Simulation study of reaction fronts

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Using random walkers on a square lattice we have simulated a diffusion-reaction process $A+B\rightarrow C$; initially, the reactants are segregated on either side of a straight boundary. Quantities studied include the position and width of the reaction front and the position-dependent reaction rates and densities of the reactants. Our results agree with the scaling theory of Gálfi and Rácz for the long-time behavior of the system indicating that the scaling assumption is valid and that the neglect in the scaling theory of concentration fluctuations and of the discrete (particle) nature of the reactants is not important. Furthermore, although the scaling theory is not explicitly constructed for the case of unequal diffusion coefficients of the two initial species, our results indicate that it is correct in this regime as well.

I. INTRODUCTION

Pattern formation in the wake of a reaction front is a phenomenon common to physical, chemical, and biological systems.[1-4] The study of the reaction front naturally serves as a first step in understanding these pattern-formation phenomena. We report simulations of a lattice model for a diffusion-reaction process $A+B\rightarrow C$ with reactants A and B initially segregated on either side of a planar (linear) boundary defined as $x=0$. A scaling theory for this system has been given by Gálfi and Rácz.[5] In their theory, the process is described by

$$\frac{\partial\rho_A}{\partial t}=D_A\nabla^2\rho_A-k\rho_A\rho_B\ , \tag{1}$$

$$\frac{\partial\rho_B}{\partial t}=D_B\nabla^2\rho_B-k\rho_A\rho_B\ , \tag{2}$$

where $\rho_\gamma(x,t)$, $\gamma=A,B$, are the concentrations of the reactants; D_γ are their diffusion constants; and k controls the rate of reactions. With initial conditions

$$\begin{aligned}&\rho_A(x,0)=\rho_A(0)\ \text{ and }\ \rho_B(x,0)=0\ \text{ for } x>0\ ,\\ &\rho_A(x,0)=0\ \text{ and }\ \rho_B(x,0)=\rho_B(0)\ \text{ for } x<0\ ,\end{aligned} \tag{3}$$

Gálfi and Rácz[5] argue that for $D_A=D_B$, the reaction rate R, which depends on x and t,

$$R(x,t)\equiv k\rho_A(x,t)\rho_B(x,t) \tag{4}$$

has, at large t, the scaling form

$$R(x,t)\sim t^{-\beta}F\left[\frac{x-x_f}{w}\right] \tag{5}$$

with $\beta=\frac{2}{3}$. Further, the width w of the reaction front scales as t^α with $\alpha=\frac{1}{6}$, and the position x_f of the front, taken as zero at $t=0$, scales as $t^{1/2}$ if $\rho_A(0)\neq\rho_B(0)$; if $\rho_A(0)=\rho_B(0)$, $x_f=0$. Similarly, the concentrations at large t have the scaling forms

$$\rho_\gamma(x,t)\sim t^{-\beta/2}G_\gamma\left[\frac{x-x_f}{w}\right]\ . \tag{6}$$

The values of α and β can be inferred[5] from the following simple argument: In the diffusion-reaction process, there is a concentration-depletion zone of width $W_d\propto t^{1/2}$ around the reaction center. Consequently, the fluxes of particles are given by

$$j_A=D_A\frac{\partial\rho_A}{\partial x}\sim j_B=D_B\frac{\partial\rho_B}{\partial x}\sim\frac{1}{W_d}\sim t^{-1/2}\ , \tag{7}$$

and the average values of ρ_A and ρ_B in the reaction front are $\rho_A\sim\rho_B\sim wt^{-1/2}$. Hence, since the reaction is fed by particles that flow into the reaction region,

$$wR\sim t^{\alpha-\beta}\sim j_A\sim t^{-1/2}\ , \tag{8}$$

and consequently

$$\alpha-\beta=-\tfrac{1}{2}\ . \tag{9}$$

On the other hand, the rate at which C is formed is

$$R\sim t^{-\beta}\sim\rho_A\rho_B\sim w^2/t\sim t^{2\alpha-1}\ ; \tag{10}$$

thus,

$$2\alpha-1=-\beta\ . \tag{11}$$

By combining Eqs. (9) and (11) one obtains $\alpha=\frac{1}{6}$ and $\beta=\frac{2}{3}$.

In this paper we present representative results from simulations of a lattice model designed to study the diffusion-reaction phenomenon described above. Our aims in doing this work were to test whether the system exhibits scaling behavior and, if so, to test the scaling theory,[5] to assess the importance of fluctuations and of the discrete nature of the reactants (which are not included in the scaling theory), and to look at cases outside of the conditions imposed in constructing the theory (for example, $D_A\neq D_B$). We know of no comparable simula-

tions for this process and geometry, although Chopard and Droz[6] are investigating the applicability of a cellular automata model. Our results agree with the scaling theory,[5] including the case of $D_A \neq D_B$.

In the remainder of the paper, we give in Sec. II a description of the model and simulations; Sec. III contains the results and a summary.

II. MODEL AND NUMERICAL TECHNIQUES

We use an $N_x \times N_y$ square lattice; the reactants A and B are initially distributed randomly on the left and right halves (in the x direction) of the lattice with concentrations $\rho_A(0)$ and $\rho_B(0)$. A site is indexed by subscripts (i,j), $1 \le i \le N_x$, $1 \le j \le N_y$. A step in the simulations is as follows: First, randomly choose a site (i,j) occupied by A or B. Next, if (i,j) is occupied by A (B) and at least one of the neighboring sites is occupied by B (A), then both A (B) and one of its randomly chosen neighbors of type B (A) are removed, and a C is introduced on either of the two original particles' sites with equal probability; or, if (i,j) is occupied by A (B) and no neighboring site is occupied by B (A), then move this particle to an empty randomly chosen neighboring site with probability P_A (P_B). Periodic boundary conditions are applied in the y direction; particles are not allowed to diffuse out of the system in the x direction. A given site can be occupied by one particle of type A or type B and by an arbitrary number of particles of type C. Time is measured in units of steps per lattice site (SPS). We have done runs of up to 10^4 SPS. Notice that $D_\gamma \propto P_\gamma$.

Quantities computed include, first, the concentration profiles $\rho_\gamma(x,t)$,

$$\rho_\gamma(x,t) = N_y^{-1} \sum_j n_{ij\gamma} \ . \tag{12}$$

The sum is over all sites in a column at given i, and $n_{ij\gamma}$ is the occupation number of particles of type γ at site (i,j) of the lattice. The index i is replaced by x for the computed quantities; $x \equiv i$. Next, the reaction rate $R(x,t)$ is defined as the number of reactions taking place within the xth column during time step t; a reaction is considered to take place within a given column if the product C winds up in that column. From $R(x,t)$, the displacement of the reaction front $\delta x_f(t)$ and the width $w(t)$ are given by

$$\delta x_f(t) = \frac{\sum_x [x - x_f(0)] R(x,t)}{\sum_x R(x,t)} \ , \tag{13}$$

$$w^2(t) = \frac{\sum_x [x - x_f(t)]^2 R(x,t)}{\sum_x R(x,t)} \ , \tag{14}$$

where $x_f(t) = x_f(0) + \delta x_f(t)$. Changes in $R(x,t)$, $\delta x_f(t)$, and $w(t)$ are sufficiently slow that what we report are really averages over 100 time steps centered at t. Fluctuations in R, δx_f, and w are reduced further by making N_r computer runs, $N_r \le 70$, for a given set of parameters and different initial configurations. The lattice size used is typically $N_x = 200$ and $N_y = 100$. Comparison with runs done on systems of size 100×100, and with $N_x = 100$ and $N_y = 200$ showed no evidence of size effects.

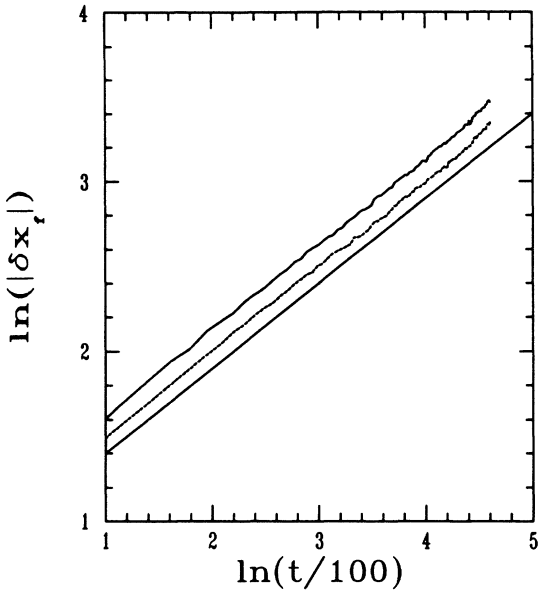

FIG. 1. We plot $\ln(\delta x_f)$ vs $\ln(t/100)$ for $P_A = P_B = 1$ and $\rho_A(0) = 0.6$, $\rho_B(0) = 0.3$ (solid curve) and for $P_A = 0.7$, $P_B = 1.0$, $\rho_A(0) = 0.7$, and $\rho_B(0) = 0.3$ (dashed curve). Each set of data is the average of 67 separate computer runs using $N_x = 100$, $N_y = 200$. A line of slope $\frac{1}{2}$ is shown for comparison.

III. RESULTS

We present first our results with equal diffusion coefficients. Figures 1 and 2 show, respectively,

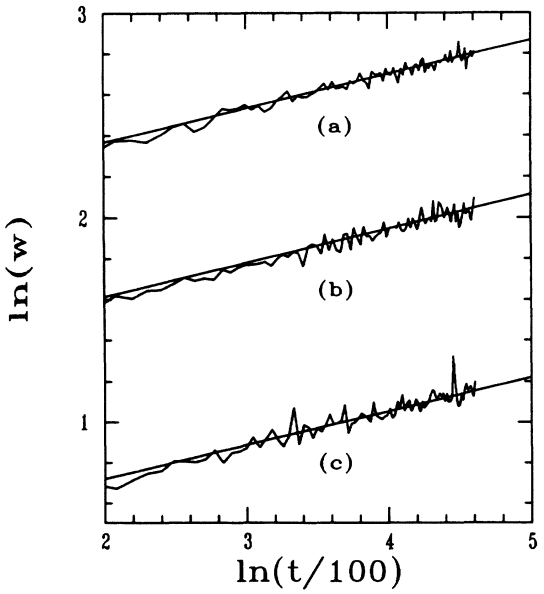

FIG. 2. For (a) $P_A = P_B = 1$, $\rho_A(0) = 0.6$, and $\rho_B(0) = 0.3$; (b) $P_A = 0.7$, $P_B = 1.0$, $\rho_A(0) = 0.7$, and $\rho_B(0) = 0.3$; and (c) $P_A = 0.5$, $P_B = 1.0$, $\rho_A(0) = 0.8$, and $\rho_B(0) = \sqrt{0.32}$, $\ln(w)$ is plotted against $\ln(t/100)$. For clarity, curves (a) and (b) are shifted vertically by $\ln(4)$ and $\ln(2)$, respectively.

$\ln[|\delta x_f(t)|]$ (solid curve) and $\ln[4w(t)]$ versus $\ln(t/100)$ [curve (a)] for $\rho_A(0)=0.6$ and $\rho_B(0)=0.3$. For the former, the data fit a line of slope 0.508 ± 0.006, consistent with the predicted value of $\frac{1}{2}$. For the latter the data at longer times fit a line with a slope 0.173 ± 0.016, close to the predicted value of $\frac{1}{6}$. For the same parameters, Fig. 3 shows plots of the scaled reaction rate $100t^{2/3}R(x,t)$ and the scaled densities $t^{1/3}\rho_\gamma(x,t)$ as functions of the scaled position $[x-x_f(t)]t^{-1/6}$ at $t=800$, 3000, and 5000 SPS. The curves for $t^{2/3}R(x,t)$ very nearly superpose as do those for the densities in the active reaction area, aside from fluctuations, consistent with the scaling relations.

For $P_A\neq P_B$, or $D_A\neq D_B$, also, our simulations support the scaling predictions as can be seen from Figs. 1 (dashed line) and 2 [curve (b)] that present results for $P_A=0.7$, $P_B=1.0$, $\rho_A(0)=0.7$, and $\rho_B(0)=0.3$. These curves fit lines of slopes 0.504 ± 0.007 and 0.178 ± 0.020, respectively. Figure 4 shows the reaction rates and densities for this case at times of 1000, 3000, and 5000 SPS; one sees that the curves at different times superpose nicely.

We find that the general condition for the center of the reaction zone not to move, i.e., $\delta x_f(t)=0$, is

$$r_{AB}\equiv\frac{P_A^{1/2}\rho_A(0)}{P_B^{1/2}\rho_B(0)}=1\ . \tag{15}$$

The center always moves to the side with the smaller value of $P_\gamma^{1/2}\rho_\gamma(0)$. As examples, we show in Fig. 5 δx_f versus t for three cases with $r_{AB}>1$, $r_{AB}=1$, and $r_{AB}<1$, respectively. For the case $P_A=0.5$, $P_B=1.0$, $\rho_A(0)=0.8$, and $\rho_B(0)=\sqrt{0.32}$, which corresponds to $r_{AB}=1$, curve (c) of Fig. 2 presents $\ln[w(t)]$ versus $\ln(t/100)$. A least-squares fit yields a slope of 0.178 ± 0.027, consistent with $w\sim t^{1/6}$.

We have done other runs, albeit with poorer statistics, using different initial concentrations and diffusion constants. In every case, for $D_\gamma\neq0$, the results are consistent with those reported above. As one of the D_γ ap-

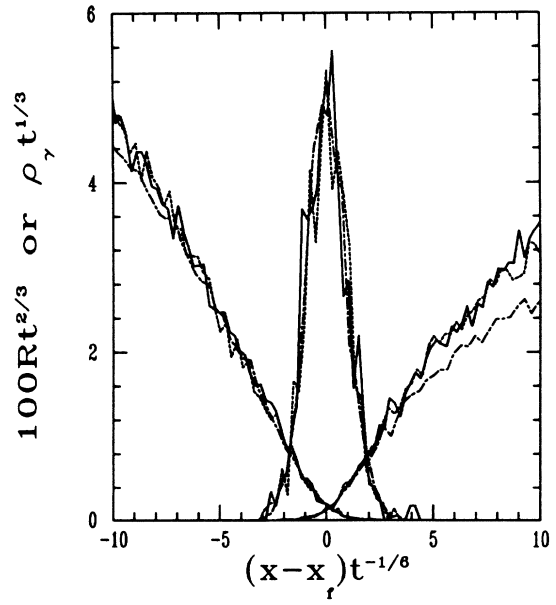

FIG. 3. For $P_A=P_B=1$, $\rho_A(0)=0.6$, and $\rho_B(0)=0.3$, $100t^{2/3}R(x,t)$ and $t^{1/3}\rho_\gamma(x,t)$ are shown as functions of $[x-x_f(t)]t^{-1/6}$ for the three times 800 (·–·–·), 3000 (– – –), and 5000 (——) SPS.

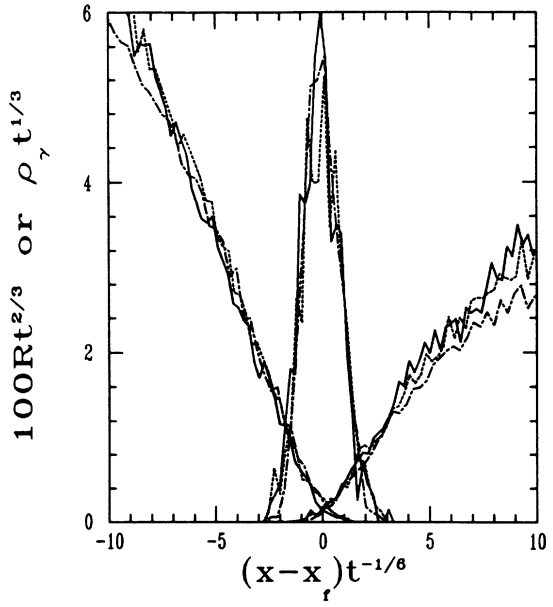

FIG. 4. The same as Fig. 3 except that $P_A=0.7$, $P_B=1.0$, $\rho_A(0)=0.7$, and $\rho_B(0)=0.3$. Also, the curves are for times 1000 (·–·–·), 3000 (– – –), and 5000 (——) SPS.

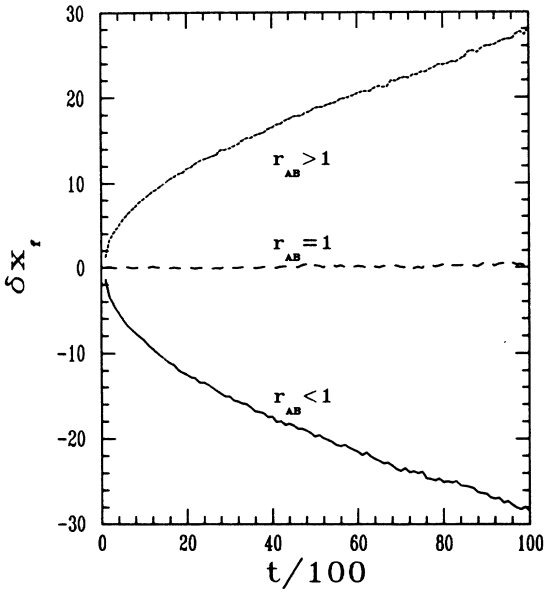

FIG. 5. The displacement $\delta x_f(t)$ is plotted against t for three cases: $r_{AB}>1$ [$P_A=0.7$, $P_B=1.0$, $\rho_A(0)=0.7$, $\rho_B(0)=0.3$]; $r_{AB}=1$ [$P_A=0.5$, $P_B=1.0$, $\rho_A(0)=0.8$, $\rho_B(0)=\sqrt{0.32}$]; and $r_{AB}<1$ [$P_A=0.7$, $P_B=1.0$, $\rho_A(0)=0.3$, $\rho_B(0)=0.5$]. For the case with $r_{AB}=1$, the reaction front is not displaced, but its width broadens as $t^{1/6}$ which is demonstrated by curve (c) of Fig. 2.

proaches zero, we find that $w(t)$ quickly saturates at a small value with significant fluctuations. It is then true that $\delta x_f(t) \sim t^{1/2}$, which is expected because in this limit Eq. (11) should be replaced by

$$\alpha - \tfrac{1}{2} = -\beta \ . \tag{16}$$

Combining Eqs. (16) and (11) one obtains $\alpha = 0$ and $\beta = \frac{1}{2}$.

To summarize, we have simulated, in two dimensions, a model of a diffusion-limited irreversible reaction $A + B \rightarrow C$ with A and B initially separated by a planar interface. The results of the simulations, which were done with both equal and unequal initial densities and diffusion constants, expressed through the probabilities P_A and P_B, support the scaling theory of Gálfi and Rácz, the latter being made for the particular case $D_A = D_B$ and with neglect of fluctuations in the reactants' concentrations and of the discrete character of the reactants. Hence we may conclude that fluctuations and the discrete nature of the system are not important and, for that matter, that the very assumption of scaling behavior is valid. We expect that these conclusions will carry over to the more physical case of three dimensions where fluctuations should be even less important.

ACKNOWLEDGMENTS

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[1] R. E. Liesegang, Naturwiss. Wochenschr. **11**, 353 (1986).

[2] D. Avnir and M. Kagan, Nature (London) **307**, 717 (1984), and references therein.

[3] B. Heidel, C. M. Knobler, R. Hilfer, and R. Bruinsma, Phys. Rev. Lett. **60**, 2492 (1988); B. Heidel and C. M. Knobler, Physica A **162**, 334 (1990).

[4] G. T. Gee, Phys. Rev. Lett. **57**, 275 (1986); J. Stat. Phys. **39**, 705 (1985).

[5] L. Gálfi and Z. Rácz, Phys. Rev. A **38**, 3151 (1988).

[6] B. Chopard and M. Droz, in *Cellular Automata and Modeling of Complex Physical Systems*, edited by P. Mannevill *et al.* (Springer-Verlag, Berlin, 1990), p. 130.