Mixing Effects in the $A+B \rightarrow 0$ Reaction-Diffusion Scheme

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We study analytically the irreversible reaction $A+B \rightarrow 0$ under laminar stirring, for equal overall particle concentrations. In contrast to the usually found algebraic decays, here the reactant concentrations display exponential patterns, which stem from the mixing kinetics. The crossover from this short-time behavior to the classical kinetic law in a fully mixed system is also investigated. Furthermore, disorder effects are fundamental, since for strictly regular patterns the short-time decay shows an exponentially exponential time dependence.

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In recent years diffusion-controlled reactions have received much attention, triggered by the realization that often the decay laws deviate quantitatively from the chemical-kinetics forms. Thus for the $A+B \rightarrow 0$ reaction with equal numbers of A and B particles the kinetic scheme predicts at long times a t^{-1} behavior, while more consistent theoretical approaches and numerical simulations find (in the absence of stirring) more general patterns, such as a $t^{-d/4}$ law (where d is the spatial dimension), a fact due to the random fluctuations in the particle distribution.[1-6] The usual assumption is that under vigorous stirring the standard classical kinetics should again apply. In this Letter we show that the situation is not so simple in that stirring does not necessarily lead to algebraic decay.

Here we mimic stirring by laminar mixing models.[7-11] Basically, mechanical mixing of two initially separated liquids often produces a quasi-one-dimensional lamellar structure.[7-9] Thus the irreversible $A+B \rightarrow 0$ reaction was investigated in Refs. 10–13 by first creating the striation pattern and then letting the reaction develop. Using Ranz's methods[14] we solve here the problem of simultaneous reaction and mixing by using so-called warped-time transformations. Note that one may envisage mixing by picking particles randomly and placing them in new positions;[15,16] although this procedure leads to the classical-kinetics results, it does not mirror real mixing closely.

In standard situations, laminar mixing of two liquids gives rise to a structure of alternating striations, which get thinner in time because of folding and squeezing. In fact, thinning of lamellar arrangements of striations occurs generally under mixing conditions and may be found even in turbulent flow. The striation thickness distribution (STD) is random, its mean decreasing, in general, exponentially with time.[9]

We use here the fact that the so-called warped-time transformation[9,14] allows one to map the diffusion problem in a steadily thinning array of striations onto a diffusion problem in a static lamellar system.[10-12] This allows us to implement our recent analytical results for the static problem[13] to investigate the $A+B \rightarrow 0$ reaction under mixing, both in the case of infinite local reaction rates and also for finite ones. Specifically, we display the decay behavior under mixing and we determine the dependence of the overall decay rate on the reacting species (concentrations, diffusion constants, local reaction rates) and on the mixing procedure (squeezing rate and STD). Furthermore, we determine the characteristic crossover time from the initial regime (dominated by fluctuations and mixing) to a fully mixed situation.

We model mixing (following Refs. 7 and 9) by considering an array of parallel striations (say, along the x axis), which is also squeezed in the x direction. This model represents quite well both the local structure of a mixed specimen and also its dynamics.[9] If squeezing makes the characteristic scale e times smaller each θ seconds, then in the absence of reaction, full mixing is achieved at a time T, when the striation thickness becomes comparable to the intermolecular distances; for $\theta = 1$ s, $T \approx -\theta \ln 10^{-8} \approx 18$ s for initial length scales l_0 of 1 cm.

Now the bimolecular irreversible reaction $A+B \rightarrow 0$ in a system *without external constraints* can be described by

$$\frac{\partial c_A}{\partial t} = D\Delta c_A - R, \quad \frac{\partial c_B}{\partial t} = D\Delta c_B - R, \tag{1}$$

where $c_A(\mathbf{r},t)$ and $c_B(\mathbf{r},t)$ are the local concentrations of reactants, and D is the diffusion constant. In standard chemical kinetics R is often taken to be equal to $\kappa c_A c_B$, where κ is the microscopic reaction rate coefficient. In fact, this is only an approximation (see Ref. 12 for other forms) and in general the situation is much more complicated,[17,18] since the reaction rate depends on the joint probability to find one A and one B particle within the reaction radius, a probability which in general does not factorize as $c_A(\mathbf{r},t)c_B(\mathbf{r},t)$. To fix the ideas we take equal concentrations (say $c_0 \approx 10^{22}$ cm^{-3}) of reactants and set D equal to 10^{-5} cm^2/s, typical for aqueous solutions (e.g., Ref. 19). In this case, assuming as usual $\kappa = 8\pi D r_0$, with a reaction radius $r_0 \approx 10^{-8}$ cm, we have $\kappa \sim 10^{-13}$ cm^3/s.

Squeezing is modeled with the help of a velocity field $\mathbf{v}$. For reactions in moving liquids, Eq. (1) holds *locally* in a system of coordinates moving together with the liquid domain considered. The change from this moving (Lagrangian) system of coordinates to the fixed (Eulerian) one is provided by the operator (called the *material* derivative in Ref. 7)

$$\frac{\mathcal{D}}{\mathcal{D}t} = \frac{\partial}{\partial t} + \mathbf{v}\cdot\nabla\,, \tag{2}$$

which replaces the partial time derivative in Eq. (1).

For a parallel array of striations perpendicular to the x axis the problem is essentially one dimensional; thus only the x component of the velocity is significant. For a continuous contraction this component depends only on the location x, and is

$$v(x) = -ax\,, \tag{3}$$

with the squeezing rate being $a = 1/\theta$. Using Eqs. (2) and (3) we can now rewrite the one-dimensional equivalent of Eq. (1) as a pair of equations for $q(x,t) = c_A(x,t) - c_B(x,t)$ and for $s(x,t) = c_A(x,t) + c_B(x,t)$. Thus

$$\frac{\mathcal{D}q}{\mathcal{D}t} = \frac{\partial q}{\partial t} - ax\frac{\partial q}{\partial x} = D\frac{\partial^2 q}{\partial x^2} \tag{4}$$

and

$$\frac{\mathcal{D}s}{\mathcal{D}t} = \frac{\partial s}{\partial t} - ax\frac{\partial s}{\partial x} = D\frac{\partial^2 s}{\partial x^2} - \frac{\kappa}{2}(s^2 - q^2)\,. \tag{5}$$

Note that the first equation is linear and depends on $q(x,t)$ only, and that the second one contains q as a parameter. Equations (4) and (5) allow now a straightforward analysis.

Let us consider first Eq. (4), which is also of great interest by itself, because it describes the limiting case of very fast reactions, $\kappa \to \infty$. (For a discussion of the experimental significance of this assumption see Ref. 9, pp. 13 and 282ff.) For $\kappa \to \infty$ Eq. (5) reverts to a similar form as Eq. (4). Under general conditions it follows that $s^2 = q^2$, or $s = |q|$ everywhere: The system consists of domains occupied either by A or B particles; hence one has

$$c_A = q\Theta(q),\quad c_B = -q\Theta(-q)\,, \tag{6}$$

with $\Theta(x)$ being the Heaviside step function. Now by the change of variables (warped-time transformation[9,14])

$$\xi = x\exp(at),\quad \tau = \tfrac{1}{2}\theta[\exp(2at) - 1]\,. \tag{7}$$

Equation (4) reduces to an ordinary diffusion equation with partial, *not material,* derivatives:

$$\frac{\partial q}{\partial \tau} = D\frac{\partial^2 q}{\partial \xi^2}\,. \tag{8}$$

In Eq. (7) ξ and τ are chosen so that ξ and x coincide at $t = \tau = 0$. Such a diffusion problem in the absence of mixing was considered in Refs. 10 and 11. A straightforward procedure would now require the solution of Eq. (8) for all possible initial conditions. We circumvent the problem in that we consider directly ensemble-averaged quantities, which we denote by $\langle \cdots \rangle_e$. In Ref. 13 we have shown how to deal with this problem theoretically. Here we have to pay attention to the fact that we need also to average over x. Fortunately, all the spatial averages are the same when averaging over x or over ξ: $\langle f(q(x,t))\rangle_x = \langle f(q(\xi,\tau(t)))\rangle_\xi$, where f is an arbitrary function of q only, since no singularities occur in the change of variables from (x,t) to (ξ,τ) and since the variable τ depends only on t (but not on x). Furthermore both averages coincide with $\langle f(q(x,t))\rangle_e$ [or $\langle f(q(\xi,\tau(t)))\rangle_e$]. Because in Eq. (7) both sets of variables coincide at $t = 0$ the initial realization of the A and B domains, $q(x,0)$, is identical to $q(\xi,0)$. Therefore, paralleling Ref. 13, we can obtain $c(\tau) = \langle |q(\xi,\tau)|\rangle$ as the solution of Eq. (8) with the initial condition $q(\xi,0) \equiv q(x,0)$ and then revert from τ to t to get $c(t)$. Here we present a heuristic argument, which (up to constants of order unity) leads to the same qualitative results as in Ref. 13 for the "long-time" ($\tau \gg 1$) behavior.

Paralleling Ref. 3 we use scaling ideas and view τ in Eq. (8) as the time and ξ as the space variable. The characteristic diffusion length ξ_D in ξ space is then $\xi_D \sim \sqrt{D\tau}$. At time τ the profile of the concentrations is smoothed out by diffusion on the scale ξ_D, but fluctuations on scales larger than ξ_D survive. Thus, at time τ the system can be viewed as consisting of independent compartments of length ξ_D, each compartment containing only the reactant that was initially in excess in this part. This residual amount of reactant is of the order of $c_0|\xi_A - \xi_B|$, where ξ_A and ξ_B are the total initial widths of the A and the B lamellae in the compartment considered. If $\xi_D \gg l_0$, the mean number of A and B striations inside a compartment of length ξ_D is $n = \xi_D/l_0$ each, the mean value of the difference $\xi_A - \xi_B$ is, of course, zero, and the variance of this difference, $\langle(\xi_A - \xi_B)^2\rangle$, is of the order of $2n\sigma^2$, where $\sigma^2 = S - L^2$ is the variance in striation widths, L being the average width and S the average square width of the striations.

In general $\sigma > 0$, i.e., $S > L^2$. Then the average amount of the residual reactant is

$$\langle |q(\xi,\tau)|\rangle \sim c_0\langle |\xi_A - \xi_B|\rangle \sim c_0\langle(\xi_A - \xi_B)^2\rangle^{1/2}\,,$$

and its average concentration,

$$c(\tau) \sim \langle |q(\xi,\tau)|\rangle \sim c_0\langle |\xi_A - \xi_B|\rangle/\xi_D\,,$$

is of the order of

$$c(\tau)\sim c_0\left(\frac{S-L^2}{L}\right)^{1/2}\xi_D^{1/2}$$
$$\sim c_0\left(\frac{S-L^2}{L}\right)^{1/2}(D\tau)^{-1/4}. \qquad (9)$$

The "time" τ dependence, $c\sim\tau^{-1/4}$, is typical for fluctuation-dominated kinetics in one-dimensional disordered systems,[2-5,10,11] and the dependence on c_0, L, and S is as found by us in Ref. 13; in fact, a more detailed theoretical analysis[13] also gives the values of the numerical coefficients:

$$\langle q^2(\tau)\rangle = c_0^2(S-L^2)L^{-1}(8\pi D\tau)^{-1/2},$$
$$c(t)=2^{-5/4}\pi^{-3/4}c_0(S-L^2)L^{-1}(D\tau)^{-1/4}.$$

On the other hand, the case $\sigma=0$ is special. Here $S=L^2$, which corresponds to a strictly ordered system; then the reactant concentration in each lamella decays according to the same law. The solution may be found from the diffusion equation in intervals with absorbing boundaries. For large enough τ the decay is *exponential in* τ:

$$c(\tau)=\langle|q(\xi,\tau)|\rangle\sim c_0\exp(-\pi^2D\tau/L^2). \qquad (10)$$

Substituting $\tau(t)$ (inverse warped-time transformation) into Eqs. (9) and (10) one obtains at long times

$$c(t)\sim c_0\exp[-(\pi D/2\alpha L^2)\exp(2\alpha t)], \qquad (11)$$

i.e., the exponential of an exponential law (EE decay). On the other hand, for a random situation one has an exponential decay:

$$c(t)\sim c_0\left(\frac{S-L^2}{L}\right)^{1/2}\left(\frac{D}{\alpha}\right)^{-1/4}\exp\left(-\frac{t\alpha}{2}\right). \qquad (12)$$

Both Eq. (11) and Eq. (12) set in only when the diffusion length ξ_D becomes comparable to L: This corresponds to times of the order of $T_0\sim\ln(2\alpha L^2/D)/2\alpha\simeq 6\theta$, i.e., for our choice of parameters to ≈ 6 s.

We now get back to the general case where κ is finite. Then Eq. (6) holds only in the early reaction stages. We now have to solve Eq. (5). In an ensemble-averaged situation $\langle s\rangle$ is independent of x. Therefore one gets by averaging Eq. (5) over the ensemble of realizations,

$$\frac{d\langle s\rangle}{dt}=-\frac{\kappa}{2}(\langle s^2\rangle-\langle q^2\rangle). \qquad (13)$$

We note that s is independent of x both in the initial state, where (apart from the boundaries between the domains) $s(x,0)=c_0$, and also in the late, fully mixed states of the reaction. In both these limiting cases the relation $\langle s^2\rangle=\langle s\rangle^2$ is strict. In the intermediate regime (since s is well behaved) $\langle s^2\rangle$ and $\langle s^2\rangle$ can differ only by a factor of order of unity. We thus set $\hat{s}(t)=\langle s\rangle=\langle s^2\rangle^{1/2}$ in Eq. (13) and obtain an ordinary differential equation for $\hat{s}(t)$.

Now, as long as σ^2 does not vanish, one has, for times larger than a few θ units, $\langle q^2(t)\rangle=a\exp(-\alpha t)$, with a being of the order of $c_0^2[(S-L^2)/L](D/\alpha)^{-1/2}$. Setting $z\equiv\exp(-\alpha t)$ one obtains for $\hat{s}$ the Ricatti equation:

$$\frac{d\hat{s}}{dz}=\frac{\kappa}{2\alpha z}\hat{s}^2-\frac{a\kappa}{2\alpha}. \qquad (14)$$

Using a standard method, see Ref. 20, we introduce the auxiliary function

$$\phi(z)=\exp\left(-\int_0^z\frac{\kappa\hat{s}(z')}{2\alpha z'}dz'\right)$$

and get a Bessel equation for ϕ. Then reverting to $\hat{s}$ and using that $\hat{s}$ is bounded and real we obtain

$$\hat{s}(z)=\sqrt{az}\,K_1(\kappa\sqrt{az}/\alpha)/K_0(\kappa\sqrt{az}/\alpha), \qquad (15)$$

where K_0 and K_1 are modified Bessel functions, Eq. (9.6.1)ff of Ref. 21. Now the coefficient $\kappa\sqrt{a}/\alpha$ is large and for moderately long times t, $t<2\ln(\kappa\sqrt{a}/\alpha)/\alpha$, one obtains from the asympotic (large argument) forms of K_i,

$$\hat{s}(z)=\sqrt{az}. \qquad (16)$$

This agrees with the former results for $\kappa\to\infty$. For larger times $t>2\ln(\kappa\sqrt{a}/\alpha)/\alpha$ the small-argument expansion of Eq. (15) gives

$$\hat{s}(z)=-2/\kappa\alpha\ln z=2/\kappa t, \qquad (17)$$

which is the standard chemical-kinetics form. The change from Eq. (16) to Eq. (17) occurs for arguments around unity, i.e., for times around T_1, where $T_1=2\ln(\kappa\sqrt{a}/\alpha)/\alpha$. With our parameters discussed above one has $T_1\approx 37\theta\approx 37$ s for a very fast, almost purely diffusion-controlled reaction. Note that T_1 is twice as large as T, the full mixing time in the absence of the reaction.

The behavior of the solution, Eq. (15), for different values of κ is shown in Fig. 1. All curves correspond to the value of $a=c_0^2(S-L^2)/L\sqrt{4\pi D/\alpha}=10^{46}$ cm^{-6} and the values of κ vary from 10^{-18} cm^3/s (slow, reaction-controlled regime) to 10^{-13} cm^3/s (fast, diffusion-controlled reaction). One can easily see that the initial, exponential behavior is universal. The crossover effects at larger times are also quite obvious. For $\kappa=10^{-13}$ cm^3/s the crossover time T_1 is around half a minute and $c(T_1)/c(0)\sim 10^{-10}$, $c(T_1)$ being well outside experimental detection means.

Let us also look at the exceptional case where $\sigma^2=0$. Evidently, we can expect an EE decay only for times larger than T_0. For finite κ, we again have to analyze Eq. (13), now with $\langle q^2\rangle$ expressed through Eq. (11). Comparison of the terms on the right-hand side of Eq. (13) shows that the EE decay may hold only up to times around T_2, where now T_2 obeys $c_0\exp[-(\pi D/2\alpha L^2)$

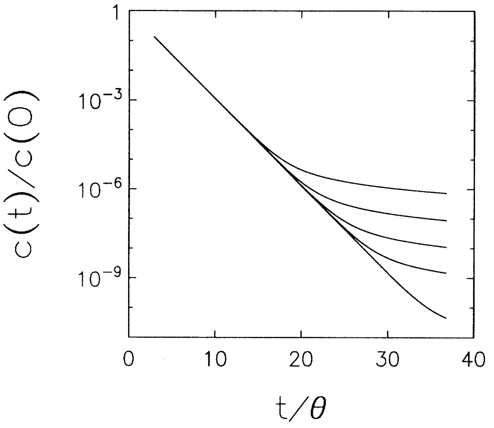

FIG. 1. The analytical solution for the concentration decay. The values of the local reaction rate coefficient are $\kappa=10^{-18}$, 10^{-17}, 10^{-16}, 10^{-15}, and 10^{-13} cm^3/s (top to bottom). Other parameters are $c_0=10^{22}$ cm^{-3}, $D=10^{-5}$ cm^2/s, $\theta=1$ s, and $S\sim L\sim 1$ cm.

$\times\exp(2\alpha T_2)]\sim 1/\kappa T_2$. With our values of parameters T_2 is around 7θ so that the region between T_0 and T_2 is quite small. Furthermore, for an *almost* ordered system, the EE decay requires that the fluctuations in L are very small, so that $c(t)\gtrsim c_0\Delta L/L$ holds. For our parameters this means $\Delta L/L\sim 10^{-10}$, i.e., atomically flat boundaries. We conclude that in reacting systems the fluctuations of striation thicknesses are of great importance and that mixing models neglecting these fluctuations (e.g., the regular baker's transformation) must be viewed with suspicion.

Summarizing, mixing usually governs the initial stages of the reaction and the standard, diffusion-controlled regime is often reached quite late. Furthermore, the concentration fluctuations caused by the random nature of mixing play a very important role: Neglecting these fluctuations can lead to a drastic change in the decay behavior at short times.

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