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Properties of the reaction front in an $A+B \rightarrow C$ type reaction-diffusion process

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We study the motion of a reaction front formed by a process, $A+B \rightarrow C$, in which the reagents are transported by diffusion and the reaction kinetics is of second order. A scaling description valid in the long-time limit is derived analytically, and it is found that the center (x_f) and the width (w) of the front scale with time as $x_f \sim \sqrt{t}$ and $w \sim t^{1/6}$, while the production rate of C at x_f is proportional to $t^{-2/3}$.

The presence of a reaction front is a characteristic feature of a variety of physical, chemical, and biological processes. For example, a chemical-reaction-type process $A+B \rightarrow C$ exhibits a front (i.e., a spatially localized region where the production of C is nonzero) provided the diffusing reagents A and B are initially separated in space. Interest in these fronts has increased recently since it has been realized that pattern formation in the wake of a moving front is a quite general phenomenon.[1,2] A classic case associated with the $A+B \rightarrow C$ reaction is the Liesegang-band formation[3] which is thought to be a complex process of interplay between the dynamics of the reaction front and the nucleation kinetics of the precipitate (C). Another much studied example where a reaction-diffusion front produces nontrivial structure is the diffusion-limited aggregation.[4] In that case, one of the species (B) plays the role of the precipitate ($C=B$) while the density of the other reagent (A) is negligibly small.

It is quite clear that the first stage in understanding pattern formation in the processes discussed above is the description and calculation of the properties of the reaction zone, i.e., answering the question of where and at what rate the reaction product C appears. This question has been studied for a long time. Simplified theories of Liesegang-band formation derive the pattern from the properties of the front alone[5] and phenomenological theories of diffusion-limited aggregation[6] rely on some unproven and often contradictory assumptions about the screening length which is the width of the reaction front. Unfortunately, most of the works in these fields consist of numerical simulations[7] and a convincing answer to the above question has not been found.

In view of the scarcity of analytical results about the reaction zone, here we study in detail a reaction process $A+B \rightarrow C$ in which the transport kinetics of the reagents is dominated by diffusion and the reaction kinetics is of second order. Our aim is to present an analytical calculation of the spatial distribution of the production rate of C.

The mathematical description of the process we consider is given by the set of reaction-diffusion equations

$$\dot{a} = D_a \Delta a - kab, \tag{1}$$

$$\dot{b} = D_b \Delta b - kab, \tag{2}$$

where the concentrations of the reactants A and B are denoted by a and b, respectively, D_a and D_b are the corresponding diffusion constants, and the reaction rate parameter is k. As an initial condition, we choose the reagents to be separated with constant densities for both $x<0$ ($a=a_0$ and $b=0$) and $x>0$ ($a=0$ and $b=b_0$). For this choice of initial state, the solution of (1) and (2) depends only on the x spatial coordinate at all times, t, i.e., the system effectively becomes one dimensional. Denoting the solution by $a(x,t)$ and $b(x,t)$, the production rate of C which is the object of our investigation is obtained through $R(x,t)=ka(x,t)b(x,t)$. Our main result is that $R(x,t)$ assumes the scaling form in the large time limit

$$R(x,t) = ka(x,t)b(x,t) \sim t^{-\beta} F\left(\frac{x-x_f}{t^{\alpha}}\right), \tag{3}$$

where the position of the center of the front, x_f, scales with time as $x_f \sim \sqrt{t}$ (if $a_0=b_0$ the front does not move and $x_f=0$), the width of the reaction front is proportional to t^{α} with $\alpha=\frac{1}{6}$, and the scaling exponent of the production rate of C at $x=x_f$ is $\beta=\frac{2}{3}$.

In order to make the mathematics more transparent, we shall simplify the calculation of $R(x,t)$ by assuming that the diffusion constants are equal, $D_a=D_b=D$. The derivation can be carried through for the case of $D_a \neq D_b$ and the conclusions about the scaling properties of the reaction front [Eq. (3)] and about the numerical values of the exponents are not changed. The ratio D_a/D_b is an irrelevant variable in the sense of critical phenomena, it plays a role only in producing some unimportant shape corrections in the scaling function $F(z)$.

A simplifying feature of the $D_a=D_b$ assumption is that by measuring length, time, and particle density in units of $l=\sqrt{D/(ka_0)}$, $\tau=1/(ka_0)$, and a_0, respectively, we eliminate all the material constants and the only control parameter left in the problem is $q=b_0/a_0$. A more important consequence of the $D_a=D_b$ choice is that after subtracting (2) from (1), one obtains a diffusion equation for $u=a-b$. It can be solved with the appropriate initial condition ($u=1$ for $x<0$ and $u=-q$ for $x>0$) and the result is given by

$$u(x,t) = a-b = \frac{1-q}{2} - \frac{1+q}{2} \operatorname{erf}\left(\frac{x}{2\sqrt{t}}\right) \tag{4}$$

where $\operatorname{erf}(x)$ is the error function.[8] Two points are important about this solution. The first one is that the width of the depletion zone (W_d) defined as the region where a and b are significantly smaller than their initial values (Fig. 1) scales with time as $\sqrt{t}$. The second one follows from the observation that the production rate of C is expected to be largest in the region where $a \approx b$ (Fig. 1). Thus, Eq. (4) can be used to determine a reference point (x_f) in the reaction zone which we shall call the center of the reaction zone, by requiring that $a(x_f,t) = b(x_f,t)$. From $u(x_f,t) = 0$, the time dependence of x_f is found to be

$$x_f = \sqrt{2D_f t}\,, \qquad (5)$$

where the "diffusion constant" of the front D_f is determined from the equation erf $(\sqrt{D_f/2}) = (1-q)/(1+q)$. It should be noted that the results embodied in Eqs. (4) and (5) are well known for the case of an infinitely thin reaction zone.[9]

Substituting Eq. (4) into Eq. (1), a nonlinear partial differential equation is obtained,

$$\dot{a} = a'' - a^2 + ua\,, \qquad (6)$$

which we are unable to solve in general. The derivation of the scaling form (3) is nevertheless possible if we make the assumption that the width of the reaction front w increases with time not faster than t^α where $\alpha < \frac{1}{2}$. In other words, this assumption means that in the long time limit, the width of the reaction zone is negligible compared to the width of the depletion zone ($w \ll W_d$). A justification for this assumption comes from the numerical solution of Eqs. (1) and (2) (Fig. 1) where one finds that w, which is defined through the second moment of $R(x,t)$

$$w^2 = \frac{\int_{-\infty}^{\infty}(x-x_f)^2R(x,t)dx}{\int_{-\infty}^{\infty}R(x,t)dx}\,, \qquad (7)$$

scales with time as $w \sim t^\alpha$ and $\alpha \approx \frac{1}{6}$. An *a posteriori* justification is the self-consistency of our result $\alpha = \frac{1}{6}$ with the above assumption.

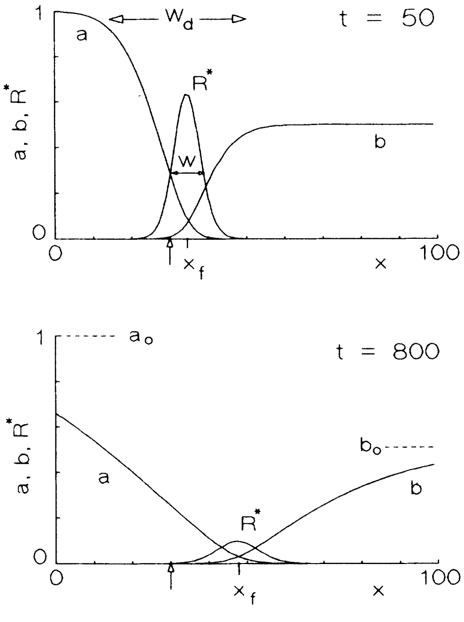

FIG. 1. Numerical results for Eqs. (1) and (2) demonstrating that the width of the depletion zone (W_d) increases with time much faster than the width of the reaction zone (w). Length (x), time (t), the densities (a,b) of the reagents (A,B), and the magnified production rate ($R^* = 100R = 100kab$) of C are all dimensionless since they are scaled by l, τ, a_0, and a_0/τ, respectively [for definition of these quantities see discussion preceding Eq. (4)]. As an initial condition, we used: $a = 1$, $b = 0$ for $x < 30$, and $a = 0$, $b = 0.5$ for $x > 30$ (the $t = 0$ position of the center of the front, x_f is shown by an arrow).

Once $w \ll W_d$ is assumed, we may expand $u(x,t)$ around x_f and keep only the first term in the expansion

$$u(x,t) \approx -K(x-x_f)/\sqrt{t}\,, \qquad (8)$$

where K is given by $K = (1+q)\exp(-D_f/2)/(2\sqrt{\pi})$. The terms neglected in Eq. (8) are of the form $(a_n/n!)[(x-x_f)/\sqrt{t}]^n$, where a_n is the nth derivative of erf(x) at $x = D_f/2$. Taking into account that in the region of interest we have $x - x_f \approx t^\alpha \ll \sqrt{t}$, one can see that the correction terms are of the order of $t^{n(\alpha-1/2)}$ and they indeed can be neglected in the limit of large times.

Since we make the approximation (8) for $u(x,t)$ we must reconsider the boundary condition for $a(x,t)$ at $x \to -\infty$. As we get out of the reaction front in the region $x < x_f$, we have $b = 0$ and, thus, $u(x,t) = a(x,t)$. Consequently, the solution of Eq. (6) must match $u(x,t)$ [Eq. (8)] for $-\sqrt{t} \ll x - x_f \ll -t^\alpha$. In the scaling limit [$t \to \infty$ and $z = (x-x_f)/t^\alpha$ fixed] which will be considered below, the matching region extends to $x \to -\infty$ and, thus, we have the following boundary condition: $a(x,t) \to -K(x-x_f)/\sqrt{t}$ for $x \to -\infty$. The other boundary condition [$a(x,t) \to 0$ for $x \to +\infty$] remains unchanged since it is independent of the approximation made for u.

Now the solution of Eq. (6) satisfying the boundary conditions discussed above is obtained by using a scaling ansatz

$$a(x,t) = t^{-\beta/2}G\left(\frac{x-x_f}{t^\alpha}\right). \qquad (9)$$

It can be easily seen that the boundary conditions imply the following asymptotics for the scaling function $G(z)$,

$$G(z) \to -Kz \text{ for } z \to -\infty \text{ and } G(z) = 0 \text{ for } z \to +\infty\,. \qquad (10)$$

Furthermore, they force the exponents to satisfy a scaling law

$$\alpha + \beta/2 = \tfrac{1}{2}\,. \qquad (11)$$

Substituting (9) into Eq. (6) and introducing the notation $z = (x-x_f)/t^\alpha$, one finds an equation

$$t^{-\alpha-1/2}\left(-\frac{\beta}{2}G(z) - \alpha zG'(z)\right) + t^{-2\alpha}\sqrt{D_f/2}\,G'(z) = t^{-3\alpha+1/2}G''(z) - G^2(z) - KzG(z)\,, \qquad (12)$$

in which the terms resulting from the time derivative in Eq. (6) (left-hand side) can be neglected in the scaling limit $t \to \infty$ and $z = (x-x_f)/t^\alpha$ fixed. In order to obtain an equation for $G(z)$ which has a solution with the correct asymptotics [Eq. (10)], one needs the first term on the right-hand side of Eq. (12). Since that term alone is not enough to obtain a meaningful solution, we arrive at the conclusion that the exponent of t in front of $G''(z)$ must be zero and thus $\alpha=\frac{1}{6}$. Then the value of the other exponent $\beta=\frac{2}{3}$ is also determined through Eq. (11) and, furthermore, we find that $G(z)$ satisfies the equation

$$G''(z)=G^2(z)+KzG(z)\,. \qquad (13)$$

This equation with the boundary conditions (10) can be solved numerically and, for example, the value of $G(0)$ which we shall use below can be determined to be $G(0)=K^{2/3}0.5454\ldots$. It can also be seen from (13) that for large z where $G^2(z)$ can be neglected as compared to $zG(z)$, the asymptotes of $G(z)$ are given by the Airy function[8] $G(z)\approx \mathrm{Ai}(K^{1/3}z)$.

Now we proceed by determining $b=a-u$ from Eqs. (8) and (9),

$$b(x,t)=t^{-\beta/2}[G(z)+Kz]\,, \qquad (14)$$

and then by finding $R(x,t)=kab$ using Eq. (9). One can see our main result immediately: $R(x,t)$ is indeed described by the scaling form given in Eq. (3) with $x_f\sim\sqrt{t}$, $\alpha=\frac{1}{6}$ and $\beta=\frac{2}{3}$. A few explanatory notes remain to complete the derivation.

The scaling function $F(z)=kG(z)[G(z)+Kz]$ is obtained from Eqs. (9) and (14). Since $F(z)$ is a symmetric function of z [Eqs. (13) and (10) yield $G(z)+Kz=G(-z)$ and, consequently, $F(z)=kG(z)G(-z)$], we conclude that the reaction front is symmetric about the point x_f. This observation justifies the name "center of the reaction front" we introduced for x_f.

The production rate of C at x_f can be obtained through the numerical value of $G(0)$,

$$R(x_f,t)=kG(0)^2/t^{2/3}\approx 0.298kK^{4/3}/t^{2/3}\,.$$

Using the scaling form [Eq. (3)] for the evaluating the width of the front [Eq. (7)] it is a matter of change of variables in the integrals to show that $w\sim Qt^{1/6}/K^{1/3}$ as claimed (the constant of proportionality $Q\approx 2$ can be determined numerically). This result may be used to estimate the time domain where the approximation $w\ll W_d$ which yields scaling is valid. Since $W_d\approx t^{1/2}$ [see Eq. (4)], we have $w\sim t^{1/6}/K^{1/3}\ll W_d\sim t^{1/2}$ or, in dimensional form, $t_0\equiv(ka_0K)^{-1}\ll t$. Taking the values of $k\approx 10^3\,\mathrm{mol}^{-1}\mathrm{sec}^{-1}$, $a_0=100b_0\approx 10^{-2}$ mol from a theory[10] which reproduces the formation of Liesegang bands, we find $K\approx 10^{-2}$, and, consequently, $t_0\approx 10$ sec. Thus, the scaling regime seems to set in fast on the timescale (hours) of the band formation.

Having finished the mathematical derivation of Eq. (3), we now present a simple argument which yields the same values of α and β as obtained above. The derivation is based on the following assumptions: (i) The width of the depletion zone, W_d, is proportional to $\sqrt{t}$. Since the particles can diffuse to the reaction zone from a distance proportional to $\sqrt{t}$ (Fig. 1), this is a natural assumption. (ii) The width of the reaction zone scales with time as $w\sim t^{\alpha}$ and $\alpha<\frac{1}{2}$, i.e., $w\ll W_d$. (iii) The scaling of the production rate of C in the central region of the reaction zone is given by $t^{-\beta}$. The last two points are scaling assumptions based on studying the numerical solution of Eqs. (1) and (2).

The values of α and β are calculated by deriving two scaling laws connecting these exponents. The first one follows from a conservation law: the number of particles C produced in the reaction zone is equal to the number of A- and B-type particles entering the zone. The number of C particles produced in a unit of time can be estimated as $wR\sim t^{\alpha-\beta}$, while the number of A and B particles entering the reaction zone in a unit time is given by their currents $j_a=-D_a\partial a/\partial x$ and $j_b=-D_b\partial b/\partial x$ towards the reaction zone. Since a and b decrease from their initial value to zero in a distance proportional to W_d (Fig. 1), we can estimate j_a and j_b to be proportional to W_d^{-1}, i.e., we obtain $j_a\sim j_b\sim t^{-1/2}$ (note that this is a known result in case of an infinitely thin reaction zone[11]). Comparing now the exponents in $wR\sim j_a$ we have the first scaling relation

$$\alpha-\beta=-\tfrac{1}{2}\,. \qquad (15)$$

The second scaling law is obtained by noting that the $j_a\sim\partial a/\partial x\sim j_b\sim\partial b/\partial x\sim t^{-1/2}$ relation can be used to estimate the average values of a and b in the reaction front $a\sim b\sim w/t^{1/2}$. Thus, the production rate of C particles can be obtained as $R\sim t^{-\beta}\sim ab\sim w^2/t\sim t^{2\alpha-1}$ and comparison of the exponents leads to the scaling relation $2\alpha-1=-\beta$ which we have already met in the discussion of the boundary condition for the equation determining the scaling function [see Eq. (11)]. The solution of Eqs. (15) and (11) is $\alpha=\frac{1}{6}$ and $\beta=\frac{2}{3}$. Thus, our analytical results are recovered from a simple physical argument.

A problem where the results of this paper can help to simplify the calculation is the formation of Liesegang bands. The equations to be solved in that case are Eqs. (1) and (2) and an equation governing the kinetics of the product C:

$$\dot{c}=D_c\Delta c+kab-u(c)\,. \qquad (16)$$

Here c and D_c denote the concentration and the diffusion constant of C, respectively, and $u(c)$ describes the depletion of C's resulting from their nucleation and from the growth of their droplets. Since a and b appear in (16) only through the source term (kab) calculated above, Eqs. (1) and (2) do not have to be considered any more. This simplification makes it possible to extend previous studies[10,12] and to investigate how the details of the reaction zone affect the formation of bands in the asymptotic time domain.[13]

A less obvious problem to be explored is how to apply our results to the theory of diffusion-limited aggregation.

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