

Boundary Effects on Chaotic Advection-Diffusion Chemical Reactions

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A theory of a fast binary chemical reaction, $\mathcal{A} + \mathcal{B} \rightarrow C$, in a statistically stationary bounded chaotic flow at large Peclet number Pe and large Damköhler number Da is described. The first stage correspondent to formation of the developed lamellar structure in the bulk part of the flow is terminated by an exponential decay, $\propto \exp(-\lambda t)$ (where λ is the Lyapunov exponent of the flow), of the chemicals in the bulk. The second and the third stages are due to the chemicals remaining in the boundary region. During the second stage, the amounts of \mathcal{A} and \mathcal{B} decay $\propto 1/\sqrt{t}$, whereas the decay law during the third stage is exponential, $\propto \exp(-\gamma t)$, where $\gamma \sim \lambda/\sqrt{Pe}$.

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A common expectation is that random advection should essentially accelerate chemical reactions rate in fluid phase, since it should lead to homogenization of the reaction mixtures. Then dynamics is determined by an interplay of three factors: diffusion, advection, and chemical reaction. Typical situation realizing in chemical reactors is that the chemical reaction itself is much faster than mixing and diffusion, i.e., the Damköhler number Da , which is defined as the ratio of the mixing time to the characteristic time of the reaction [1], is large. For the binary reaction this separation of temporal scales results in formation of lamellar structure, built of stripes, populated solely by one chemical. The stripes of different chemicals are separated from each other by an interface of complicated shape, and the chemicals coexist only in the narrow interface domain where the chemical reaction occurs. The reaction is limited by diffusion in the sense that diffusion controls fluxes of the chemicals into the interfacial reaction zone [2–4]. The physical picture of the acceleration due to the random advection is that it stretches domains populated by one chemical into thin sheets, so that the chemical reaction driven by diffusion proceeds more efficiently because of an essential increase of the interface area. In this Letter, we explain how this general physical picture formulated initially for unbounded flows applies to chaotic flows confined to a finite geometry.

We consider a binary chemical reaction, $\mathcal{A} + \mathcal{B} \rightarrow C$, in a dilute solution of two chemicals. We study a decay problem, with an initial distribution of the chemicals \mathcal{A} and \mathcal{B} , created by injecting solution of one chemical, say, of \mathcal{A} , into a solution of the other chemical, \mathcal{B} . It is assumed that the inverse reaction $C \rightarrow \mathcal{A} + \mathcal{B}$ is negligible, i.e., there is no back influence of C on the distribution of \mathcal{A} and \mathcal{B} . Then molecular concentrations of the chemicals, n_a and n_b , vary according to the following nonlinear governing equations (see, e.g., [5]):

$$\partial_t n_{a,b} + (\mathbf{v} \cdot \nabla) n_{a,b} = \kappa_{a,b} \nabla^2 n_{a,b} - R n_a n_b, \quad (1)$$

where R is the reaction rate coefficient, \mathbf{v} is the velocity of the flow (which is assumed to be incompressible), and $\kappa_{a,b}$ are the diffusion coefficients of the chemicals. We assume that the fluid dynamics is independent of the chemical reaction; that is, the velocity does not sense changes in the chemical concentrations nor heat released in the result of the chemical reaction. Our approach is also applicable to the case, realized in tubular chemical reactors, when the solution of the chemicals, prepared at the entrance, is then pushed through a pipe. In this case, the position along the pipe plays the role of time in the decay problem.

The major question addressed in this Letter is: how do the total amounts of chemicals, $N_{a,b} = \int d\mathbf{r} n_{a,b}(t, \mathbf{r})$, decay as time t advances? We focus primarily on the stoichiometric case $N_a = N_b$. This case is of major interest for applications as it allows one to get pure product C (not mixed with the reagents) by the time reaction is completed. (An effect of a mismatch between N_a and N_b is also briefly discussed.) We identify major stages of the chemical reaction and relate them to the chemical decay in different parts of the flow. An essential part of the evolution is related to the boundary region. We discuss mainly the case of $\kappa_a = \kappa_b = \kappa$ (it is argued later in the text that $\kappa_a \neq \kappa_b$ does not lead to significant changes in the theory). Then one obtains a closed equation for the difference field, $n = n_a - n_b$,

$$\partial_t n + (\mathbf{v} \cdot \nabla) n = \kappa \nabla^2 n, \quad (2)$$

from Eq. (1), i.e., one finds that $n(t, \mathbf{r})$ is a passive scalar field. Note that n has no definite sign and that $\int d\mathbf{r} n = 0$ in the stoichiometric case, $N_a = N_b$.

We assume that the chaotic statistically steady velocity field $\mathbf{v}(t, \mathbf{r})$ contains only few harmonics of the reservoir size; i.e., the flow is smooth. This regime can be realized in chemical reactors with mechanically rotating mixers or externally driven magnets stirring the fluid in the perfect mixing devices and also in the tubular reactors at moderate Reynolds numbers. (See [6] for a discussion of the chemical engineering principles behind various

reactor designs.) The passive scalar advection in a smooth chaotic flow is a well studied (by both theoretical [7–11] and experimental [12–14] means) subfield of statistical hydrodynamics (see also reviews [15,16]). The passive scalar decay theory, developed in [11,17] for an unbounded flow, was recently modified for bounded flows, i.e., for chaotic flows with suitable (no slip) conditions on the boundary [18]. Smoothness of the flow allows one to approximate the velocity difference between close points by a linear, although fluctuating in time, profile. In the bulk region, the linear profile approximation is valid for separations smaller than the system size L . In the periphery, i.e., close to the solid boundary (wall), the linear profile approximation is valid for velocity fluctuations on a scale smaller than a distance to the boundary. An important consequence of the linear velocity profile approximation is that close Lagrangian trajectories diverge exponentially in time. The mean logarithmic rate of the nearby Lagrangian trajectories divergence defines the Lyapunov exponent of the flow, λ . Notice that in the peripheral domain advection is essentially anisotropic, and the stretching rate along the boundary is estimated by λ , while the stretching rate in the direction normal to the boundary is significantly smaller.

It is straightforward to derive from Eq. (2) equations for correlation functions of n (the derivation procedure is similar to the one described in [10,11]). The equation for the mean value of n , $\langle n \rangle$, derived by averaging over times larger than the correlation time of the flow τ_0 , is

$$\partial_t \langle n \rangle = \nabla_\alpha (D_{\alpha\beta} \nabla_\beta \langle n \rangle) + \kappa \nabla^2 \langle n \rangle. \quad (3)$$

In the case of a short-correlated (in time) flow, $\lambda\tau_0 \ll 1$, the turbulent diffusion tensor D is expressed through the velocity pair correlation function: $D_{\alpha\beta}(\mathbf{r}) = \int_0^\infty dt \langle v_\alpha(t, \mathbf{r}) v_\beta(0, \mathbf{r}) \rangle$. Equation (3) remains valid in the general case. However, for $\lambda\tau_0 \sim 1$ the relation between the eddy-diffusivity tensor and the velocity correlations becomes more complicated. In the boundary domain longitudinal and transverse to the boundary components of the velocity behave as $v_\parallel \propto q$ and $v_\perp \propto q^2$ (where q is the separation from the boundary); thus, the corresponding components of the tensor D are $D_\parallel \sim \lambda q^2$ and $D_\perp \sim \lambda q^4/L^2$. Description of the chemical reaction problem is based on the solutions of Eq. (3) in different spatiotemporal domains. The eigenvalue problem set by linear Eq. (3) requires explicit resolution in the peripheral domain. This problem was solved in [18]. Let us stress that the solution of Eq. (3) is sensitive to velocity fluctuations and cannot be obtained in the framework of any dimensional arguments. Here we use the results of [18] for $\langle n \rangle$ to establish the dependence of $N_{a,b}$ on t . The brief style of this Letter does not allow us to present the complete analysis here. Therefore, below we report final results, omitting details of the derivation. To clarify the results, we also pay special attention to presenting a clear physical picture of the phenomenon.

First we discuss characteristic spatial scales in the problem. The size of the system, L , which is also the chaotic flow typical eddy scale, is the largest scale in the problem. A comparison of the advection and diffusion terms in Eq. (1) sets the dissipative scale of the flow, which in the bulk region is $r_d = \sqrt{\kappa/\lambda}$. We assume that the Peclet number, $Pe \sim (L/r_d)^2$, is large; i.e., in the asymptotically wide range of scales, $L \gg r \gg r_d$, advection dominates diffusion. The width of the diffusive boundary layer r_{bl} is found from the balance condition between the molecular diffusion κ and the transverse component of the turbulent diffusion tensor D_\perp . One finds $r_{bl} \sim Pe^{1/4} r_d$, i.e., $r_{bl} > r_d$. Yet another important scale, associated with the chemical reaction itself, is the size of the reaction zone r_{ch} (the width of the interfacial domain where the chemical reaction occurs). In the bulk region the scale is estimated by $r_{ch} = r_d [\lambda / (R n_m)]^{1/3}$, where n_m is a typical concentration of the chemicals inside the layers [2]. (The estimate for the width of the reaction zone should be modified near the boundary, where it appears to be larger than in the bulk.) Initially, r_{ch} is much smaller than r_d ; the inequality is a consequence of the $Da \gg 1$ assumption. (Indeed, in accordance with the definition, the Damköhler number can be estimated as $Da \sim R n_0 / \lambda$, where n_0 is a typical value of the initial chemical concentration. Thus, at $t = 0$, $r_{ch} \sim Da^{-1/3} r_d$.) However, r_{ch} grows as n_m decreases. Thus, even though the separation of scales is perfect initially, it eventually breaks down at the latest stage of the chemical reaction. A cartoon illustration of the scale hierarchy is shown in Fig. 1. The magnified striped structure is shown on the chart in the upper right corner of the figure. Regions populated by one chemical are single-colored. To resolve the interface domain, even stronger magnification is needed. Dependence of the chemicals concentrations on the coordinate normal to the interface is shown schematically on the chart in the lower right corner of the figure.

The separation of scales, $r_{ch} \ll r_d, L$, allows an important simplification in the description. Indeed, the chemical reaction takes place in the r_{ch} -narrow interface domain, where the values of n_a and n_b are comparable. Outside this narrow region, i.e., in the region dominated by one of the chemicals, the presence of the other chemical is negligible. Thus, in the limit $r_{ch} \rightarrow 0$, i.e., when the reaction zone becomes infinitesimally thin, one obtains $n_a = n, n_b = 0$ for $n > 0$ and $n_a = 0, n_b = -n$ for $n < 0$. These relations imply a remarkable conclusion [2,4]: the fast chemical reaction can be described in terms of the linear setting (2) which does not contain the chemical reaction rate coefficient R . The reaction rate is determined by the diffusion fluxes of \mathcal{A} and \mathcal{B} to the $n = 0$ interface. These fluxes are equal to each other and opposite in sign, which is translated, at $r_{ch} \rightarrow 0$, into a continuity condition for ∇n at the interface. This observation also means that, while r_{ch} is much smaller than all other relevant scales, our problem is reduced to the problem of scalar decay in chaotic bounded flow.

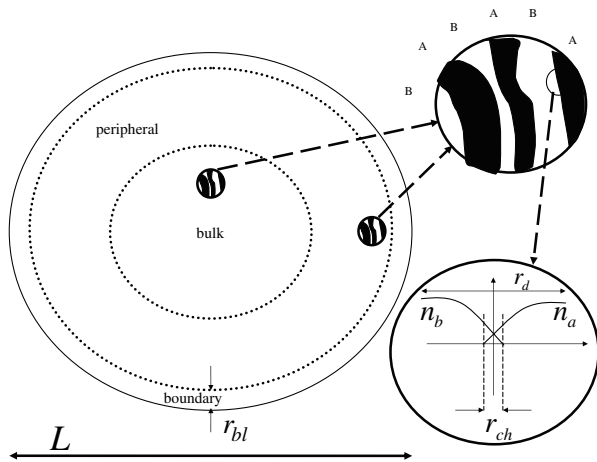


FIG. 1. The chemical reactor boundary is drawn by a solid line on the main chart. Dotted lines separate bulk, peripheral, and boundary domains of the flow. The chart in the upper right corner shows schematically the stripe structure magnified from the bulk and/or peripheral domains. Black and white regions are the ones populated by \mathcal{A} and \mathcal{B} , respectively. The chart in the low right corner shows (under even stronger magnified glass) distribution of chemicals normal to their contact interface.

We find that the chemical reaction (which starts at $t = 0$) undergoes the following four stages.

I. *Formation of stripes in the bulk.*—Advection creates from an initially smooth distribution a striped structure of alternating domains of \mathcal{A} and \mathcal{B} [4]. The stripes become dynamically thinner; i.e., inhomogeneities of smaller and smaller scales are produced. Once the width of the stripe decreases down to the diffusive scale r_d , the stripe collapses (wiped out by the diffusion-limited chemical reaction) in a time $\sim \lambda^{-1}$. Since the stretching (contraction) process leading to creation of the stripes is exponential in time [7–10,15,16], the initial stage (when the r_d stripes are formed) lasts for $\tau_1 \sim \ln(\text{Pe})/\lambda$, i.e., just the time required for the cascade of passive scalar to run from L down scale to r_d . Even though the interfacial area increases exponentially during the first stage, $N_{a,b}$ do not vary significantly. By the end of this stage the bulk parts of $N_{a,b}$ begin to decay rapidly (exponentially), with a decrement of the order of λ , according to the law of the passive scalar decay in an unbounded spatially smooth flow [11,17]. Thus, after the first stage the chemicals remain mainly in the peripheral region.

Notice also that after the first stage, stripes of different widths, distributed between r_d and L , are present in the bulk. (This multiscale structure is also seen in the passive scalar decay experiment [13,14] and in binary-reaction numerics [19].) When the r_d -wide stripe, say, of the chemical \mathcal{A} , collapses, then two nearby stripes of the chemical \mathcal{B} form one wider stripe. Thus, collapse of r_d -narrow stripes is accompanied by creation of wider stripes, which are shrunk by the flow in turn.

II. *Peripheral-region-dominated dynamics.*—The same process of layered structure formation takes place in the peripheral domain as well. However, advection, which is statistically isotropic in the bulk, is strongly anisotropic in the peripheral domain, where advection is more efficient in the direction along the boundary than in the normal direction. This anisotropy causes the layers in the peripheral domain to stretch mainly along the boundary. The stripes closer to the boundary shrink slower than the remote ones, since the normal to the boundary component of the stretching rate decreases as one approaches the boundary. Therefore, the developed layered structure (i.e., the one which contains stripes of the diffusive scale width) occupies a part of the peripheral region where the amounts of \mathcal{A} and \mathcal{B} become negligible. Thus, the empty of chemicals region, formed in the bulk by the end of the first stage, starts to expand towards the boundary. As a result, the chemicals are arranged mainly within a δ vicinity of the boundary (wall), $\delta \sim L/\sqrt{\lambda t}$, where the concentrations of the chemicals remain practically unchanged. Outside this layer, at $L \gg q \gg \delta$, the concentration of chemicals decreases algebraically $\langle n_{a,b} \rangle \propto t^{-3/2} q^{-3}$. During this stage the overall amounts of chemicals decrease as $\delta(t)$, that is, $\propto 1/\sqrt{t}$. The spatiotemporal picture explained above follows from the universal form of the velocity field profile in the proximity of the boundary. This stage lasts for $\tau_2 \sim \sqrt{\text{Pe}}/\lambda$, i.e., until δ shrinks to the width of the boundary layer r_{bl} .

III. *Boundary-layer-dominated dynamics.*—Chemicals remain mainly within the r_{bl} -thin (not varying with time) vicinity of the boundary. The boundary layer width r_{bl} is still much larger than the reaction zone size (defined for the boundary region), so that the passive scalar description applies. The interfacial area where the chemicals interact does not change significantly anymore. Thus, due to linear relation between flux of chemicals to the interface and their concentrations, the algebraic decay switches to an exponential one, i.e., $\langle n_{a,b} \rangle \propto \exp(-\gamma t)$, for $t \gg \tau_2$, where $\gamma \sim \lambda/\sqrt{\text{Pe}} \sim L^{-1}\sqrt{\lambda\kappa}$. This estimate for the decrement γ follows from the condition that the temporal derivative term and the diffusive terms in Eq. (3) are of the same order scale r_{bl} away from the boundary. Then $N_{a,b}(t) \propto \exp(-\gamma t)$. Chemicals are mainly concentrated inside the diffusion boundary layer. Outside the boundary layer (at $q \gg r_{bl}$), one of the chemicals prevails and its concentration decays algebraically, $\propto 1/q^3$. The passive scalar description in the vicinity of the boundary layer is broken when r_{ch} , which grows exponentially with time, becomes of the order of r_{bl} , i.e., when at the boundary $n_{a,b}$ becomes $\sim \lambda/(R\sqrt{\text{Pe}})$. One concludes that the duration of the boundary-layer-dominated stage is $\tau_3 \sim \gamma^{-1} \ln(Rn_0\sqrt{\text{Pe}}/\lambda)$, where n_0 is the initial concentration of the chemicals.

IV. *Nonlinear stage.*—By the end of the previous stage, advection and diffusion homogenize the remaining amounts of the chemicals, first within the boundary layer and later over the entire reservoir. After that there are no

inhomogeneities of $n_{a,b}$ left in the system. A purely homogeneous kinetic process takes over: $dN_{a,b}/dt = -RVN_aN_b$ (where V is the chemical reactor volume). Thus, $N_{a,b} \propto 1/t$ during the final stage.

If $N_a \neq N_b$, then the proposed scheme is valid until $N_{a,b}$ become of the order of $|N_a - N_b|$. Then N_a saturates to a constant (if $N_a > N_b$) and N_b disappears exponentially, $\propto \exp(-RN_a t/V)$. (Note that the exponential decay starts after a short intermediate stage characterized by complete homogenization of \mathcal{A} due to advection and diffusion.)

Let us now discuss the effect of unequal diffusion coefficients, still assuming that $\sqrt{\kappa_{a,b}/\lambda} \ll L$. If $Da \gg 1$, then during the first stages, the chemical length r_{ch} is (as above) much smaller than all other scales. This problem can also be reduced to a linear one considering the advection-diffusion equations in domains populated by different species, supplemented by the condition that fluxes of the two chemicals towards the interface are equal. During the first two stages, the evolution is controlled by the stripe formation process which is insensitive to the diffusion. During the latter, third and fourth, stages of the evolution in the uneven $\kappa_a \sim \kappa_b$ case, the chemicals evolve similarly to what was described above for the $\kappa_a = \kappa_b$ case. Thus, the above description applies to the general, $\kappa_a \neq \kappa_b$, case as well.

We conclude with some general remarks. A complicated spatiotemporal behavior for the binary chemical reaction in a chaotic flow is established. Evolution of the chemicals near the boundary (where mixing is slower than in the bulk) determines the intermediate stages of the reaction. Those boundary-dominated stages were not singled out in previous publications on the subject simply because the stages are not observed in an infinite [4] or periodic [19] flow systems. In our setting, the lamellar structure (which is statistically isotropic in bulk and strongly anisotropic near boundaries) is dynamically generated by advection. (This situation is essentially different from the one considered in [20], where the lamellar structure is created initially and no advection participates in subsequent evolution.) We focused here on large scale chaotic flows with the size of the box being of the order of the major scale of the flow. However, it is also of interest for applications to describe chemical reaction acceleration in turbulent flows, which are smooth only inside the viscous range of scales. In this case, with a large value of the viscous to dissipative scales ratio, a consideration similar to those presented in this Letter is applicable. We plan to examine the more complicated case in the future. Also, the approach developed in this Letter is generalizable for other, more complicated, types of chemical reaction, e.g., competing chemical reactions. For completeness, let us also mention another case of interest which is realized at moderate Da , large Pe , and if one of chemicals is present in abundance. The joint effect of advection and chemistry is different in this case (than in the problem discussed in this Letter), even though rich

multiscale structure of spatial correlations is also revealed [21]. A final remark concerns the validity of the hydrodynamic description of the chemical reaction dynamics. It is known that the character of spatial fluctuations in the initial distribution of chemicals may essentially influence the long-time behavior in diffusion-limited chemical systems [22,23]. In some cases (of low space dimensionality, $d \leq 2$) large scale renormalization of the concentration fields due to the small scale fluctuations could be important (see, e.g., [24]). In our case, however, this does not happen because the long-time correlations are completely destroyed by chaotic advection.

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