PHYSICAL REVIEW E VOLUME 57, NUMBER 2 FEBRUARY 1998

BRIEF REPORTS

Brief Reports are accounts of completed research which do not warrant regular articles or the priority handling given to Rapid Communications; however, the same standards of scientific quality apply. (Addenda are included in Brief Reports.) A Brief Report may be no longer than four printed pages and must be accompanied by an abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.

Early-time scaling for the reaction front of a ternary, $A+2B\rightarrow C$, reaction-diffusion system

Andrew Yen, Zhong-You Shi, and Raoul Kopelman
Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109-1055

(Received 21 July 1997)

We study the ternary $A+2B\rightarrow C$ reaction-diffusion process with initially separated reactants. A perturbation approach gives a scaling of the global reaction rate with $t^{1/2}$ at early time, followed by a crossover to $t^{-1/2}$ in the asymptotic time regime, a behavior which is the same as for the binary $A+B\rightarrow C$ reaction under initial segregation. Monte Carlo simulations are in good agreement with the predicted scaling.
[S1063-651X(98)01402-0]

PACS number(s): 82.40.−g

I. INTRODUCTION

We studied the early-time reaction front propagation of a ternary reaction-diffusion system under the initial segregation of reactants. Previously, such studies were limited to binary elementary reactions. The presence of such a reaction interface is characteristic of many processes in nature [1–5] and recently it became possible to study such processes for ternary reactions [6].

Galfi and Racz [7] considered a simple binary $A+B\rightarrow C$ reaction under initial segregation and developed their theory based on the assumption that the reaction-diffusion equations have a solution approaching an asymptotic scaling form. In the asymptotic regime, the center of the reaction front x_f and the width w of the front scale with time as $x_f\sim t^{1/2}$ and $w\sim t^{1/6}$, respectively, while the local production rate of C at x_f is proportional to $t^{-2/3}$. Their theory has been confirmed by experiments and computer simulations [8–11]. The early-time behavior of this system was studied by Taitelbaum *et al.* [12]. At very early times little reaction occurs before the reactants mix effectively; thus, the formation of C is treated as a small perturbation to the normal diffusion equation. It was found that both the global reaction rate and the reaction front grow as $t^{1/2}$.

The generalized and more complicated $nA+mB\rightarrow C$ reactions under initially separated reactant conditions were studied theoretically by Cornell, Droz, and Chopard [13,14]. They found the width of the reaction front to scale as $t^{n+m-1/2(n+m+1)}$ and the production rate of C at x_f, namely $R(x_f,t)$, to scale as $t^{-(n+m)/(n+m+1)}$, in the asymptotic regime. From the width and the local reaction-rate exponents it was concluded that the global reaction rate would decrease as $t^{-1/2}$, independent of n,m [9]. In this paper we first derive an early-time theory for the global reaction-rate exponent based on a perturbation theory for the $A+2B\rightarrow C$ system. We found the global reaction rate at early time to go as $t^{1/2}$, the same as for the $A+B\rightarrow C$ case. This is confirmed by Monte Carlo simulations, which also show that there is indeed a crossover from such an early-time behavior to the asymptotic-time behavior.

II. THEORY

The following set of diffusion equations describes the $A+2B\rightarrow C$ system under initial reactant segregation:

$$\frac{\partial a}{\partial t}=D_a\nabla^2 a-kab^2,$$
$$\frac{\partial b}{\partial t}=D_b\nabla^2 b-2kab^2, \tag{1}$$

where D_a and D_b are the diffusion coefficients for reactants a and b, and k is the microscopic reaction constant. The equations are subject to the initial reactant separation condition along the separation axis x,

$$a=a_0H(x),\quad b=b_0[1-H(x)], \tag{2}$$

where a_0 and b_0 are the initial concentrations and $H(x)$ is the Heaviside step function. The initial separation of reactants makes the system effectively one dimensional. In order to study the short-time behavior, we develop a perturbation theory based on the idea that reactive effects are small compared to diffusive effects.

To apply perturbation analysis, we reparametrized Eq. (1) in terms of dimensionless concentration and diffusion coefficients. First we write

$$\rho_a(x,t)=a_0\alpha(x,t),\quad \rho_b(x,t)=\beta_0(x,t), \tag{3}$$

where α and β are now dimensionless concentrations. Following Ref. [11] we also define two dimensionless constants in terms of diffusion constants and initial concentrations.

$$D=(D_a/D_b)^{1/2}, \quad r=(a_0/b_0). \tag{4}$$

At sufficiently early times, the mixing of A and B particles is minimal; consequently, the amount of product C will be small. We can approximate the early-time behavior by treating the reaction term as a perturbation to the diffusion equations. The perturbation parameter is denoted by

$$\varepsilon=k/(D_aD_b)^{1/2}. \tag{5}$$

We also introduce dimensionless time and space variables

$$\tau=ta_0b_0(D_aD_b)^{1/2}, \quad \xi=x(a_0b_0)^{1/2}. \tag{6}$$

Equation (1) can be rewritten in terms of the new variables as

$$\begin{aligned} \frac{\partial\alpha}{\partial\tau}&=D\frac{\partial^2\alpha}{\partial\xi^2}-\frac{\varepsilon}{r}\alpha\beta^2, \\ \frac{\partial\beta}{\partial\tau}&=\frac{1}{D}\frac{\partial^2\beta}{\partial\xi^2}-2\varepsilon\alpha\beta^2. \end{aligned} \tag{7}$$

For reaction-limited reactions, the reaction coefficient is small. Thus, the perturbation coefficient is small, i.e., $\varepsilon \ll 1$. We expand α and β in series

$$\alpha=\sum_{j=0}^{\infty}\alpha_j\varepsilon^j, \quad \beta=\sum_{j=0}^{\infty}\beta_j\varepsilon^j, \tag{8}$$

where α_0 and β_0 each satisfies an ordinary diffusion equation that is subject to the initial separation condition. The solution is given by

$$\alpha(\xi,\tau)=\Phi\left[\frac{\xi}{(2D\tau)^{1/2}}\right], \quad \beta(\xi,\tau)=1-\Phi\left[\xi\left(\frac{D}{2\tau}\right)^{1/2}\right], \tag{9}$$

where

$$\Phi(z)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{z}e^{-u^2}du. \tag{10}$$

The local reaction rate is defined as $R(x,t)=ka(x,t)b^2(x,t)$. We define the global reaction rate as

$$R(t)=\int_{-\infty}^{+\infty}R(x,t)\ dx. \tag{11}$$

The local reaction rate can be expanded in a series that goes as powers of ε. Useful information on the early-time behavior can be obtained from the lowest order of perturbation theory:

$$R(\tau)=a_0^{1/2}b_0^{2/3}(DaDb)^{1/2}\varepsilon[R_0+\varepsilon R_1+\cdots]. \tag{12}$$

From the lowest term in the expansion we find that

$$R_0(\tau)\sim\sqrt{\tau}. \tag{13}$$

From this perturbation approach we predict that for the $A+2B\rightarrow C$ reaction-diffusion system under initial segregation the global reaction rate will cross over from an early-time behavior given by $t^{1/2}$ to the asymptotic $t^{-1/2}$ behavior given by scaling arguments [13].

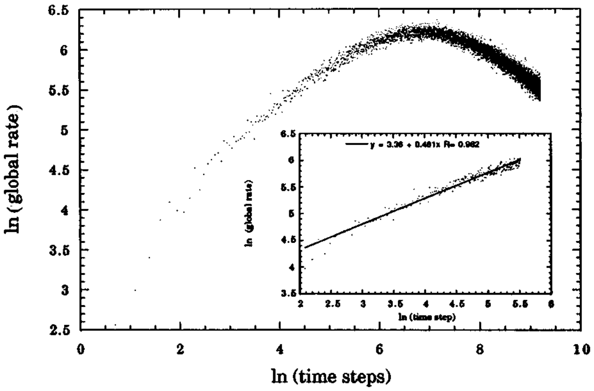

FIG. 1. Simulation result for ln (global rate) vs ln t. We fit the slope before and after the crossover. The slope before crossover is around 0.48 and after crossover is -0.45. Particle densities of 40% for A and 80% for B are placed at opposite sides of the origin at time 0. The diffusion coefficients are the same for A and B. We introduce a reaction probability of 0.001 for the $A+B\rightarrow AB$ step. The inset shows that the slope before crossover is 0.48, compared to 0.5 predicted by perturbation theory.

The above theory is based on a set of mean-field equations. In this approximation one neglects the fluctuations and assumes that the reaction term factorizes into the local densities of A and B. It has been shown by Cornell *et al.* [13] that for the $A+2B\rightarrow C$ reaction-diffusion system with initially separated reactants, the upper critical dimension is $d=2$. This result was confirmed by their cellular-automata (CA) algorithm for the long-time limit. We note that *strictly* one-dimensional cellular automata calculations made by Cornell *et al.* [13] for this $A+2B\rightarrow C$ reaction gave only *slight* deviations for the mean-field behavior. Our Monte Carlo simulations (below) are performed on a two-dimensional square lattice. Therefore, we expect these simulations to give mean-field results, which they do.

III. SIMULATIONS

We simulated the $A+2B\rightarrow C$ reaction-diffusion process, under the condition of an initial separation of reactants, on two-dimensional lattices. In order to check the early-time behavior, we use the ''intermediate'' approach where $A+B\rightarrow AB$ first and then $AB+B\rightarrow C$. For our simulation we introduce a reaction probability of 0.001 for the $A+B\rightarrow AB$ step. The global reaction rate is defined as the number of reactions that occurred on the lattice during a given time step. Figure 1 shows global rate vs time data on a log-log scale simulated on a square lattice (200×200) under initial reactant separation, using the Monte Carlo method. Particle densities of 40% for A and 80% for B are placed at opposite sides of the origin at time 0. The diffusion coefficients are the same for A and B. When A and B meet, an *intermediate* (AB) may be formed. Then, if the intermediate meets with a B particle they will react and leave the system. The result is averaged over 1000 runs. Figure 1 shows a clear crossover of the global reaction rate from a positive slope to a negative slope. We fit the slope before and after the crossover. Before crossover the slope is 0.48, which is close to 0.5, the result derived from perturbation (mean-field) theory. After crossover the slope is -0.48, which follows the asymptotic result obtained from scaling arguments. However, the main task for the simulation was the testing of the early-time regime, as there is overall agreement in the literature [13–14] concerning the asymptotic behavior. We note that the simulation would give a much better *asymptotic* behavior for a diffusion-limited reaction (reaction probability$=1$) [6].

IV. SUMMARY

Our mean-field perturbation theory predicts that for $A+2B\rightarrow C$, under initial separation of A and B, the global rate exponent should increase at early time as $t^{1/2}$ and then cross over to a universal $t^{-1/2}$ asymptotic behavior. Our Monte Carlo simulations show that with a small reaction probability (reaction-limited reaction), we indeed observe such a crossover of the global reaction rate. The results indicate that, for a reaction-limited reaction at early time, the kinetics do follow the mean-field perturbation-theory prediction of a $t^{1/2}$ behavior, which is the classical expectation based on the Einstein diffusion equation.

ACKNOWLEDGMENT

We appreciate support from NSF through Grant No. DMR-9410709.

[1] H. K. Henisch, *Crystals in Gels and Liesegang Rings* (Cambridge University Press, Cambridge, England, 1988).

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

[3] G. T. Dee, Phys. Rev. Lett. **57**, 275 (1986).

[4] B. Heidel, C. M. Knobler, R. Hilfer, and R. Bruinsma, Phys. Rev. Lett. **60**, 2492 (1988).

[5] K. F. Mueller, Science **225**, 1021 (1986).

[6] A. Yen and R. Kopelman, Phys. Rev. E **56**, 3694 (1997).

[7] L. Galfi and Z. Racz, Phys. Rev. A **38**, 3151 (1988).

[8] Y. E. Koo, L. Li, and R. Kopelman, Mol. Cryst. Liq. Cryst. **183**, 187 (1990).

[9] Y. E. L. Koo and R. Kopelman, J. Stat. Phys. **65**, 893 (1991).

[10] A. Yen, Y. E. L. Koo, and R. Kopelman, Phys. Rev. E **54**, 2447 (1996).

[11] Z. Jiang and C. Ebner, Phys. Rev. A **42**, 7483 (1990).

[12] H. Taitelbaum, S. Havlin, J. E. Kiefer, B. Trus, and G. Weiss, J. Stat. Phys. **65**, 573 (1991).

[13] S. Cornell, M. Droz, and B. Chopard, Physica A **188**, 322 (1992).

[14] S. Cornell, M. Droz, and B. Chopard, Phys. Rev. A **44**, 4826 (1991).