Segregation in Annihilation Reactions without Diffusion: Analysis of Correlations

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We study binary one-dimensional exchange-mediated $A + B \rightarrow 0$ reactions in the absence of diffusion. Using the Kirkwood superposition approximation to decouple the infinite hierarchy of many-particle densities a closed set of integrodifferential equations is derived. A comparison to simulation calculations shows that the approximation reproduces the correct long-time asymptotic decay of reactant concentration as well as the correct spatial correlations of the segregation pattern.

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Recent years have seen a drastic increase in interest in the $A + B \rightarrow 0$ reaction scheme, following the realization that segregation of like particles occurs,[1-4] which leads to long-time behavior different from the classical kinetic scheme. A recent review article summarizes the findings.[4] In contrast to the $A + A \rightarrow A$, $A + A \rightarrow 0$, and $A + B \rightarrow B$ diffusion-limited reactions, for which in the last years several *exact* 1D solutions have become available,[5-9] the analytic work for $A + B \rightarrow 0$ reactions is still based (even in 1D) on approximate (although increasingly reliable) analytical methods.[4,10]

Most of the analyses have centered on *diffusion-limited* reactions in which the reactants move (either diffusionally or as a random walk) before reacting on contact. By contrast, far less attention has been paid to reactions in which the particles annihilate via longer-ranged interactions, such as exchange, in the *absence* of motion. Since motion and reaction often cause adverse effects on segregation,[1,2,10] we consider here only reactions with immobile reactants. Such reactions, especially when taking place in spaces of low dimensions, provide a stringent test of approximate analytical approaches, since possible deviations of the theory from the computer experiments are not obscured by diffusion effects or by the (often milder) behavior in higher dimensions.

Interestingly, we find expressions which use the Kirkwood superposition approximation[11] for the three-center correlation functions to perform exceedingly well even for short-range exchange reactions in 1D, and to provide both the correct long-time asymptotic behavior of the reaction, as well as the correct AB-particle segregation pattern. This fact is quite remarkable, since then the method may represent a powerful *analytical* approach to the $A + B \rightarrow 0$ problem, even when diffusion is involved. By contrast, neglect of the segregation aspect leads to (even qualitatively) wrong asymptotic forms.

In the following we consider randomly distributed A and B particles, which react via exchange, $w(\mathbf{r}) = w(r) = w_0 \exp(-r/r_0)$, where w is the probability rate that A and B situated at distance r react and r_0 is a constant, which determines the interaction range. The exponential

form is typical for exchange-dominated reactions in solids, like scavenging or recombination of electrons and holes via tunneling.[3] For describing the recombination kinetics we follow the ideas of Kuzovkov and Kotomin,[4] where the following infinite system of coupled differential equations for the many-point densities $\rho_{m,m'}$ derived (p. 1485ff of Ref. 4):

$$\frac{\partial}{\partial t} \rho_{m,m'} = - \sum_{i=1}^{m} \sum_{j=1}^{m'} w(\mathbf{r}_i - \mathbf{r}_j') \rho_{m,m'}$$
$$- \sum_{i=1}^{m} \int w(\mathbf{r}_i' - \mathbf{r}_{m'+1}') \rho_{m,m'+1} d\mathbf{r}_{m'+1}'$$
$$- \sum_{j=1}^{m'} \int w(\mathbf{r}_j' - \mathbf{r}_{m+1}) \rho_{m+1,m'} d\mathbf{r}_{m+1}. \quad (1)$$

The $\rho_{m,m'}$ are ensemble-averaged products of reactant concentrations, where m and m' denote the number of A and B particles involved in the product. With $n(\mathbf{r},t)$ being the microscopic particle density, one has thus for the single- and two-point densities,

$$\rho_{1,0} = \langle n_A(\mathbf{r},t) \rangle \equiv n_A(t), \quad \rho_{0,1} = \langle n_B(\mathbf{r},t) \rangle \equiv n_B(t), \quad (2)$$

and

$$\rho_{2,0} = \langle n_A(\mathbf{r}_1,t) n_A(\mathbf{r}_2,t) \rangle \equiv n_A^2(t) X_A(\mathbf{r}_1 - \mathbf{r}_2,t),$$
$$\rho_{0,2} = \langle n_B(\mathbf{r}_1,t) n_B(\mathbf{r}_2,t) \rangle \equiv n_B^2(t) X_B(\mathbf{r}_1 - \mathbf{r}_2,t), \quad (3)$$
$$\rho_{1,1} = \langle n_A(\mathbf{r}_1,t) n_B(\mathbf{r}_2,t) \rangle \equiv n_A(t) n_B(t) Y(\mathbf{r}_1 - \mathbf{r}_2,t).$$

Note that in Eq. (3) we have introduced the pair correlation functions $X_A(\mathbf{r},t)$, $X_B(\mathbf{r},t)$, and $Y(\mathbf{r},t)$. In this Letter we consider strictly bimolecular reactions, so that one has for the number of particles $A(0) = B(0)$, and thus also $A(t) = B(t)$ at all times. This implies $n_A(t) = n_B(t) \equiv n(t)$ and $X_A(\mathbf{r},t) = X_B(\mathbf{r},t) \equiv X(\mathbf{r},t)$.

We revert now to one dimension. Inserting Eqs. (2) and (3) into Eq. (1) leads to the following exact expression for $n(t)$:

$$\frac{dn(t)}{dt} = -n^2(t) \int_{-\infty}^{\infty} w(r') Y(r',t) dr'. \quad (4)$$

Following Refs. 4 and 12 we now make use of the Kirkwood superposition principle to decouple all three-center correlation functions (see Eq. 7.4.6 of Ref. 11); thus, for instance,

$$\rho_{2,1} = \langle n_A(\mathbf{r}_1,t) n_A(\mathbf{r}_2,t) n_B(\mathbf{r}_1',t) \rangle \simeq n^3(t) X(\mathbf{r}_1 - \mathbf{r}_2,t) Y(\mathbf{r}_1 - \mathbf{r}_1',t) Y(\mathbf{r}_2 - \mathbf{r}_1',t) . \tag{5}$$

This approximation leads here to a closed set of equations for X and Y:

$$\frac{\partial \ln Y(r,t)}{\partial t} = -w(r) - 2n(t) \int_{-\infty}^{\infty} w(r') Y(r',t) [X(r-r',t) - 1] dr' , \tag{6}$$

$$\frac{\partial \ln X(r,t)}{\partial t} = -2n(t) \int_{-\infty}^{\infty} w(r') Y(r',t) [Y(r-r',t) - 1] dr' . \tag{7}$$

A simple way to visualize, say, Eq. (6), is to observe that a given AB pair may disappear [$d(n^2 Y)/dt$] either through direct annihilation ($-wn^2 Y$) or by having one of the partners annihilate with a third particle, whose position distribution is given in the Kirkwood approximation by a $n^3 YYX$-type product. The factor 2 accounts for the two channels for third-particle annihilation and the -1 in the square brackets stems from the dn/dt terms in the $d(n^2 Y)/dt$ expression, where use was made of Eq. (4).

The starting point both for the simulation and also for the analytical development according to Eqs. (4), (6), and (7) is an uncorrelated distribution of A and B particles with initial densities $n(0) = n_0$ and $Y(r,0) = X(r,0) \equiv 1$. Evidently in the course of the reaction one has at all times

$$\lim_{|r| \to \infty} X(r,t) = \lim_{|r| \to \infty} Y(r,t) = 1 . \tag{8}$$

A lower-level approximation than Eqs. (6) and (7) consists in decoupling at an earlier stage, e.g., by setting $X(r,t) \equiv 1$ in Eq. (6). This implies the neglect of correlations between like particles, i.e., neglect of cluster formation. Such a procedure, although sometimes encountered,[13] does not display the proper asymptotic behavior. The approximation implies, from Eq. (6), that

$$Y(r,t) = \exp[-w(r)t] , \tag{9}$$

with which Eq. (4) can be integrated by separation of variables, yielding

$$[n(t)]^{-1} = n_0^{-1} + \int_{-\infty}^{\infty} dr (1 - e^{-w(r)t}) \sim C \ln(w_0 t) , \tag{10}$$

the last integral being of common occurrence in the theory of energy transfer.[14] However, we find (vide infra) that both simulation calculations and the full system of Eqs. (4), (6), and (7) lead to

$$n(t) \sim C \ln^{-1/2}(w_0 t) , \tag{11}$$

in accordance with a change of $\frac{1}{2}$ in the time-decay exponents for strictly bimolecular reactions; see Refs. 1–4. In higher dimensions the exponent in Eq. (11) is $-d/2$.

The starting point for the simulations are random distributions of A and B particles (N_0 each) on a chain of L sites under periodic boundary conditions. Here and in the following a shift-register random-number generator[15] ($p = 98$, $q = 27$) was used. The random mutual annihila-

tion of unlike particles was simulated through a minimal process method.[16] From all AB pairs at each reaction step one pair was selected randomly, according to its reaction rate; the time increment τ for this step was computed as $\tau = -(\ln T)/R$, with R being the sum of the rates of all AB pairs present and T a random number from the homogeneous distribution in the unit interval. The time was measured in units of w_0^{-1} and we stopped the procedure after a maximal time of 10^{30}.

Figure 1 shows the buildup of correlations after starting with 1000 A and 1000 B particles on a segment $L = 10000$. The interaction parameter r_0 was set to $r_0 = 5$, which corresponds to typical exchange interactions in organic molecular crystals. Already at $t = 10^5$ correlation regions are clearly visible, a finding comparable for instance to the results for diffusion-limited reactions under pulsed excitation,[2,3,17] and also for steady-state situations.[10,18]

To quantify these findings we present in Fig. 2 the evolution of the number of A (or B) particles, followed over more than thirty decades in time. The decay (curve a) was obtained by averaging over ten different initial configurations, and we indicate the standard variation of the data by dashed lines. Asymptotically, the simulations follow very closely a $\ln^{-1/2}(w_0 t)$ behavior, as verified by us by replotting the data of Fig. 2.
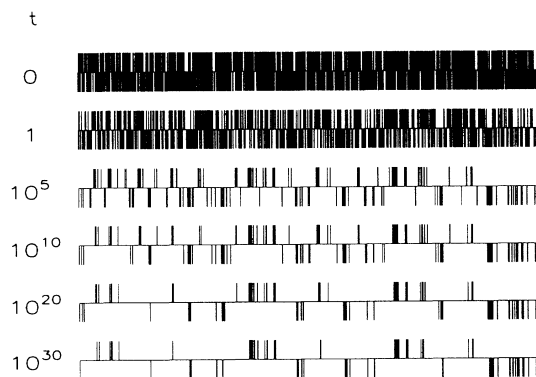

FIG. 1. Distribution of A and B particles (initially 1000 of each kind on a chain with $L = 10000$ sites) during a numerical simulation. Each vertical line represents one A (up) or B (down) particle.
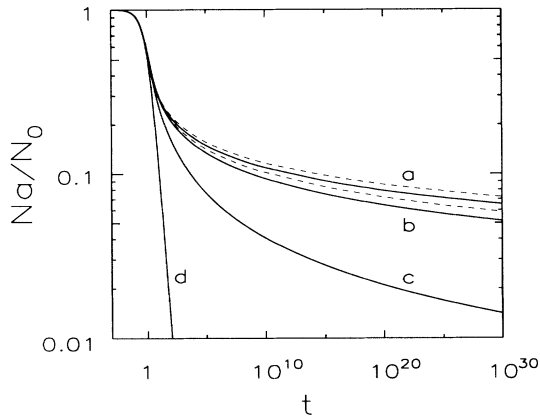
FIG. 2. Decay of the number of A (B) particles resulting from (curve a) averaging over 10 numerical simulations ($N_0 = 10^4$, $L = 10^5$, the dashed lines show the standard deviation), (curve b) the numerical evaluation of Eqs. (4), (6), and (7) using the Kirkwood superposition approximation, and (curve c) a raw approximation, Eq. (10), which neglects correlations between like particles. Curve d is the solution of the simple kinetic approach [Eq. (13)], neglecting all spatial inhomogeneities.

A very good description of this decay is provided by Eqs. (4), (6), and (7). Here the numerical evaluation involved the discretization of the time and space variables, and use was made of the symmetry of the integrals with respect to inversion. To improve the accuracy, for each discretized time interval the derivatives were expressed as symmetric functions of the interval's boundaries. This leads to a nonlinear set of iteration functions, which converge very fast under a quasilinearization procedure.[19]

The resulting decay is also given in Fig. 2 (curve b). One observes that simulation and numerical solution agree closely over the whole range investigated; the decays are practically indistinguishable over the first four decades in time, and differ by at most a factor of 1.2 in the very late stages (times of the order of 10^{20}–10^{30}). Moreover, the asymptotic behavior which follows from Eqs. (4), (6), and (7) also obeys a $\ln^{-1/2}(w_0 t)$ behavior.

By contrast, setting $X(r,t) \equiv 1$ in Eq. (6), which is equivalent to neglecting correlations between like particles, leads to very different behavior, given in Fig. 2 as curve c. The range of agreement to the simulation shrinks to the domain of very short times ($t \sim 1$); furthermore, at longer times a $\ln^{-1}(w_0 t)$ pattern dominates.

In Fig. 2 we also plotted the solution of the simple kinetic approach (curve d), which implies neglect of all spatial inhomogeneities [$X(r,t) \equiv 1$ and $Y(r,t) \equiv 1$]. In this case Eq. (4) reduces to

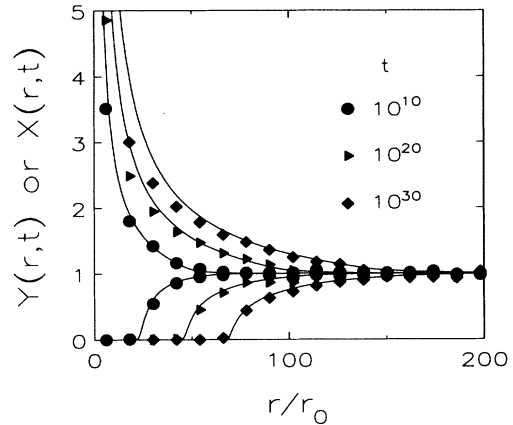$$\frac{dn(t)}{dt} = -2w_0 r_0 n^2(t),$$
(12)

FIG. 3. Correlation functions for like (X) and unlike (Y) particles, calculated numerically from Eqs. (4), (6), and (7) (solid lines). The symbols mark the results from numerical simulations, each value averaged over 10 realizations and over a distance of $5r_0$ ($N_0 = 10^4$, $L = 10^5$, $r_0 = 5$).

a kinetic-scheme expression, which has the solution

$$n(t) = \frac{n(0)}{1 + 2r_0 n(0) w_0 t}.$$
(13)

This approximation is valid only up to $w_0 t \approx 1$, as demonstrated in Fig. 2. Then the assumption of spatial homogeneity breaks down.

A further, stringent test of Eqs. (4), (6), and (7) is provided by comparing the correlation functions $X(r,t)$ and $Y(r,t)$ to the simulation data, which in raw form are as in Fig. 1. In Fig. 3 we present the X and Y functions, evaluated at three given times ($t = 10^{10}$, 10^{20}, and 10^{30}), and contrast them with the simulation results, obtained, as before, by averaging over ten different realizations of the process. The scatter of the simulated data was inhibited by averaging over length intervals comparable to the width of the symbols used in Fig. 3; under these circumstances the error in the data is around 1%, much below the height of the same symbols. The agreement between $Y(r,t)$ and simulation is strikingly good, considering that, after all, $Y(r,t)$ was obtained from the Kirkwood approximation, and that we have a 1D system with no diffusion. Furthermore, the $Y(r,t)$ data show that the typical domain size ξ, defined by $tw(\xi) = 1$, grows as $\ln(w_0 t)$; this is a consequence of the assumed exponential form for $w(r)$. Also $X(r,t)$ performs remarkably well. Up to times $t = 10^{10}$ the agreement is very good; at longer times ($t \sim 10^{30}$) deviations begin to appear in the small-r regime.

In this Letter we have analyzed the $A + B \rightarrow 0$ strictly bimolecular reaction in 1D under exchange interactions in the absence of diffusion. We find that an analytical development in terms of the superposition approximation leads to astonishing accurate results. We consider our conditions (1D system and no diffusion) to be particular-

ly stringent, so that one may use with confidence the analytical method in applications to experiments.

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