Scaling Anomalies in Reaction Front Dynamics of Confined Systems

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We study the kinetics of the reaction front for diffusion-reaction systems of the form $A + B \rightarrow C$ which are confined to one dimension, and in which the reactants are initially separated. For the case in which both A and B diffuse, the spatial moments of the reaction front are characterized by a hierarchy of exponents, bounded by the exponents $\sigma = 1/4$ and $\delta = 3/8$ characterizing the asymptotic time dependence of the distance $\ell_{AB}(t)$ between nearest neighbor A and B particles and the fluctuations of the midpoint $m(t)$ between them, respectively. We argue that this behavior arises from confinement effects and will appear in other confined systems.

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Diffusion-reaction systems of the form $A + B \rightarrow C$(inert) in which the reactants are initially separated in space have been the subject of many experimental and theoretical studies [1–13]. The behavior of the "reaction front" is well understood within a "mean field" theory when the dimension of the system is greater than or equal to 2 [5,7]. When the system is confined to one dimension, however, the correlations in the concentration fluctuations that arise from the confinement of the reactants invalidate the "mean field" assumptions. Thus, the question of how to describe such systems is still open.

The reaction front $R(x,t)$ is the localized region where the reaction takes place; it is defined as the average number of C particles produced at position x at time t. Most of the analytical results for the reaction front kinetics to date are based on the mean field assumption that the probability for a reaction to occur at a given time and place is proportional to the product of the average concentrations of the reactants [1]. This assumption leads to a scaling form for the reaction front $R(x,t) \sim t^{-\beta} f(|x|/t^{\alpha})$ with $\alpha = 1/6$ and $\beta = 2/3$.

Deviations from the mean field behavior of the reaction front appear in true 1D systems, due to correlations among the fluctuations associated with the diffusive motion of the reactant species. The correlations, which give rise to an unexpectedly complex behavior of the reaction front, arise from the confinement of the reactants upon a line, and may be present in other confined systems (i.e., quasi-one-dimensional systems and fractals).

In this paper we undertake the study of the kinetics of the reaction front for the limiting case of true 1D systems. We consider systems in which initially the A species is located to the left of the origin and the B species to the right. We assume that both species have the same diffusion constant, and we compare our results with the case in which one of them is static.

Though the correlations that arise from confinement effects will be present for any nonzero reaction probability, they are maximized when the reaction probability is 1. In this limiting case the presence of a particle of species A at position x precludes the possibility of finding particles of species B at any position to the left of x. We therefore focus on the situation in which the reaction probability is 1. Thus, in the systems we are considering, reactions can only take place between the rightmost A particle (RMA) and the leftmost B particle (LMB).

As the system becomes less confined, it becomes easier for particles to walk around each other without meeting. As the "thickness" of the systems goes to infinity, the correlations become negligible and the mean field assumption of uncorrelated overlapping concentrations becomes valid. This is what makes the mean field form of $R(x,t)$ valid only for systems whose dimension is $d \geq 2$, and explains why an expression for $R(x,t)$ in terms of the average reactant concentrations cannot be written for 1D systems.

To properly describe the systems we are considering, we use the fact that the only possibility of reaction is between the RMA and the LMB. We define the coordinate $m(t)$ to be the midpoint between the RMA and the LMB; $m(t)$ is closely related to the reaction front since every time a reaction occurs, it perforce must occur at a position given by $m(t)$. Thus, the fluctuations in the value of $m(t)$ will be an important contribution to the width of $R(x,t)$ [14]. The midpoint $m(t)$ may be defined for any system, but as the confinement increases, the connection between $m(t)$ and the reaction front becomes more significant.

To study the statistics of $m(t)$, we perform Monte Carlo simulations. The number of particles on each site is chosen from a Poisson distribution with the same concentration, $c_0 = 1$, for both species. We consider the case in which both reactants have the same diffusion constant $D_A = D_B = 1/2$, so that each particle can move to one of its neighbors with equal probability. At each unit step, we move the particles sequentially keeping track of the position of the RMA and LMB, $m(t)$ and ℓ_{AB}; then we check for the occurrence of reaction in the re-

gion LMB$\leq x \leq$RMA. Our simulations are for times up to 25 000 steps in systems whose size was big enough to guarantee that there are no finite size effects, averaging over 6000–15 000 configurations. We find that the moments of $m(t)$, $\xi(t) \equiv \langle m^q(t)\rangle^{1/q}$, scale with time as t^δ with $\delta \approx 3/8$ independent of q (see Fig. 1 for the data for $q = 2$).

The result $\delta = 3/8$ can be derived from the following scaling argument. In the absence of fluctuations, we expect that the concentration profiles of the reactants would be given by error functions vanishing at the origin, and, thus, in the vicinity of the origin they would be of the form $c(x,t) \sim x/t^{1/2}$. The fluctuations can be described by noting that up to time t, only the particles within a characteristic distance $\ell \sim t^{1/2}$ could have "participated" in the reaction; the actual number of A and B particles within this distance will be given by $n_i \sim t^{1/2} \pm c_1 t^{1/4}$ with $i = A, B$ (c_1 is a constant). Let us assume that there is a local majority of A particles so that the difference $n_A - n_B$ scales as $t^{1/4}$. This excess of A particles will "invade" the right hand side of the system, thus moving $m(t)$ to the right until they react with enough B particles to stop their advance. This will happen at a distance ξ from the center of the reaction front at which

$$t^{1/4} \sim n_A - n_B \sim \int_0^\xi c(x,t)dx \sim \frac{\xi^2}{t^{1/2}}, \tag{1}$$

from which we obtain

$$\xi \sim t^{3/8}. \tag{2}$$

In unconfined systems, these fluctuations cannot survive since the "invading particles" would be surrounded on all sides by the other reactant; this acts as a stabilizing effect that suppresses large fluctuations and it is weaker in confined systems. This stabilizing effect is absent in the systems we are considering. This provides a qualitative explanation for the larger width of the reaction front in 1D systems compared with higher dimensional systems.

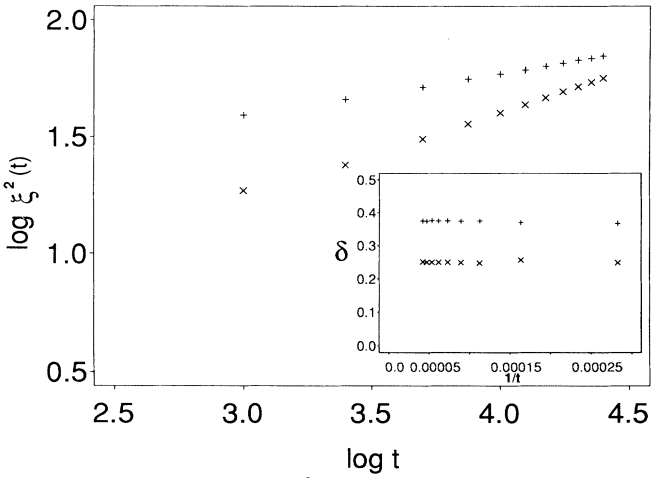

FIG. 1. Log-log plot of ξ^2 as a function of time for the case in which both species diffuse (+), and for the case in which one is static (×). Inset shows the exponent δ obtained as the slope between successive points of the curves as a function of $1/t$, from which we conclude that $\delta \sim 0.375$ when both reactants diffuse (+) and $\delta \sim 0.25$ when one is static (×).

Another quantity that is complementary to $m(t)$ in the characterization of $R(x,t)$ is the distance $\ell_{AB}(t)$ between the RMA and LMB. At time t, a reaction will occur at position $m(t)$ providing $\ell_{AB}(t) = 0$. A complete knowledge of the behavior of $m(t)$ and $\ell_{AB}(t)$ would suffice to determine the form of the reaction front [15]. We calculated $\ell_{AB}(t)$, and found that for all q, $\langle \ell_{AB}^q(t)\rangle^{1/q}$ scales as t^σ, with $\sigma \approx 1/4$ (Fig. 2). This result is also similar to that found by Weiss *et al.* [15] for a similar quantity in the one dimensional trapping reaction $A+B \to B$, where an initially randomly distributed ensemble of Brownian particles A diffuse in the presence of a single stationary trap.

We performed analogous calculations for the case where one of the reactants is static. We find numerically that in this case the two exponents coincide: $\delta = \sigma = 1/4$. Also, a scaling argument analogous to the case in which both reactions diffuse leads to the result $\delta = 1/4$, in agreement with previous results for this case [9].

Next we study the spatial moments of the reaction front for the case in which both reactant species diffuse. From the Monte Carlo simulations we measured the integral in time of the reaction front [which is the concentration profile $C_C(x,t)$ of the inert C particles]. Using this quantity, we can calculate the moments $\langle |x|^q\rangle^{1/q}$ of the reaction front:

$$\begin{aligned}\langle |x|^q\rangle &\equiv 2\frac{\int_0^\infty x^q R(x,t)dx}{\int_0^\infty R(x,t)dx} \\ &\sim t^{1/2}\frac{d}{dt}\int_0^\infty x^q C_C(x,t)dx \\ &\sim t^{\gamma_q - 1/2} \equiv t^{q\alpha_q}.\end{aligned} \tag{3}$$

Here we used the fact that the total number of reactions per unit time decays as $t^{-1/2}$ [1,3,5]. We find that the moments indeed have a power law dependence with time which we can write as

$$\langle |x|^q\rangle^{1/q} \sim t^{\alpha_q}. \tag{4}$$

Yet, while the distributions of both $m(t)$ and $\ell_{AB}(t)$ seemed to be describable in terms of single length scales, we notice that the moments of the reaction front do not follow a simple scaling relation. Indeed, the small moments, i.e., as $q \to 0$, appear to approach the value $\alpha_0 = 1/4$, whereas the higher moments appear to approach the value $\alpha_\infty = 3/8$ (Fig. 3). In particular the exponent of the second moment coincides with the value ($\simeq 0.3$) obtained in previous studies [5,7].

In Fig. 3 we also show the behavior in time of the suc-

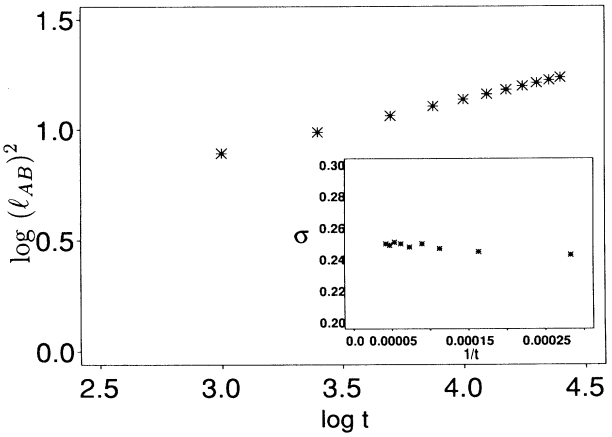

FIG. 2. Log-log plot of ℓ_{AB}^2 as a function of time for the case in which both species diffuse. Inset shows the exponent σ obtained as the slope between successive points of the curve as a function of $1/t$, which shows that $\sigma \sim 0.25$.

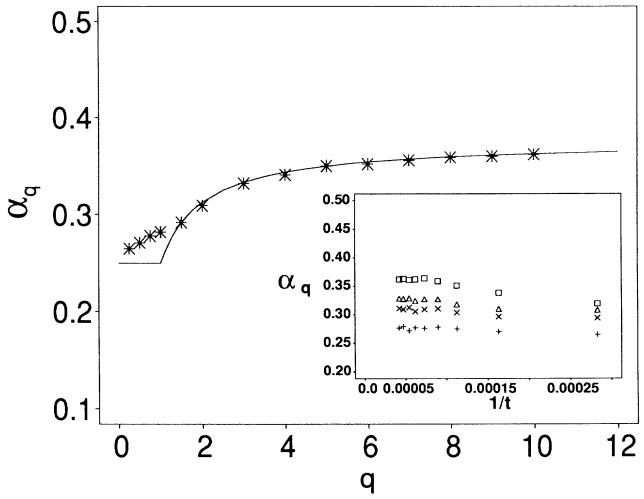

FIG. 3. Successive values of the exponents α_q which characterize the moments $\langle x^q \rangle^{1/q}$ of the reaction front obtained from extrapolation to infinite times for values of q ranging from 1/4 to 10. The solid line represents the theoretical prediction of Eq. (5). Inset shows α_q as a function of $1/t$ for $q = 1/2$ (+), 2 (×), 4 (△), 8 (□).

cessive slopes from pairs of points in a plot of $\log\langle |x|^q \rangle^{1/q}$ against $\log t$, from which we discard the possibility that there is a trend to either of the exponents, as would have happened in a "transient" situation, unless the transition occurs at extraordinarily long times. Finite size effects can also be discarded since they would cause a monotonic *decrease* of α_q as a function of q instead of the monotonic *increase* that is observed.

A qualitative argument for how each of the length scales affects the reaction front can be made by noting that when the midpoint is far from the origin, say to the right, then there is a high probability of there being a B particle near it. By definition of the midpoint, this implies that there is an A particle nearby as well, thus increasing the probability of having a reaction. Since the large-q moments probe the reaction front in the region in which reactions occur at large m, where the reaction becomes increasingly certain, these moments will approach the scaling behavior of the distribution of m. On the other hand, if the midpoint is near the origin, the rate of reaction will be controlled solely by the distribution of distances between the LMB and the RMA. Since the small-q moments probe the complete distribution evenly, and thus are dominated by the maximum of the distribution at the origin, we expect that $\langle |x|^q \rangle^{1/q}$ will scale as ℓ_{AB} for $q \to 0$. This argument provides some understanding for the limiting behaviors for the moments of the reaction front as $q \to 0$ and $q \to \infty$, yet it is far from explaining how the length scales "mix."

To explain quantitatively the behavior of α_q, we studied numerically the form of $R(x,t)$. Our data suggest that

$$\bar{R}(x,t) \equiv \frac{R(x,t)}{\int_0^\infty R(x,t)dx} \sim u^{-2} e^{-|u|/t^{1/8}}, \tag{5}$$

where $u = x/t^{1/4}$. Substituting this expression into Eq. (3) we obtain

$$\alpha_q = \begin{cases} 1/4, & q < 1, \\ 3/8 - (1/8q), & q \geq 1, \end{cases} \tag{6}$$

where for $q = 1$

$$\langle x \rangle \sim t^{1/4} \ln t.$$

Our results for $q \geq 1$ are in very good agreement with these theoretical predictions (see Fig. 3). However, for $q < 1$ our results are slightly larger than 1/4, which is probably due to not reaching the asymptotic limit [16].

In summary, in an attempt to find the correct description of the diffusion-reaction kinetics for true 1D systems, we have introduced two quantities which are closely related to the reaction front, $m(t)$, and ℓ_{AB}. We found that when both reactants diffuse, the reaction front appears not to be describable in terms of a single characteristic length, while the distributions of m and ℓ_{AB} are. The presence of "multiple scales" is reflected in the q dependence of the moments of the reaction front obtained from Monte Carlo simulations; that is $\langle |x|^q \rangle \sim t^{\alpha_q}$. We find that as $q \to 0$, $\alpha_q \to 1/4$, whereas, as $q \to \infty$, $\alpha_q \to 3/8$. These limits coincide with the values of the exponents that characterize the scaling of the nearest-neighbor distribution and the midpoint distribution, respectively. This situation contrasts with the case in which one of the reactants is static, for which ℓ_{AB} and the fluctuations of $m(t)$ scale in time as $t^{1/4}$ resulting in a reaction front for which $\alpha_q \equiv 1/4$ as expected [9].

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[14] There are differences between the distribution of $m(t)$ and the reaction front, the clearest being their "normalizations": since $m(t)$ is ever present, its distribution is normalized to unity, whereas the integral over space of $R(x,t)$ corresponds to the average number of reactions at time t and, thus, vanishes in time. As we will show later, the differences run much deeper.

[15] Note that the distance ℓ_{AB} can also be used as a measure of the "segregation" or separation of the reactants due to the diffusion-reaction process; see, e.g., G.H. Weiss, R. Kopelman, and S. Havlin, Phys. Rev. A **39**, 466 (1989); S. Redner and F. Leyvraz, J. Stat. Phys. **65**, 1043 (1991).

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