Reaction Kinetics of Diffusing Particles Injected into a d-Dimensional Reactive Substrate

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We study a system in which diffusing particles (species A) are injected into a reactive d-dimensional substrate (species B) at rate λ, with the rule that A+B→ C(inert). The amount of species C, $C(t)$, and the number of surviving A particles, $A(t)$, are calculated for substrate dimensions $d = 1$, 2, and 3. We find the surprising results $A(t) \sim t^{2/3}$ for $d = 3$ and $C(t) \sim \sqrt{t \ln t}$ for $d = 1$. We confirm our predictions by performing Monte Carlo simulations for $d = 1$, 2, and 3 and experiments for the reaction $I_{2(gas)} + 2Ag_{(solid)} \rightarrow 2AgI_{(solid)}$ for $d = 2$.

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What governs the growth dynamics of the disk-shaped structures one often sees after a salt crystal is dropped on an icy pavement? There are countless systems in nature in which a reactant A is "injected" into a d-dimensional substrate B whereupon it reacts to form some inert product C. Examples range from corrosive processes [1] to exciton trapping [2, 3] and defect annealing [4]. Other systems in which this process occurs are solid state chemical reactions, such as the oxidation of silicon $[O_{2(gas)} + Si_{(solid)} \rightarrow SiO_{2(solid)}]$ in the processing of semiconductors [5]. A concrete $d = 2$ example is the following experiment: inject iodine at a point of a large silver plate and monitor the reaction $I_{2(gas)} + 2Ag_{(solid)} \rightarrow 2AgI_{(solid)}$. In general, such systems are described by the rule A(diffusing) + B(substrate) → C(inert).

Here we report a theoretical, numerical, and experimental study of a general model in which A particles are continuously injected at a rate of λ particles per unit time at a single point. Each A particle performs an independent random walk (we ignore excluded volume effects) on a d-dimensional Euclidean lattice, and the B particles are fixed at every site of the lattice. Upon contact, an A and a B undergo an irreversible reaction (instantaneously) to form an inert and immobile compound C. Thus the A particles can actually "diffuse" only in the region of the lattice that has been "cleared" of B particles by the reactions of other A particles. In general, this model describes any process which depends on first passage events of diffusing particles in which both the substrate and the diffusing particles are "spent" upon reaction (in distinction to "trapping" models in which certain sites on the substrate act as eternal reacting sites [6]).

We present results for the amount of the compound C present in the system at time t, $C(t)$; and for $A(t)$, the number of A particles that have "survived" (that have not yet reacted) up to time t; for substrate dimensions $d = 1, 2, 3$. The quantities $A(t)$ and $C(t)$ are related by

$$A(t) = \lambda t - C(t). \tag{1}$$

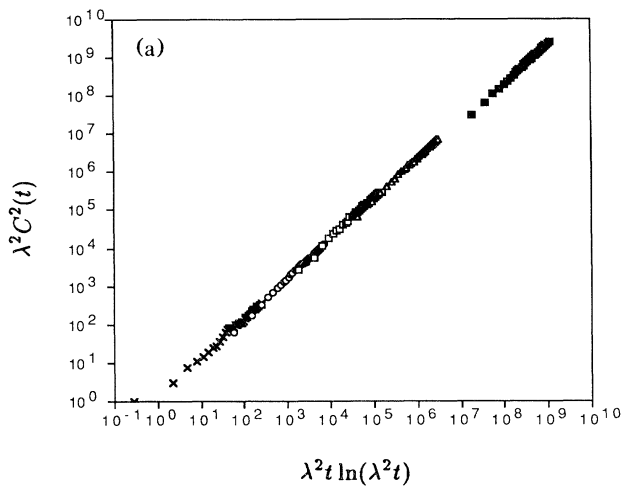
We find that $C(t)$ and $A(t)$ have complex growth behaviors with various distinct growth regimes. The initial growth regime is due to the discreteness of the lattice, in this regime $C(t) \sim t^d$, which is apparent when λ is large. This behavior lasts as long as the inverse of the probability to find an A particle near the boundary of the reacted area is much smaller than the injection rate λ. Thus this regime ends at a crossover time given roughly by $t_\times \sim \ln \lambda$ for very large values of λ [7].

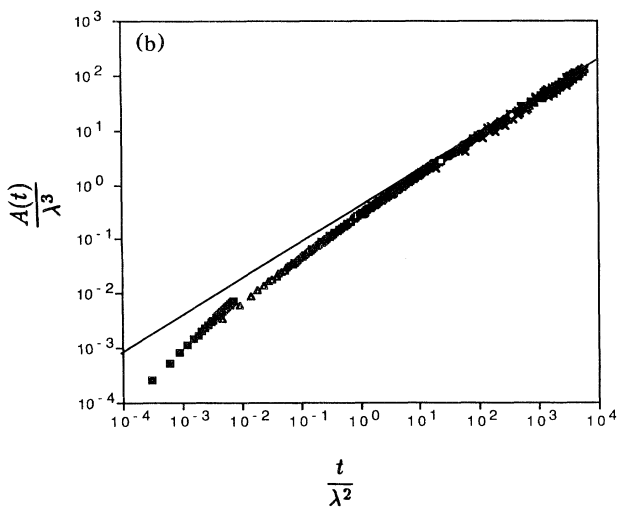
The long time behavior can be analyzed using the continuum version of the problem, which yields a Stefan problem [5, 8],

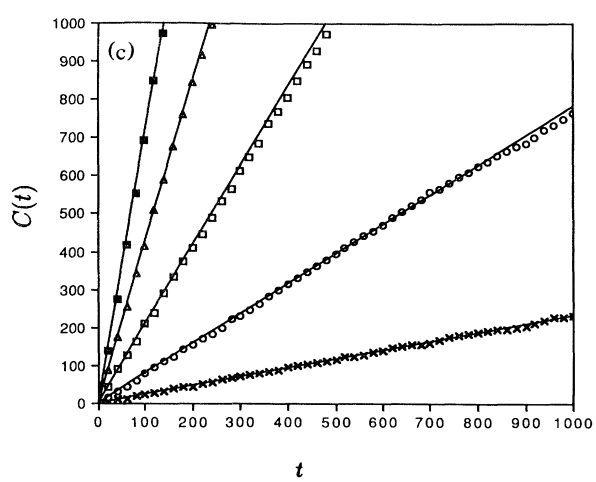
$$\frac{\partial c_A}{\partial t} = D \nabla^2 c_A, \tag{2}$$

with the conditions (i) $\lim_{\epsilon \rightarrow 0}[-D \int_{s(\epsilon)} \nabla c_A \cdot ds] = \lambda$, (ii) $c_A(r = R(t), t) = 0$, and (iii) $\dot{R} = -D \partial c_A / \partial r|_{r=R}$. Here $c_A(r, t)$ denotes the concentration of A particles at a distance r from the origin at time t, D is their diffusion coefficient, and $R(t)$ is the radius of the region where reactions have occurred. Condition (i) specifies that there is a constant input at the origin, and $s(\epsilon)$ is defined as the surface of the d-dimensional sphere of radius ϵ around the origin. Condition (ii) is the trapping condition at the boundary between the reacted (reached by an A particle) and nonreacted (nonreached) regions [9]. Condition (iii) specifies the motion of the boundary; it is obtained by equating the number of C particles that are created at a given time with the number of A particles that react at that time [10].

By defining $y \equiv r/R$ we convert Eq. (2) into a fixed boundary problem in the variable y. Assuming that







$c_A(y,t)$ approaches its stationary state (an assumption which can be verified for the case $d = 2$ by the exact solution presented below), we set $\partial c_A(y,t)/\partial t = 0$. The resulting equation can be solved by integration, subject to the conditions (i) and (ii),

$$c_A(y,t) = \frac{\lambda}{2Dd\Omega R^{d-2}} \left(\frac{R\dot{R}}{2D}\right)^{d/2-1} \times \left[\Gamma\left(1-\frac{d}{2}, y^2\frac{R\dot{R}}{2D}\right) - \Gamma\left(1-\frac{d}{2}, \frac{R\dot{R}}{2D}\right)\right]. \tag{3}$$

Here $\Gamma(a,x)$ is the incomplete gamma function and Ω is defined through the relation

$$C(t) \equiv \Omega(d) R^d \qquad [\Omega = 2, \pi, 3\pi/4; d = 1,2,3]. \tag{4}$$

From Eq. (3) and condition (iii), we obtain the relation

$$\dot{R} = \frac{\lambda}{d\Omega R^{d-1}} e^{-R\dot{R}/2D}. \tag{5}$$

For $d \neq 2$, we note directly from Eq. (5) that $C(t)$ must obey the scaling expression

$$C(t) \sim \lambda^{d/(d-2)} g(t/\lambda^{2/(d-2)}). \tag{6}$$

For a more detailed analysis of the long time behavior of $C(t)$ we treat each dimension separately. We first consider the long time behavior for $d = 1$ and 3; and then obtain the exact solution for $d = 2$.

d = 1. For $d = 1$, we expect $\dot{R} \to 0$ as $t \to \infty$. Therefore, according to Eq. (5), $R\dot{R}$ must diverge in time, which implies that $R/t^{1/2} \to \infty$. However, R is asymptotically bounded by a function of the form $(t \ln t)^{1/2}$ [11]. Thus, we argue that R has the asymptotic form

$$R(t) \sim [4D\alpha t \ln(t/t_0)]^{1/2}. \tag{7}$$

Substituting Eq. (7) into Eq. (5) and equating the leading

FIG. 1. (a) Scaling plot of $\lambda^2 C^2(t)$ as a function of $\lambda^2 t \ln(\lambda^2 t)$ for the case $d = 1$ for several values of the injection rate λ: $\lambda = 1/4$ (×), 1 (○), 4 (□), 16 (△), 64 (■). The data collapse and straight line with slope $\simeq 1$ are in agreement with Eqs. (5) and (7). (b) Scaling plot for the number of surviving A particles, $A(t)$, for $d = 3$ for injection rates $\lambda = 1$ (×), 4 (○), 16 (□), 64 (△), 256 (■). The data tend asymptotically to a straight line with slope 2/3 (indicated by the solid line), supporting Eq. (11). (c) Plot of the number of C particles, $C(t)$, as a function of time for $d = 2$ and a range of injection rates λ [same symbols as in part (a)]. The straight lines which pass through the data correspond to Eq. (13) with $\alpha = (\lambda/\pi)\exp(-\alpha/4D)$ (in all the simulations $D = 1/2d$ where d is the dimension of the substrate). The results obtained for all dimensions are from *single* Monte Carlo runs, indicating that the fluctuations are negligible and that the systems tend to self-average.

orders gives $\alpha = 1/2$ and $t_0 = 2D/\lambda^2$. Thus, for very long times, we obtain

$$C(t) \sim 2\left[2Dt\ln\left(\frac{\lambda^2 t}{2D}\right)\right]^{1/2} \qquad [d=1]\ . \tag{8}$$

Equation (8) is supported by Monte Carlo simulations shown in Fig. 1(a).

d = 3. Since $R \le t^{1/3}$ [11], then $R\dot{R} \to 0$ as $t \to \infty$. Therefore we can expand the exponential in Eq. (5) to first order in $R\dot{R}$ and solve for R,

$$\frac{4\pi R^3}{3} + \frac{\lambda R^2}{4D} \simeq \lambda t. \tag{9}$$

From this expression we can see that the leading behavior of $C(t) = 4\pi R^3/3$ at large times will be given by

$$C(t) \sim \lambda t - \frac{\lambda}{4D}\left(\frac{3\lambda}{4\pi}\right)^{2/3} t^{2/3} \qquad [d=3]. \tag{10}$$

The total number of surviving A particles, $A(t)$, will be

$$A(t) \sim \frac{\lambda}{4D}\left(\frac{3\lambda}{4\pi}\right)^{2/3} t^{2/3}. \tag{11}$$

Thus, for $d = 3$ the reaction-diffusion processes conspire in such a way that in spite of having a constant input, the total density of A particles within the C-region actually vanishes as $t^{-1/3}$. Equation (11) is supported by simulations shown in Fig. 1(b).

d = 2. For the case $d = 2$, $\Gamma(0,x) = E_1(x)$ (the exponential integral), and Eq. (3) becomes

$$c_A(y,t) = \frac{\lambda}{4\pi D}\left[E_1\left(y^2\frac{R\dot{R}}{2D}\right) - E_1\left(\frac{R\dot{R}}{2D}\right)\right]. \tag{12}$$

Equation (5) can be solved by letting $R = (\alpha t)^{1/2}$, where α satisfies $\alpha = \frac{\lambda}{\pi}e^{-\alpha/4D}$.

Equation (12) together with R and α turns out to be the *exact* solution of Eq. (2) [supporting the assumption leading to Eq. (3)]. Finally, $C(t)$ can be calculated using $C(t) = \pi R^2$; the result,

$$C(t) = \pi\alpha t \qquad [d=2], \tag{13}$$

is compared with simulations in Fig. 1(c).

The analytic results presented above are amenable to direct experimental test. In order that the experiments could be described by our theory, we took into account the following considerations: (i) The advancing diffusing/reaction front should not be influenced by surface tension, (ii) constant injection rate, and (iii) accurate measurability of either $C(t)$ or $A(t)$ as a function of time.

We found that the following experiment is well suited to meet the above requirements as well as to demonstrate the theoretical model for the two-dimensional case: a Petri dish 10 cm in diameter is coated by about 0.1 μm of silver by evaporation. A 1–2 mm piece of solid iodine is placed on the thin layer of silver. At room temperature and at atmospheric pressure the iodine sublimizes, and since the duration of the experiment is not very long, the piece of iodine acts as a relatively constant and localized source of iodine. Since the iodine gas is heavier than air, it creeps on the surface of the silver substrate, and as a gas it diffuses with no surface tension. From the surface the iodine penetrates and reacts with the silver according to the reaction $I_{2(gas)} + 2Ag_{(solid)} \to 2AgI_{(solid)}$. Since the diffusion-reaction process takes place mainly upon the surface of the silver, the system is essentially two dimensional, which greatly simplifies the measuring process: the AgI is a transparent material, whereas the silver is highly reflective. As a result, colored rings are created due to the interference of light reflected from the inner and outer surfaces of the AgI. The furthermost ring (which marks the range of the reacted area) is created by a layer of AgI approximately 500 Å in depth. This indicates that all the iodine gas that reaches a region of unreacted silver must be absorbed until this depth is achieved (the amount of iodine required to form such a layer is equivalent to a column of approximately 1 cm per unit area, at $\sim$ 1 torr partial vapor pressure of I_2 at equilibrium). Thus almost no iodine gas diffuses far beyond the boundary of the AgI.

Since the diffusion on the surface of the plate is quite fast, the system evolves in a reasonable time and can be filmed, thus providing a relatively simple and accurate means to measure the time dependence of the amount of compound AgI [corresponding to $C(t)$].

Figure 2 shows the increasing radius $R(t)$ of the outermost ring, which marks the range of the AgI compound on the silver substrate. We find that $R \sim t^{1/2}$, in agreement with our results for 2D systems.

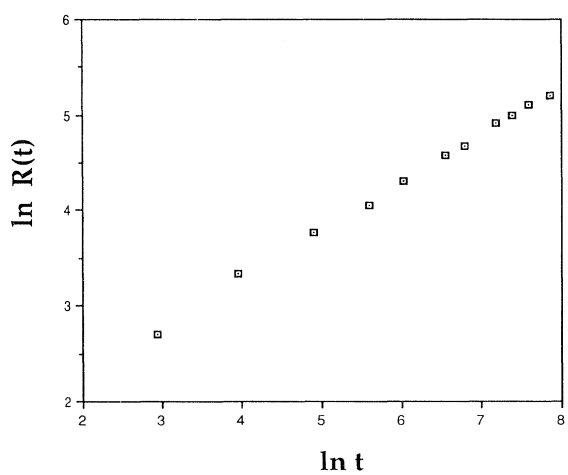


FIG. 2. Logarithmic plot of the experimental $R(t)$, the radius of the outermost interference ring, which marks the range of the AgI compound on the silver substrate. The best line fit yields a slope of 0.5028, in agreement with our $d = 2$ result $R = (\alpha t)^{1/2}$.

Before concluding, we note that a transient regime between the initial and long time growth regimes discussed above can be expected by noticing that the system has two "natural" length scales: a diffusive length scale $\xi_D = (4Dt)^{1/2}$, and a volume (or mass balance) length scale $\xi_V = (\lambda t/\Omega)^{1/d}$ which corresponds to a strict upper bound for $R(t)$ as discussed above. When $\xi_V > \xi_D$, the growth of $C(t)$ will be determined by the "rare events" in which A particles wander further than the characteristic diffusion length. This is the case for the long time regime of 1D systems. On the other hand, when $\xi_V < \xi_D$, then $C(t)$ is limited by its upper bound which is the case for the long time growth of 3D systems. In 2D systems, the relation between ξ_V and ξ_D is fixed for all times and it is reflected in the values of α in the large λ limit $[\alpha \sim 4D\ln(\lambda/\Omega)]$, and the small λ limit $(\alpha \sim \lambda/\pi)$. In 1 and 3D systems there is a crossover time $t'_\times$ at which both length scales are equal: $t'_\times = (4D)^{d/(d-2)}(\lambda/\Omega)^{2/(d-2)}$. It is for times $t \gg t'_\times$ that our asymptotic results hold.

In summary, we have found the long time behavior of the amount $C(t)$ of reactant and the number $A(t)$ of surviving A particles for the reaction $\mathrm{A}_{(\mathrm{diffusing})} + \mathrm{B}_{(\mathrm{substrate})} \rightarrow \mathrm{C}_{(\mathrm{inert})}$. Our results can be easily extended to general d (≥ 2) by solving Eq. (5), $A(t) = (\lambda/4D)[\lambda t/\Omega(d)]^{2/d}$ and $C(t) = \lambda t - A(t)$. While our results strictly refer to either characteristic or average quantities, they may be useful for the description of single systems. This is due to the fact that for long enough times, the systems appear to be self-averaging to such a degree that remarkably good "statistics" can be obtained from a *single* Monte Carlo run. We support our theoretical results by numerical simulations in $d = 1, 2, 3$ and by experiments in $d = 2$.

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[9] Through both the experiments and the Monte Carlo simulations, we find that the region marked by C particles (C-region) has radial symmetry as expected (except at very short times when the structure of the lattice and the details of the random walk determine the shape of the C-region), and that the boundary of the C-region is remarkably smooth. These observations validate the symmetry assumptions that are used in the analytical treatment of the problem, but most important, they justify our assumption that the boundary can be treated as a relatively sharp locus at a distance $R(t)$ from the origin.

[10] A factor indicating the "size" (length, area, or volume according to the dimension of the system) of the compound particle C should appear on the right hand side of condition (iii). Throughout this paper we set this factor, which takes care of the appropriate units of D and R, to unity.

[11] Since there can be at most one reaction per A particle, then the total number of reactions $C(t) \leq \lambda t$. Thus the radius $R(t)$ of the C-region can grow at best as $R(t) \sim t^{1/d}$. For 1D systems an even lower bound can be found for $R(t)$ by considering systems without reaction, for which the typical position of the furthermost particle from the origin grows as $(t\ln t)^{1/2}$ at very large values of t [see [7] and E. ben-Naim (private communication)]. The presence of reaction cannot increase this distance, therefore we expect $R(t) \leq (t\ln t)^{1/2}$. This argument holds for other dimensions as well but yields a weaker bound than $t^{1/d}$ except at relatively short times.