\Psi}$ denotes Kronecker delta symbol and equals one

for $\Phi = \Psi$, being zero otherwise. The \sum_e denotes sum over over nearest neighbors, which can be reached by one-step diffusion process.

The first three rows of eq A3 describe probability change due to diffusion, and the last two rows describe influence of the A + B reaction. For example, the last row in eq A3 is a loss term, indicating that the probability of configurations with particles present vanish, provided particles are within reaction range. The first three rows describing diffusion will ensure the flow of probabilities into such configurations.

Appendix B: Derivation of the Reaction Rate $k(t)$

With initial condition $Y(x, 0) = 1$, the Laplace transform of eq 11 becomes

$$sY(x, s) - 1 = (D_A + D_B)Y''(x, s) - \sigma(x)Y(x, s) \quad (\text{B1})$$

The correlation functions are symmetric around the origin, that is, $Y(x, t) = Y(-x, t)$. They are also periodic in L . This implies that it is sufficient to focus on the positive x axis and impose boundary conditions $(\partial/\partial x)Y(x, s) = 0$ for $x = 0$ and $x = L/2$. Equation B1 is an ordinary second-order differential equation, which is easily solved by solving it in regions $0 < x < a$ and $a < x < L/2$ separately and then matching solutions at the end. After some algebra, one obtains

$$Y_1(x, s) = \frac{1}{D} \left(\frac{1}{\nu} - \frac{1}{\mu} \right) \times \left(\frac{\text{ch}(x\sqrt{\mu})}{\text{ch}(a\sqrt{\mu}) + \sqrt{\frac{\mu}{\nu}} \text{sh}(a\sqrt{\mu}) \text{ch}\left[\sqrt{\nu}\left(\frac{L}{2} - a\right)\right]} \right) + \frac{1}{D\mu} \quad (\text{B2})$$

and

$$Y_2(x, s) = \frac{1}{D} \left(\frac{1}{\mu} - \frac{1}{\nu} \right) \times \left(\frac{\text{ch}\left[\left(\frac{L}{2} - x\right)\sqrt{\nu}\right]}{\text{ch}\left[\left(\frac{L}{2} - a\right)\sqrt{\nu}\right] + \sqrt{\frac{\nu}{\mu}} \text{sh}\left[\left(\frac{L}{2} - a\right)\sqrt{\nu}\right] \text{ch}(a\sqrt{\mu})} \right) + \frac{1}{D\nu} \quad (\text{B3})$$

where $Y(x, s) = Y_1(x, s)$ for $0 \leq x \leq a$ and $Y(x, s) = Y_2(x, s)$ for $a \leq x \leq L/2$ with $\mu = (s + \sigma_0)/D$ and $\nu = s/D$. The reaction rate $k(s)$ is given by

$$k(s) = 2\sigma_0 \int_0^a dx Y_1(x, s)$$

and equals

$$k(s) = \frac{2\sigma_0}{D} \left(\frac{1}{\nu} - \frac{1}{\mu} \right) \frac{\text{sh}(a\sqrt{\mu})}{\sqrt{\mu}} \times \frac{\text{ch}(x\sqrt{\mu})}{\text{ch}(a\sqrt{\mu}) + \sqrt{\frac{\mu}{\nu}} \text{sh}(a\sqrt{\mu}) \text{ch}\left[\sqrt{\nu}\left(\frac{L}{2} - a\right)\right]} + \frac{2\sigma_0}{D\mu} \quad (\text{B4})$$

We could not find the inverse Laplace transform of the expression above in closed analytic form. However, this is possible when $\sigma_0 \rightarrow \infty$. In such a case, one has

$$k(s) \approx 2\sqrt{\frac{D}{s}} \frac{1}{\text{cth}\left[(L/2 - a)\sqrt{\frac{s}{D}}\right]} + \frac{2\sigma_0 a}{\sigma_0 + s} + \mathcal{O}(1/\sigma_0) \quad (\text{B5})$$

The inverse Laplace transform of the approximate expression for $k(s)$ can be found by a residuum method. The $s = 0$ is not a branching point nor a pole. The only poles come from zeros of hyperbolic cosine, coming from \cosh term in the denominator of eq B5. Zeros occur at $s_m = -\pi^2(2m - 1)^2 D/(L - 2a)^2$. This fully fixes the form of $k(t)$ in eq 12.

Appendix C: Computer Experiment via Monte Carlo Simulations

We have chosen the minimal process algorithm for the simulations for two reasons. The first reason is that the algorithm reproduces the master equation (eq 2).³⁴ Second, our goal is to study a whole range of particle sizes and relatively large numbers of particles at the same time. Clearly, there are other possibilities to carry out Monte Carlo simulations, but the main advantage of the minimal process algorithm is that it can be applied for systems containing a relatively large number of particles. An original algorithm was devised for the situation where $a \approx h$, that is, particles react at the same lattice site or when nearest neighbors. We had to modify the original version of the algorithm to account for finite reaction range when $a \gg h$. A detailed description of the algorithm is given in the following.

Algorithm. (1) Site i is chosen at random. (2) If the site is empty, go to step 5. (3) For a chosen site i , one has to calculate the rate W_i for a certain process to occur (diffusion or reaction). Also, one needs a null rate N_i at which nothing happens (the so-called “null process”). The null rate is defined from $W_i + N_i = Q$, where Q is arbitrary but known at each simulation step. Q is chosen in such a way that none of the N_i is negative. In practice, the case when Q is taken as the largest of W_i works best because this leads to the smallest possible values for N_i , that is, the chance that nothing is done in the course of the simulation is reduced. (Please note that this requires that Q is updated as simulation proceeds, but this can be done in a straightforward manner as explained in ref 34). $W_i = D_i + R_i$ accounts for possibilities that a particle at the site diffuses to the neighboring site with rate D_i or reacts with a particle in some other site with rate $R_i = \sum_{j \in \Omega_i} \sigma(r_{ij})$. Ω_i denotes a set of sites that are within reaction range of the site i . The calculation of R_i is by far the most costly step when a is large. In that case, a large region has to be searched to find all particles within Ω_i . This step costs $M_{\text{search}} \approx (a/h)^d$ computational steps if the sites are checked one by one. The cost can be reduced further by introducing a list that specifies which sites contain particles within the reaction range of the particle at site i . In that case, one has to update the list for each diffusion step made. The best algorithm that we have so far updates the list in roughly $M_{\text{search}} \approx (a/h)^{d-1}$ steps. (4) Once the rates for the site i have been calculated, one can use them to evaluate probabilities for specific process $p^{(D)} = D_i/Q$, $p^{(R)} = R_i/Q$, and $p^{(\text{null})} = N_i/Q$. Once the probabilities are calculated, a certain process is chosen by a linear selection algorithm. First, one decides whether diffusion, reaction, or nothing is going to happen. If diffusion is to happen, then the particle is moved to one of the randomly chosen $2d$ nearest neighbors. If reaction was chosen, then one of the sites containing particles in reaction range is chosen at random, for example, at site j , and a pair of particles from sites i and j are annihilated. (5) Time is updated according to the formula $t \rightarrow t + \Delta t$ where $\Delta t = 1/LQ$ where L was specified before and Q is the maximum rate at the present step. (6) Move back to step 1 unless some criteria to stop is invoked.

Applying the same type of reasoning as in ref 34, one can see that the algorithm proposed here reproduces the behavior

described by the master equation (eq 2). As time of the simulation progresses, we monitor the number of particles and calculate all of the statistics.

As the original minimal process algorithm, the present simulation method is not that efficient at the later stages of dynamics when the lattice becomes sparse. The quantity that governs computational cost of this method is the number of Monte Carlo steps needed to see some change in the number of particles. We describe it by the number of Monte Carlo steps needed to annihilate the *last* pair of particles.

To make such an estimate, it is best to move to the reference frame of one of these particles. Then one particle is fixed and another one is trying to find it. The number of diffusion steps that the moving particle needs to find the one that sits still is roughly given by $M(\text{diff}) \approx L^d/a$ (here and in the following it is implicitly assumed that every length variable is measured in units of lattice spacing h). Each diffusion step bears $M(\text{step}/\text{diff})$ computational steps, which gives the total number of steps to annihilate the pair of particles equal to $M(\text{tot}) = M(\text{diff}) \cdot M(\text{step}/\text{diff})$. The number of Monte Carlo steps per one diffusion step is roughly 1, $M(\text{step}/\text{diff}) \approx 1$. However, calculation of R_i requires updating the internal list, which costs $M_{\text{search}} \approx a^{d-1}$ search steps whenever the particle is moved. Thus, the true number of computational steps per diffusion step is given by $M(\text{step}/\text{diff}) \approx M_{\text{search}} \approx a^{d-1}$. Finally, one gets an estimate for the number of computational steps needed to annihilate the last pair of particles as $M(\text{tot}) \approx L^d a^{d-2}$.

The algorithm has an interesting property that for $d = 1$ there is a reduction in the computational cost when comparing large and small a cases. For larger a , the algorithm works more efficiently. For $d = 2$, the computational cost does not depend on a . Simulating a large a situation for $d = 3$ is more costly. One could avoid this growing cost problem at $d = 3$ by browsing through particles instead of searching for sites when calculating R_i . This is clearly the preferred option when the number of particles in the system is not that large.

References and Notes

- (1) Luby-Phelps, K. *Int. Rev. Cytol.* **2000**, 192, 189.
- (2) Kotomin E.; Kuzovkov, V. *Rep. Prog. Phys.* **1992**, 55, 2079.
- (3) Kotomin E.; Kuzovkov V. In *Modern aspects of diffusion-controlled reactions*; Comprehensive Chemical Kinetics, Vol. 34; Compton, R. G., Hancock, G., Eds.; Elsevier: Amsterdam, 1996.
- (4) Kuzovkov, V. N.; Kotomin, E. A. *Chem. Phys.* **1983**, 81, 335.
- (5) Kotomin, E.; Kuzovkov, V.; Frank, W.; Seeger, A. *J. Phys. A* **1994**, 27, 1453.
- (6) Chiu, D. T.; Wilson, C.; Ryttsén, F.; Strömberg, A.; Karlsson, A.; Nordholm, S.; Hsiao, A.; Gagg, A.; Garzia-López, R.; Moscho, A.; Orwar, O.; Zare, R. N. *Science* **1999**, 283, 1892.
- (7) Chiu, D. T.; Wilson, C.; Karlsson, A.; Danielsson, A.; Lundqvist, A.; Strömberg, A.; Ryttsén, F.; Davidson, M.; Nordholm, S.; Orwar, O.; Zare, R. N. *Chem. Phys.* **1999**, 247, 133.
- (8) Karlsson, A.; Karlsson, M.; Karlsson, R.; Cans, A.-S.; Strömberg, A.; Ryttsén, F.; Orwar, O. *Nature* **2001**, 409, 150.
- (9) Karlsson, R.; Karlsson, A.; Karlsson, M.; Cans, A.-S.; Voinova, M.; Bergenholtz, J.; Ewing, A. G.; Åkerman, B.; Orwar, O. *Langmuir* **2002**, 18, 4186.
- (10) Park, H.; Park, J.; Lim, A. K. L.; Anderson, E. H.; Alivisatos, A. P.; McEuen, P. L. *Nature* **2000**, 407, 57.
- (11) Alcaraz, F. C.; Droz, M.; Henkel, M.; Rittenberg, V. *Ann. Phys.* **1994**, 230, 250–302.
- (12) Konkoli, Z.; Johannesson, H.; Lee B. P. *Phys. Rev. E* **1999**, 59, R3787.
- (13) Konkoli, Z.; Johannesson, H. *Phys. Rev. E* **2000**, 62, 3276.
- (14) *Diffusion-limited reactions*; Comprehensive Chemical Kinetics, Vol. 25; Bamford, C. H., Tipper, C. F. H., Compton, R. G., Eds.; Elsevier: Amsterdam, 1985.
- (15) Khairutdinov, R. F.; Serpone, N. *Prog. React. Kinet.* **1996**, 21, 1–68.
- (16) Khairutdinov, R. F.; Burshtein, K. Ya.; Serpone, N. *J. Photochem. Photobiol., A* **1996**, 98, 1.
- (17) Tachiya, M. *Chem. Phys. Lett.* **1980**, 69, 605.

- (18) *Photochemistry in Organized and Constrained Media*; Ramamurthy, V., Ed.; VCH Publishers: New York, 1991.
- (19) Lee, B. P. *J. Phys. A* **1994**, 27, 2633.
- (20) Lee, B. P.; Cardy, J. *Stat. Phys.* **1995**, 80, 971.
- (21) Havlin, S.; Ben-Avraham, D. *Adv. Phys.* **1987**, 36, 695.
- (22) Burlatskii, S. F.; Ovchinnikov, A. A. *Russ. J. Phys. Chem.* **1978**, 52, 1635.
- (23) Ovchinnikov, A. A.; Zeldovich, Ya. B. *Chem. Phys.* **1978**, 28, 215.
- (24) Toussaint, D.; Wilczek, F. *J. Chem. Phys.* **1983**, 78, 2642.
- (25) Burlatskii, S. F.; Ovchinnikov, A. A.; Pronin, K. A. *JETP* **1987**, 92, 625.
- (26) Gutin, A. M.; Mikhailov, A. S.; Yashin, V. V. *JETP* **1987**, 92, 941.
- (27) Bramson, M.; Lebowitz, J. L. *Phys. Rev. Lett.* **1988**, 61, 2397.
- (28) Oerding, K. *J. Phys. A* **1996**, 29, 7051.
- (29) Mattis, D. C.; Glasser, M. L. *Rev. Mod. Phys.* **1998**, 70, 979.
- (30) Koo, Y. E. L.; Kopelman, R. *J. Stat. Phys.* **1991**, 65, 893–918.
- (31) Calef, D. F.; Deutch, M. *Annu. Rev. Phys. Chem.* **1983**, 34, 493.
- (32) Berg, H. C.; Purcell, E. M. *Biophys. J.* **1977**, 20, 193.
- (33) Wu, Y.-Ta.; Nitsche, J. M. *Chem. Eng. Sci.* **1995**, 50, 1467–1487.
- (34) Hanusse, P.; Blanche, A. *J. Chem. Phys.* **1981**, 74, 6148.