Steady-State Reaction-Diffusion Front Scaling for $mA+nB \rightarrow$ [inert]

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We study the front formed by the reaction $mA+nB \rightarrow$ [inert] between opposing currents of A and B, as a function of current density $J(\rightarrow 0)$, diffusion constant D, and reaction constant k. We show that the critical dimension is $d_c = 2/(m+n-1)$, above which mean-field theory is valid. Below d_c, $J \rightarrow 0$ is equivalent to $k \rightarrow \infty$. Consistency arguments give exact predictions for the scaling exponents when $d < d_c$. Our results apply also to the case of a front that moves or grows with time, or where the diffusion constants differ.

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There are many physical, chemical, and biological systems where two diffusing species react irreversibly on contact. The most common situation is the bimolecular reaction $A+B \rightarrow 0$, where one molecule of the species A reacts with one molecule of the species B [1]. Classically, such processes are described by mean-field-like reaction-diffusion equations, where the rate of reaction of the two species is assumed proportional to the product of the average densities of the two species. Recently, however, much attention has been focused upon the deviations from mean-field behavior arising from the microscopic fluctuations in the densities, and the correlations so caused [2–6]. One situation that has provoked much interest starts with the two species initially separated in space, so that they react in a confined zone which grows with time [3–13]. The inert reaction products are assumed to precipitate out, and hence not to have any further interaction with the A and B particles. Under these conditions, the reaction profile $R(x,t)$ (number of reactions occurring per unit time per unit volume at a distance x from the initial boundary between the species) is seen to exhibit scaling behavior [7] of the form

$$R(x,t) \propto t^{-\beta}\Phi\left(\frac{x}{t^{\alpha}}\right), \tag{1}$$

provided $x \ll t^{\frac{1}{2}}$. The scaling exponent α appears to assume its mean-field value [7] $\alpha = \frac{1}{6}$ in dimension greater than 2 [3,8,9], whereas data from Monte Carlo and probabilistic cellular automata (CA) simulations in one dimension suggest a value closer to $\alpha \approx 0.30 \pm 0.01$ [3,5].

The more general case of the higher-order reaction $mA+nB \rightarrow 0$, where a reaction event requires m particles of type A to coincide with n particles of type B, is equally important in chemical physics. Such reactions may describe catalysis [14], or lead to rich complex behavior such as Turing pattern formation [15]. In previous publications [3,4], we found an inconsistency between simple nonexact microscopic arguments and our CA simulations in predicting the scaling exponents for a front formed in such a system.

A convincing evaluation of the critical dimension, and the reason for departure from mean-field behavior, has so far eluded investigation.

In this Letter, we study the scaling behavior of the front formed in the steady state reached by imposing antiparallel current densities (henceforth just "currents") $J_A = m|J|$ and $J_B = -n|J|$ of A and B particles at $x = -\infty$ and $x = +\infty$, respectively. This situation is much easier to investigate, since the front is no longer time dependent and there are only three relevant parameters (J, diffusion constant D, reaction constant k). However, the results for the scaling exponents and critical dimension may be directly applied to the time-dependent case, where the front is formed quasistatically by currents $\propto t^{-\frac{1}{2}}$ [16]. We find the surprising result that dimensional analysis, coupled with consistency arguments, is sufficient to show that the critical spatial dimension is $d_c \equiv 2/(m+n-1)$. Above d_c, the scaling limit $J \rightarrow 0$ is equivalent to the mean-field limit $k \rightarrow 0$. For $d < d_c$ scaling is equivalent to $k \rightarrow \infty$, and we find an exact prediction that corresponds to $\alpha = \frac{1}{4}$ in the time-dependent case for $d = 1$, $(m,n) = (1,1)$. We suggest that the higher values obtained elsewhere [3,5] are due to short-time effects. We confirm our results by high-precision CA simulations in dimensions 1, 2, and 3. Incidentally, our results appear to be the first published computer simulations for a reaction front in $d = 3$.

In a microscopic description, the A and B particles perform random walks (described by a diffusion constant D) with a short-ranged interaction whose sole effect is to cause reaction. Using particle density operators $\hat{a}$ and $\hat{b}$, we represent the reaction in a pointlike way as $R = k\langle \hat{a}^m \hat{b}^n \rangle$, where $\langle \cdots \rangle$ is an ensemble average and k is the reaction constant. Our CA model [4] is one realization of such a system. The boundary conditions are $a(-x) \rightarrow (mJx/D)$, $a(x) \rightarrow 0$, $b(x) \rightarrow (nJx/D)$, and $b(-x) \rightarrow 0$ as $x \rightarrow \infty$ (where $a \equiv \langle \hat{a} \rangle$, $b \equiv \langle \hat{b} \rangle$); i.e., the currents are balanced so that the front is stationary. In the steady state, the equations of motion may be written as

$$\frac{D}{m}\partial_x^2 a = R = \frac{D}{n}\partial_x^2 b \tag{2}$$

(see, e.g., [3]). In the limit $J \rightarrow 0$, the densities are low

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and the profiles are characterized by a single length scale w, the *reaction width*:

$$R = \frac{J}{w}\phi\left(\frac{x}{w}\right), \tag{3}$$

$$a = \frac{wJ}{D}A\left(\frac{x}{w}\right), \tag{4}$$

$$b = \frac{wJ}{D}B\left(\frac{x}{w}\right), \tag{5}$$

which defines ϕ, A, and B. We justify (3)–(5) *a posteriori* from mean-field analysis and simulations. The prefactors are chosen to satisfy (2) and the boundary conditions.

We suppose that w is a function of J, k, and D only. The scaling regime $w \to \infty$, corresponding to the long-time behavior for the time-dependent problem, is therefore reached in the limit $J \to 0$, and for some limit of k and D—either zero or infinity, or both, as we do not expect there to be any critical value of either of these quantities. We define exponents λ, μ, and ν from the asymptotic behavior of w in the scaling limit

$$w = \frac{D^\lambda}{k^\mu J^\nu} \tag{6}$$

(up to a numerical prefactor, which we include instead in the definitions of A, B, and ϕ). In the time-dependent case, $J \sim t^{-\frac{1}{2}}$, so we equate $\nu = 2\alpha$. For the moment, we restrict ourselves to the case where the front is stationary and the diffusion constants are the same for the two species, though we shall later argue that these conditions may be relaxed without altering the exponents.

Mean-field theory.—The mean-field hypothesis is $\langle \hat{a}^m \hat{b}^n \rangle = a^m b^n$ [3]. The case $(m,n) = (1,1)$ was considered first by Ben-Naim and Redner [17]. We treat general m and n. Writing $R = ka^m b^n$, and using the dimensionless variables $\tilde{x} = x/w_{\rm mf}$, $\tilde{a}(\tilde{x}) \equiv a(x)(D/w_{\rm mf}J)$, and $\tilde{b}(\tilde{x}) \equiv b(x)(D/w_{\rm mf}J)$, where

$$w_{\rm mf} \equiv \left(\frac{D^{m+n}}{kJ^{m+n-1}}\right)^{\frac{1}{m+n+1}}, \tag{7}$$

Eq. (2) may be written in the form

$$\frac{1}{m}\tilde{a}''(\tilde{x}) = \tilde{a}^m\tilde{b}^n = \frac{1}{n}\tilde{b}''(\tilde{x}). \tag{8}$$

The boundary conditions become $\tilde{a}(-\tilde{x}) \to m\tilde{x}$, $\tilde{a}(\tilde{x}) \to 0$, $\tilde{b}(-\tilde{x}) \to 0$, and $\tilde{b}(\tilde{x}) \to n\tilde{x}$ as $\tilde{x} \to \infty$, so $\tilde{a}$ and $\tilde{b}$ depend on J, k, and D through $\tilde{x} \equiv x/w_{\rm mf}$ only. Comparing (4) and (5) with the definitions of $\tilde{a}$ and $\tilde{b}$ in terms of a and b, we identify $\tilde{a}$ and $\tilde{b}$ as A and B and $w = w_{\rm mf}$ (up to a numerical prefactor). Combining (6) and (7) gives a value for ν that, since $\nu = 2\alpha$, is equivalent to the results of Ref. [3].

As $x \to \infty$, the asymptotic decay of the A-particle profile may be found from $\partial_{\tilde{x}}^2\tilde{a} \approx mn^n\tilde{a}^m\tilde{x}^n$, giving

$$a(x) \sim \begin{cases} \exp(-\sigma x^{1+\frac{n}{2}}) & \text{for } m = 1 \\ x^{-\frac{n+2}{m-1}} & \text{for } m > 1 \end{cases} \quad \text{as } x \to \infty, \tag{9}$$

where σ is a constant.

The total reaction rate $\int R\,dx (= J)$ always exists, and, even though the moments of R do not always exist (one of the steady-state particle profiles even being nonintegrable for $|m-n| \geq 3$), the existence of scaling solutions of the form (9) has been proved in the time-dependent case [18,19]. In a typical experimental situation, the reaction profile will agree with its theoretical steady-state value up to a distance $\sim (Dt)^{\frac{1}{2}}$ from the origin, so we expect to observe deviations only when a particle profile varies as a power law.

Beyond mean-field.—We assume that the scaling behavior (3)–(5) persists (in some limit) when microscopic fluctuations are taken into account. Although we cannot solve the model explicitly, dimensional analysis and the scaling hypothesis shall give us sufficient information to determine the scaling exponents.

The dimensions of the three relevant parameters (in terms of length L and time T) are

$$[J] = L^{-(d-1)}T^{-1}, \qquad [D] = L^2T^{-1}, \qquad [k] = L^{d(n+m-1)}T^{-1}. \tag{10}$$

There is therefore only one independent dimensionless combination of these quantities, which without loss of generality we write in the form

$$u = \frac{D^{d(m+n)-1}}{k^{d+1}J^{d(m+n-1)-2}}, \tag{11}$$

and any quantity of dimension length may in general be written in the form $w = w_{\rm mf}f(u)$. Consistency with (6) requires $f \sim u^\gamma$ in the scaling limit, leading to

$$w = \frac{D^{\frac{m+n}{m+n+1}+\gamma[d(m+n)-1]}}{k^{\frac{1}{m+n+1}+\gamma[d+1]}J^{\frac{m+n-1}{m+n+1}+\gamma[d(m+n-1)-2]}}. \tag{12}$$

This form is immediately interesting, because, at spatial dimension $d = d_c \equiv 2/(m+n-1)$, u is independent of J and so all length scales vary as $J^{\frac{m+n-1}{m+n+1}}$. For $(m,n) = (1,1)$, this critical dimension is $d_c = 2$, confirming the results of Ref. [3], where we argued that, in this dimension, two different length scales both scale in the same way with time (current). For $(m,n) = (1,2)$, the critical dimension is $d_c = 1$, showing that the arguments for this case in Ref. [3] [which gave d_c=2 independently of (m,n)] are indeed invalid in this case. For $(m,n) = (2,2)$ and above, the critical dimension is less than 1. In Ref. [4], simulations for $d = 1$, $(m,n) = (1,2)$ and (2,2) found exponents $\alpha = 0.28$ and 0.35, respectively, a little higher than the mean-field values $\frac{1}{4}$ and $\frac{3}{10}$, probably due to insufficiently long times in the simulations.

We further assume that $\langle \hat{a} \rangle^m \langle \hat{b} \rangle^n \geq \langle \hat{a}^m \hat{b}^n \rangle$, since the reaction introduces anticorrelations between the species. Using (3)–(5), we find that $f(u) = u^\gamma \geq 1$. Using (11) in the scaling limit $J \to 0$, this implies $\gamma(d - d_c) \geq 0$. We consider three cases.

Above critical dimension ($d > d_c$).—Here, $\gamma \geq 0$, so

the scaling limit is $u \to \infty$, which may also be reached by $k \to 0$. However, in this limit, we expect that mean-field results should hold, so λ, μ, and ν should take their mean-field values. To confirm this, we have performed CA simulations of the reaction $(m,n) = (1,1)$ in $d = 3$. Lattice sizes between $[64 \times 128 \times 128]$ and $[256 \times 128 \times 128]$ were used. The current was varied over a range 1–2^7 (equivalent to simulations of the time-dependent case over five decades of t), and for each value of J measurements were averaged over several hundred thousand time steps. Figure 1 shows a log-log plot of w (obtained from the second moment of R) vs J, the straight line being a least-squares fit to the last five points of gradient 0.339 ± 0.001. Given that the gradient is still decreasing as J decreases, this agrees well with the mean-field prediction $\frac{1}{3}$. A scaling plot for R using the exponent $\nu = \frac{1}{3}$ may be found in Fig. 2. We found that $R = kab$ to within 1%, so we did not run simulations of different values of k or D as this result necessarily implies mean-field behavior.

Below critical dimension ($d < d_c$).—Here $\gamma \leq 0$. The case $\gamma = 0$ corresponds to mean-field behavior, which we expect to be valid as $k \to 0$. For $\gamma < 0$, the scaling regime is approached as $u \to 0$ and hence as $k \to \infty$. This implies $\mu \leq 0$, but $\mu < 0$ is unphysical, since w cannot decrease as k decreases. Hence $\mu = 0$, which from (12) gives $\nu = 1/(d+1)$. We henceforth consider only $(m,n) = (1,1)$ in $d = 1$, being the only physically realizable situation for integral dimension $d < d_c$. $\nu = \frac{1}{2}$ is equivalent to $\alpha = \frac{1}{4}$ in the time-dependent case, equal to the value found when one of the species is stationary [6], and also to the lower bound found in Ref. [3]. This gives $w = (D/J)^{\frac{1}{2}}$, which is a measure of the typical closest A-B separation as $k \to \infty$ (see [2,3]), as has been observed elsewhere in Monte Carlo simulations [10]. It is reasonable that the reaction width should approach this value as $k \to \infty$.

How does the system interpolate between these two limits? The B-particle profile grows as $x \to \infty$. The fluctuations in this profile will be proportional to $b^{\frac{1}{2}}$, and so we expect that, at sufficiently large distances, $\langle \hat{a}\hat{b} \rangle = \langle \hat{a} \rangle \langle \hat{b} \rangle + \langle \hat{a}(\hat{b} - \langle \hat{b} \rangle) \rangle \approx \langle \hat{a} \rangle \langle \hat{b} \rangle$. The profile therefore has a mean-field-like behavior at sufficiently large distances. To estimate the distance beyond which mean field should be valid, consider an A particle in a region where the B particle density is b. Within mean field, the lifetime of the A particle is $(kb)^{-1}$, during which time it will have moved a distance $\sim (D/kb)^{\frac{1}{2}}$. For the mean-field theory to be consistent, this region must contain a large number of B particles so that the relative fluctuations are small. Since $b = (J|x|/D)$, we find that the mean field is valid for $|x| \gg \ell \equiv (k/J)$. Hence, the limit $u \to 0$ has $\ell \gg (D/J)^{\frac{1}{2}} \gg w_{\mathrm{mf}}$, while $u \to \infty$ gives $\ell \ll w_{\mathrm{mf}}$. The non-mean-field behavior is therefore observed as $u \to 0$, corresponding to $k \to \infty$ or $J \to 0$ (i.e., $t \to \infty$ in the time-dependent case), while behavior is pure mean field for $u \to \infty$, e.g., for $k \to 0$ with J fixed. In the time-dependent case, $\ell \sim t^{\frac{1}{2}}$, and so $x \gg \ell$ is in the region where b is constant; the mean-field limit does not exist in this case.

We have performed simulations for $(m,n) = (1,1)$ in $d = 1$, for lattices of size 128 to 1024. The current was varied by a factor of 2^8, with $D = \frac{1}{2}$, averaging over 32 independent runs of several tens of millions of time steps each. In our simulations, we were only able to study cases where $x \ll \ell$, so we expect to be well outside the mean-field region. A log-log plot of w vs J is to be found in Fig. 1, together with a scaling plot for R. The straight line is a least-squares fit of gradient $\nu = 0.497 \pm 0.008$. Changing k by a factor $\frac{1}{2}$ or $\frac{1}{4}$ did not change R noticeably, and when the diffusion constant was changed to $D = \frac{1}{6}$ the profile again rescaled appropriately. A plot of $RJ^{-(1+\nu)}$ as a function of xJ^{ν} may be found in Fig. 2, showing good scaling collapse for $\nu = \frac{1}{2}$.

At the critical dimension ($d = d_c$).—In this case, the above arguments do not constrain the D and k exponents. We expect again, however, that the limit $k \to 0$ should again yield mean-field exponents, while the question of whether the limit $k \to \infty$ may yield a different scaling

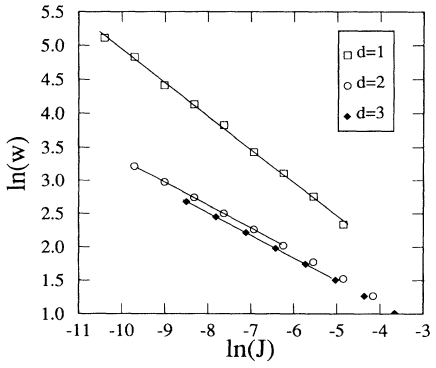

FIG. 1. Natural logarithm of the reaction width as a function of natural logarithm of the current density for the reaction $A + B \to 0$ in dimensions $d = 1$, 2, and 3.

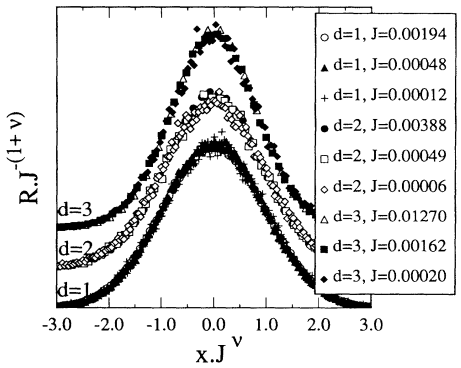

FIG. 2. Rescaled reaction profile for the diffusion-limited reaction $A + B \to 0$ in dimensions $d = 1$, 2, and 3, using $\nu = \frac{1}{2}$, $\frac{1}{3}$, and $\frac{1}{3}$, respectively. The profiles for $d = 2$ and $d = 3$ have been shifted vertically for clarity.

behavior is undetermined. It is plausible that for $d = 1$ and $(m, n) = (1, 2)$, the reaction width should again have the A-B particle distance as a lower bound, implying that as $k \to \infty$ the reaction width approaches $(D/J)^{\frac{1}{2}}$, the same value as for $(m, n) = (1, 1)$.

We have simulated the reactions (1,1) in $d = 2$ and (1,2) in $d = 1$. In the first case, we observed $R \to k\langle ab\rangle$ in the limit $k \to 0$. Figure 1 shows a log-log plot of w as a function of J. The straight line is a least-squares fit to the last five points, having gradient $\nu = 0.344 \pm 0.002$, though the gradient is successively decreasing, consistent with a slow approach to the mean-field exponent $\nu = \frac{1}{3}$. A scaling plot for R, using the mean-field exponent $\nu = \frac{1}{3}$, may be found in Fig. 2. R was found to approach kab as k was decreased, suggesting full mean-field behavior in this limit. The case (1,2) in $d = 1$, however, gave much less conclusive results. Although an analysis of the reaction profile for $x > 0$ was consistent with $\nu = \frac{1}{2}$, the power-law tail of the B particles was prone to slow equilibration and significant finite-size effects. A thorough investigation of this situation requires very high computing power.

Finally, we discuss the case of differing currents and diffusion constants. Suppose we have $(J_A/J_B) = \text{const} \neq -(m/n)$, $J_A J_B = J^2$. In the "steady" state the front will move through space at a constant velocity $v \propto J$. The particle profiles far away from the reaction zone are found by solving the diffusion equation with the condition $a = b = 0$ at a point moving with velocity v, finding v from the condition that the gradients of the profiles be in the ratio $-(n/m)$ at this point. These gradients are the total number of particles reacting per unit cross sectional area per unit time. The profile will be linear on a length scale proportional to J^{-1}, and so the quasistatic approximation is again valid since (i) the real profiles differ from the above Stefan problem only within $\sim w \propto J^{-\nu} (\ll J^{-1})$ of the front and (ii) the equilibration time of the front w^2/D is much smaller than the time w/v for the front to move over a distance w. The results for the stationary front will therefore hold for the scaling exponents as $J \to 0$. If the diffusion constants differ, we have to include a further variable D_A/D_B in our scaling theory. If this ratio is kept at a constant value (neither infinite nor zero) we expect the shape of the scaling profile to differ, but since the above arguments consider the J and k dependence only we do not expect the results of this paper for μ and ν to differ.

We shall discuss our results more fully in a future publication [20], where we shall explain our simulation methods and present further work on the properties of the reaction front, especially for the case $d = d_c$. We are also investigating the applicability of the above arguments to the case of a fractal substrate.

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