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Diffusion-reaction kinetics for $A + B(\text{static}) \rightarrow C(\text{inert})$ for one-dimensional systems with initially separated reactants

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We study analytically and numerically the reaction kinetics for diffusion-limited reactions of the type $A + B(\text{static}) \rightarrow C(\text{inert})$ in one-dimensional (1D) systems with reactants initially separated in space. We find expressions for the concentration profiles of each species, and for the reaction front. The width of the front is characterized by $w \sim t^{\alpha}$ with $\alpha = 1/4$, and its height by $h \sim t^{-\beta}$ with $\beta = 3/4$; these values differ from the "mean-field" exponents and from those obtained when both species diffuse.

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The dynamics of the reaction front observed in spatially inhomogeneous reaction systems of the form $A + B \rightarrow C(\text{inert})$ has attracted recent attention [1–8]. In these systems, the reaction takes place in the localized region where the two species meet. This region is "marked" by the production of species C and specifies the reaction front. More precisely, the reaction front $R(x,t)$ is defined as the average number of C particles produced at position x at time t. The time evolution of $R(x,t)$ is usually described by the exponents α and β that indicate how its width and height vary asymptotically with time.

From experiments [5] and simulations [2–5] of $d \geq 2$ systems in which both reactants diffuse, it has been found that the width of the front is characterized by $w \sim t^{\alpha}$ with $\alpha = 1/6$, and its height by $h \sim t^{-\beta}$ with $\beta = 2/3$, in agreement with the theory of Gálfi and Rácz [1] based on "mean-field" scaling arguments. However, numerical simulations of one-dimensional (1D) systems show that the width exponent appears to be $\alpha \simeq 0.3$ and the height exponent $\beta \simeq 0.8$ [3,6]. The origin of the difference between the exponents of 1D systems and those of higher-dimensional systems is not clear. In order to better understand this drastic change of behavior, we study analytically and numerically, for $d = 1$, the same reaction for the situation where only one of the reactant species moves. For this case we obtain $\alpha = 1/4$ and $\beta = 3/4$, which, as we shall argue, set lower bounds for the values of the exponents when both reactants diffuse.

We consider the diffusing reactant A to be located to the left of the origin and the static reactant B to the right, so that the interface separating both species is initially at $x = 0$. In the continuum approximation, the concentration of the A particles $c_A(x,t)$ is obtained as the solution of a Stefan problem [9]. From this solution, the position $r(t)$ of the boundary separating both species is found to move as $r = \gamma t^{1/2}$, where γ is a constant cho-

sen to satisfy the "Stefan condition." This continuum version does not describe what happens at small length scales, and the reaction front appears as a δ function at $r(t)$.

In order to gain insight into the microscopic dynamics of the reaction, we consider a discrete description of the problem. We concentrate on the leftmost B particle, which defines the position of the boundary between the two species. Since the B particles are static and "disappear" upon each reaction, we can describe the motion of the leftmost B particle as the motion of an imaginary particle that at each unit of time can either remain fixed with probability $1-p(x,t)$, or move to the right (when a reaction occurs) with probability $p(x,t)$. We assume that $p(x,t)$ can be written as

$$p(x,t)=\frac{\gamma}{2t^{1/2}}\left[1-2K\frac{x-\langle x\rangle}{\langle x\rangle}+\cdots\right]. \tag{1}$$

The first term of this expression arises from the average flux of particles at the boundary, as obtained from the continuum formulation of the problem. The second term is the lowest-order correction that accounts for the fact that if at a given time the leftmost B particle is to the right of its average position, more reactions than the average must have taken place. This gives rise to a depletion of the concentration near the boundary and a reduction of the flux, so in the next unit of time the probability of having a reaction is reduced. The converse is true if the leftmost B particle is to the left of its average position. Higher-order corrections are assumed to be negligible, and the constant K is used as a fitting parameter. This approach enables us to take into account the fluctuations in the position of the boundary that arise from the fluctuations inherent to the diffusive behavior of the A particles.

Next we calculate the exponents α and β that describe the asymptotic behavior of the width and height of the reaction front. Since the C particles appear only where a reaction occurs, we need to calculate the probability distribution of the position of the leftmost B particle using the probability to make a jump of Eq. (1). We begin by evaluating the central moments with respect to the average position $\langle x\rangle=\gamma t^{1/2}$. The variance of this distribution, $\sigma^2\equiv\langle(x-\langle x\rangle)^2\rangle$ also characterizes the width of the reaction front since $w\equiv\sigma$.

Using Eq. (1), we find that the conditional expectation value for $x^2(t+1)$ (the square of the position of the boundary at time $t+1$) given the position of the boundary at time t is

$$\langle x^2(t+1)|x(t)\rangle=x^2(t)[1-p(x,t)]+[x(t)+1]^2p(x,t). \tag{2}$$

Averaging over all values of $x(t)$, subtracting $\langle x(t)\rangle^2$ from both sides of the equation, and taking the continuous time limit leads to

$$\sigma^2=\frac{\gamma}{1+4K}t^{1/2}\equiv\mu t^{1/2}. \tag{3}$$

Note that the "linear" correction term in Eq. (1) only affects the value of the coefficient of $t^{1/2}$ in Eq. (3). A log-log plot of σ as a function of t from Monte Carlo (MC) simulations of the system (in which the initial concentration of each species was taken to be equal to 1) is shown in Fig. 1, from which we conclude that $\sigma\sim t^{0.250\pm0.004}$ in agreement with Eq. (3). The best fit of Eq. (3) with the numerical simulations is found for $K\simeq 2/3$.

An evaluation of the fourth central moment gives asymptotically $\langle(x-\langle x\rangle)^4\rangle\sim 3\langle(x-\langle x\rangle)^2\rangle^2$, so that for large times the probability distribution $P(x,t)$ to find the leftmost B particle at position x at time t can be approximated by a Gaussian. Using the Gaussian form we can calculate the reaction front $R(x,t)$, which is defined as the rate of reaction at position x and time t. Accordingly, we note that the changes in $P(x,t)$ are due to reactions, i.e., $P(x,t+1)-P(x,t)=R(x-1,t)-R(x,t)$ [10]. In the continuum limit, this yields

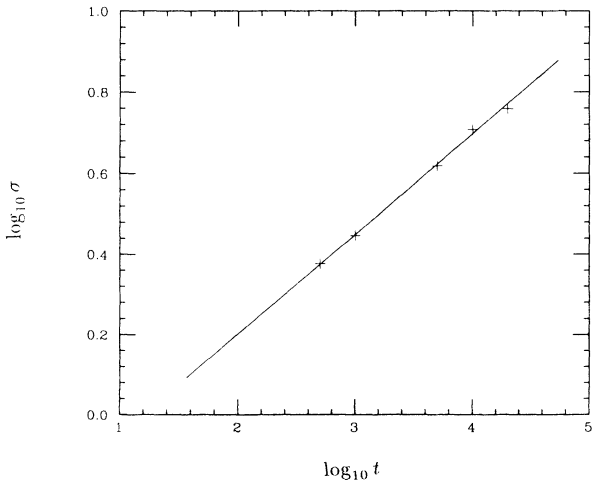

FIG. 1. Double-log plot of σ as a function of time. The best fit of the simulations to a straight line gives a slope of 0.250 ± 0.004.

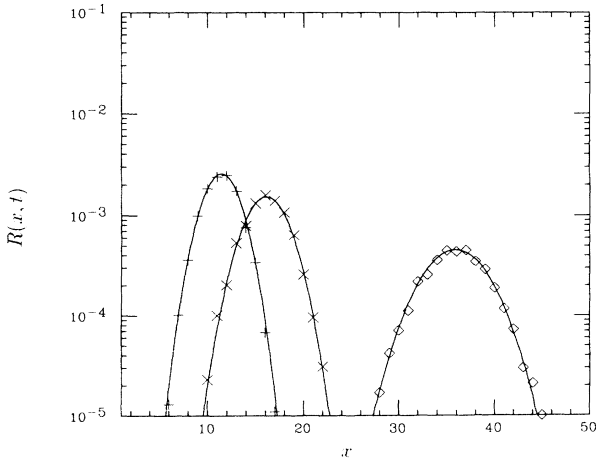

FIG. 2. Semi-log plot of the reaction front from MC simulations for $t=500$ (+), 1000 ($\times$) and 5000 ($\diamond$). The solid lines are the values obtained from Eq. (4) for the same values of time.

$$R(x,t) = \frac{1}{4t^{3/4}}\left(\frac{2\gamma^2}{\mu\pi}\right)^{1/2} \exp\left[-\frac{(x-\gamma t^{1/2})^2}{2\mu t^{1/2}}\right] \times \left[1+\frac{(x-\gamma t^{1/2})}{2\gamma t^{1/2}}\right]. \quad (4)$$

From Eq. (4) we see that the width exponent is $\alpha = 1/4$, a value smaller than the value $\alpha \simeq 0.3$ found for the case where both reactants diffuse, but larger than the mean-field value ($\alpha = 1/6$). From (4), we also see that the height exponent is $\beta = 3/4$. Note also that the center of the front moves in time as $\langle x \rangle = \gamma t^{1/2}$.

A comparison between Eq. (4) and the MC simulations is shown in Fig. 2. Since the flux of A particles into the reaction zone is proportional to $t^{-1/2}$, the two exponents α and β still satisfy one of the Gálfi and Rácz scaling relations $\alpha - \beta = -1/2$.

To further compare our results with MC simulations, we calculate the integral in time of the reaction front, which corresponds to the concentration profile of the C particles $c_C(x,t)$,

$$c_C(x,t) = \int_0^t R(x,\tau)d\tau = \frac{1}{2}\mathrm{erfc}\left(\frac{x-\gamma t^{1/2}}{\sqrt{2\mu t^{1/2}}}\right). \quad (5)$$

Figure 3 shows a plot of Eq. (5) and the numerical simulations for $t = 500, 1000, 5000$. The good agreement with the simulations supports our arguments. Note that the profile of the B particles is simply related to the profile of the C particles by $c_B(x,t) = 1 - c_C(x,t)$.

The difference between the values of the exponent α for this case where only one reactant moves ($\alpha = 1/4$), and the case in which both reactants diffuse ($\alpha \simeq 0.3$) can be understood qualitatively as follows. In the case in which one reactant is static, the width of the reaction front is solely a consequence of the fluctuations in the number of reactions that have taken place. Now consider the situation in which the B particles have a small but nonzero diffusion constant. Then, in addition to the fluctuations in the number of reactions, the width of the reaction front will have a contribution from the fluctuations in the position of the leftmost B particle, due to diffusion, that arise in the increasingly longer times between reactions. This contribution can only increase the width of the reaction front. Thus our result for the exponent $\alpha = 1/4$ must correspond to a lower bound for the more general case in which both species move.

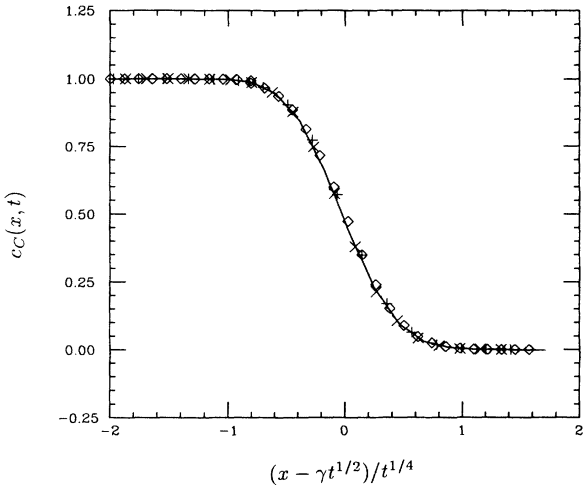

FIG. 3. Scaling plot of the integral in time of the reaction front as a function of $(x-\gamma t^{1/2})/t^{1/4}$, from MC simulations for times $t = 500$ (+), 1000 (×), and 5000 (◇). The solid line is obtained from Eq. (5).

For $d \geq 2$, the arguments and method used above for the 1D case do not hold for essentially two reasons: (a) even though one can define the leftmost B particle in each strip perpendicular to the "reaction plane," these do not necessarily pinpoint the interface between the reactants; and (b) the B particles are not necessarily reached by the A particles from the left, but can be reached in principle from any direction. Yet scaling arguments similar to those of Gálfi and Rácz suggest that if only one of the reactants diffuses, then the exponents characterizing the reaction front are $\alpha = 0$ (logarithmic in time for $d = 2$ [11]) and $\beta = 1/2$ [2].

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[1] L. Gálfi and Z. Rácz, Phys. Rev. A **38**, 3151 (1988).
[2] Z. Jiang and C. Ebner, Phys. Rev. A **42**, 7483 (1990).
[3] S. Cornell, M. Droz, and B. Chopard, Phys. Rev. A **44**, 4826 (1991).
[4] H. Taitelbaum, S. Havlin, J. Kiefer, B. L. Trus, and G. H. Weiss, J. Stat. Phys. **65**, 873 (1991); H. Taitelbaum, Y. E. Koo, S. Havlin, R. Kopelman, and G. H. Weiss, Phys. Rev. A **46**, 2151 (1992).
[5] Y. E. Koo, L. Li, and R. Kopelman, Mol. Cryst. Liq. Cryst. **183**, 187 (1990); Y. E. Koo and R. Kopelman, J. Stat. Phys. **65**, 893 (1991).
[6] M. Araujo, S. Havlin, H. Larralde, and H. E. Stanley, Phys. Rev. Lett. **68**, 1791 (1992).
[7] E. Ben-Naim and S. Redner, J. Phys. A **25**, L575 (1992).
[8] H. Larralde, M. Araujo, S. Havlin, and H. E. Stanley, Phys. Rev. A **46**, 855 (1992). See also the recent work by M. Araujo, S. Havlin, H. Larralde, and H. E. Stanley, Physica **191**, 168 (1992); S. Havlin, M. Araujo, H. Larralde, and H. E. Stanley, *ibid.* **191**, 143 (1992).
[9] J. Crank, *Free and Moving Boundary Problems* (Clarendon, Oxford, 1984).
[10] This expression is obtained by noting that an increase of $P(x,t)$ can only result from the occurrence of a reaction at $x-1$, while a decrease results from a reaction at x.
[11] J. Krug and P. Meakin, Phys. Rev. Lett. **66**, 703 (1991).