

Chemical Transients in Closed Chaotic Flows: The Role of Effective Dimensions

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We investigate chemical activity in hydrodynamical flows in closed containers. In contrast to open flows, in closed flows the chemical field does not show a well-defined fractal property; nevertheless, there is a transient filamentary structure present. We show that the effect of the filamentary patterns on the chemical activity can be modeled by the use of time-dependent effective dimensions. We derive a new chemical rate equation, which turns out to be coupled to the dynamics of the effective dimension, and predicts an exponential convergence. Previous results concerning activity in open flows are special cases of this new rate equation.

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We are witnessing an increasing interest in the experimental investigation of chemical reactions in time-periodic two-dimensional flows whose advection dynamics is chaotic. After an early attempt [1], recent studies investigate reactions in the blinking vortex flow [2], in a cellular flow [3], and in an electrolytic flow [4]. The type of reactions ranges from excitable media, via autocatalytic, to acid-base reactions. This development has been preceded by a series of theoretical works (see, e.g., Refs. [5–12]).

Although the experiments take place in closed containers, the theoretical understanding indicates that some features appear in a much cleaner form in open flows (for a review see Ref. [13]). In open flows there is a current flowing through the region of observation to which particles, once escaped downstream, cannot return within the observation time. There is a basic dichotomy between the advection dynamics in open and closed flows, as shown in Table I. In the first case (open flows) there is a very clean and time-independent fractal dimension associated with the chaotic advection dynamics. The chaotic advection dynamics itself is, however, unavoidably transient, i.e., of finite lifetime. In the second case (closed flows) chaos is permanent, but produces structures whose degree of filamentarity changes in time. Hence filamentarity is of transient character.

In open flows, the unstable manifold of the chaotic set is a filamentary fractal of zero measure, and this manifold is the skeleton of active processes [6]. In closed flows, however, the unstable filamentation is dense over the full domain, and there is no invariant set which had a well-defined dimension strictly lower than that of the flow. In the absence of fluid transport barriers in closed flows, autocatalytic [8] or excitable reactions [9,10] or even acid-base reactions lead to a steady state in which the full fluid domain is either occupied by the product or no product is present at all. The asymptotic state is thus homogeneous,

and hence much less interesting than in the open case. This is fully consistent with the observation that the product is distributed along the unstable manifolds [5]. Before reaching the asymptotic state, the chemical product appears, however, to have filamentary features [8–10,14] (see inset to Fig. 1).

A recently developed theoretical concept which we shall apply to describe the transient chemical product dynamics is that of effective dimensions. Such space or time-dependent dimensions have been used to understand the effect of transport barriers in chemical reactions [15,16] and of the overall structure of Hamiltonian phase spaces [17] as well. In the context of diffusive line dispersion in homogeneous turbulence, the concept of a time-dependent dimension has been proposed in Ref. [18]. Our approach is an extension of that of Ref. [19] in accordance with Ref. [13]. In [19], the growth of filamentary microbial colonies have been modeled by a time-dependent fractal dimension. We propose here to describe the dynamics of chemical reactions in closed flows by means of a time-dependent effective dimension, $D_{\text{eff}}(t)$. This concept gives a novel set of coupled equations for the time evolution of the chemical products and of the effective dimension, and allows a treatment analogous to that applied to the open flow case. We point out that the convergence towards the homogeneous steady state, in a broad range of reactions, is exponential with an exponent that might be different from the Lyapunov exponent of the advection dynamics. The

TABLE I. Basic difference between properties of open and closed flows.

	open flow	closed flow
chaos	transient	permanent
filamentarity	permanent	transient

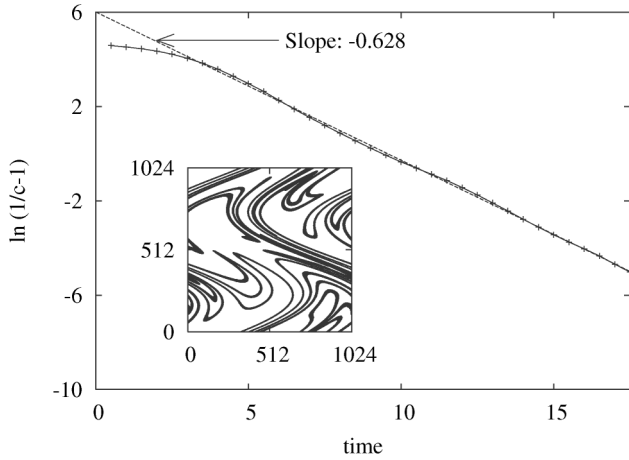


FIG. 1. Concentration of reactant B in an autocatalytic reaction in the sinusoidal shear flow [22]. Time is measured in periods of the flow. The simulations were performed on a grid of size 8192×8192 . The Lyapunov exponent of the flow is $\bar{\lambda} = 0.61 \pm 0.02$. Crosses represent results obtained from the simulation, the straight line is predicted by (18). The relaxation exponent from the plot is $\sigma = 0.628 \pm 0.01$. The inset shows a snapshot of the autocatalytic particles' distribution (black) at time $t = 8$ on a grid of size 1024×1024 .

initial growth depends on the dimension of the initial product distribution. For distributions which are essentially one-dimensional, the initial growth is typically linear in time.

Much insight can be gained into any kind of reaction dynamics by analyzing the so-called Lagrangian filament slice model [9]. The idea is to investigate a long, straight segment of the unstable manifold and follow the reaction perpendicular to this segment only, since due to a fast stretching, the distribution can be assumed to be homogeneous along the manifold. The effect of the flow transversal to the manifold is a local exponential contraction governed by the contracting Lyapunov exponent. We shall use the simplest version of this model when the dynamics can be described by ordinary differential equations [20].

Consider first reactions with front propagation, e.g., an autocatalytic reaction $A + C \rightarrow 2C$. In such cases material C is spreading into the medium of material A with a constant front velocity v and behind the front the concentration of C is approximately a constant, \bar{c} . The width of the band in which material C is distributed along the unstable manifold increases therefore with the speed of $2v$. A typical band of instantaneous width $\delta(t)$ is also shrinking at the rate $-\bar{\lambda}\delta$, where $\bar{\lambda}$ is the average positive Lyapunov exponent of the chaotic advection dynamics of the two-dimensional incompressible flow. In a domain of linear size L , the dynamics of the relative width $d = \delta/L$ is thus

$$\dot{d} = -\bar{\lambda}d + 2v/L. \quad (1)$$

This equation is expected to be valid for *any* reaction with frontal propagation. According to Luther's law [21], the

front velocity is proportional to the square root of the reaction rate k and of the diffusion coefficient D_{diff} :

$$v = \alpha(kD_{\text{diff}})^{1/2}. \quad (2)$$

With α of order unity, this law holds for an amazing variety of reactions ranging from bistable and excitable ones to flames [21].

In the case of an acid-base-type reaction $A + B \rightarrow 2C$, we imagine that components A and B are distributed uniformly on the two sides of the manifold and reaction takes place within bands of average width $\delta(t)$. Inside this band the C concentration is assumed to be a constant \bar{c} . The width is changing due to diffusion with a rate D_{diff}/δ . Note that $\dot{\delta} = D_{\text{diff}}/\delta$ has the usual $\delta = \sqrt{\delta_0^2 + 2D_{\text{diff}}t}$ solution, but this is counteracted by the simultaneous presence of exponential contraction due to the chaotic flow. The full dynamics of the dimensionless bandwidth $d = \delta/L$ is now governed by

$$\dot{d} = -\bar{\lambda}d + D_{\text{diff}}/(L^2d). \quad (3)$$

We can unify and generalize these cases by writing

$$\dot{d} = -\bar{\lambda}dg(d), \quad (4)$$

where function $g(d)$ is dimensionless. Based on the examples, we assume that there is a steady state solution $d^* > 0$ for which

$$g(d^*) \equiv 0, \quad (5)$$

and the steady state is stable [$g'(d^*) > 0$]. Note that in a reaction free case $g \equiv 1$ and no nontrivial steady state exists.

The steady state bandwidth for the particular reactions (1) and (3) is $d^* = 2U$ and $d^* = Pe^{-1/2}$, respectively. Here $Pe = L^2\bar{\lambda}/D_{\text{diff}}$ is the (Lagrangian) Péclet number, and $U = v/(\bar{\lambda}L)$ is a dimensionless front velocity, which can be written in view of (2) as $U = \alpha(Da/Pe)^{1/2}$ with $Da = k/\bar{\lambda}$ as the (Lagrangian) Damköhler number [13]. These forms show that acid-base-type reactions are basically diffusion limited, while in the frontal case the reaction rate also plays an important role.

We are applying now the width dynamics to an unstable manifold segment which is *growing* in time. Because of area preservation (incompressibility) the typical rate of contraction [$\bar{\lambda}$ in (1)] towards the unstable manifold must be the same as the stretching rate of typical line segments, which should grow initially as $\exp(\bar{\lambda}t)$.

The increase of the length \mathcal{L} of a material line of *finite width* is exponential over short times only, later saturation sets in at some \mathcal{L}^* since the width dynamics reaches its steady state d^* . In a container of area $\mathcal{H}L^2$ (for a dish of radius $L = R$ the prefactor is, e.g., $\mathcal{H} = \pi$), the total length is $\mathcal{L}^* = \mathcal{H}L/d^*$. As a simple though general form we write the equation for the dimensionless length $l = \mathcal{L}/L$ as

$$\dot{l} = \bar{\lambda} l \left(1 - f\left(\frac{ld^*}{\mathcal{H}}\right) \right). \quad (6)$$

In contrast to g , we do not specify the functional form of $f(\mathcal{L}/\mathcal{L}^*) > 0$, but require $f(0) = 0$ and $f(1) = 1$ to ensure an initial exponential growth and a saturation.

The fractal dimension of curves can be considered as a measure of their foldedness. Since a long line can fit into a finite area only if it is strongly folded, we *define* an instantaneous effective dimension $D_{\text{eff}}(t)$ by counting the number N of boxes needed to cover all the bands containing product C with boxes of size $d(t)$, and requiring that it scales as a power of d : $N(d) = \mathcal{H} d^{-D_{\text{eff}}}$ ($1 \leq D_{\text{eff}} \leq 2$). To total length can then be written as

$$l(t) = \mathcal{H} d(t)^{1-D_{\text{eff}}(t)}. \quad (7)$$

The product content in the container is $C(t) = \bar{c} \mathcal{L} \delta = \bar{c} \mathcal{H} L^2 d(t)^{2-D_{\text{eff}}(t)}$, where \bar{c} is the concentration inside the bands. The average dimensionless concentration is then $c(t) = C(t)/(\bar{c} \mathcal{H} L^2)$, and we find from (7) that

$$c(t) = d(t)l(t)/\mathcal{H} = d(t)^{2-D_{\text{eff}}(t)}. \quad (8)$$

By taking the time derivative of the left equality and using (4) and (6), we obtain

$$\dot{c} = c \bar{\lambda} [1 - g(c^{1+\beta}) - f(c^{-\beta} d^*)], \quad (9)$$

where

$$\beta(t) = \frac{D_{\text{eff}}(t) - 1}{2 - D_{\text{eff}}(t)}. \quad (10)$$

It is remarkable that a negative power ($-\beta$) of the average concentration occurs in the chemical rate equation, just like in open flows [6,13].

Differentiating the right equality of (8), and using (4), (9), and (10), an equation for the effective dimension follows:

$$\begin{aligned} \dot{\beta} &= \frac{\dot{D}_{\text{eff}}}{(2 - D_{\text{eff}})^2} \\ &= \frac{\bar{\lambda}}{\ln c} \left\{ \beta g(c^{1+\beta}) + (1 + \beta) [f(c^{-\beta} d^*) - 1] \right\}. \end{aligned} \quad (11)$$

Equations (9) and (11) give a coupled set of equations for the concentration c and the dimension-dependent exponent β .

For short times, $t \ll 1/\bar{\lambda}$, we can assume that $f \approx 0$ since saturation is not yet in effect. If the product is distributed along a line initially, so that the effective dimension is $D_{\text{eff},0} = 1$, implying $\beta_0 = 0$, we find from (9)

$$\dot{c} = \bar{\lambda} c [1 - g(c)]. \quad (12)$$

Substituting here from (1) the form $g(c) = 1 - 2U/c$ of frontal reactions, we find $\dot{c} = 2U\bar{\lambda}$, implying a linear growth:

$$c(t) = c_0 + 2U\bar{\lambda}t. \quad (13)$$

For an acid-base-type reaction [see (3)], $g(c) = 1 - 1/(c^2 \cdot Pe)$, thus $\dot{c} = \bar{\lambda}/(c \cdot Pe)$, leading to a diffusive growth

$$c(t) = \sqrt{c_0^2 + 2\bar{\lambda}t/Pe} \approx c_0 + \frac{\bar{\lambda}t}{c_0 \cdot Pe}. \quad (14)$$

Note that an exponential growth would only follow from (12) if g would be constant, which is not the case.

In order to see how the trivial $c \rightarrow 1$, $D \rightarrow 2$, $d \rightarrow d^*$ final state is reached, we take into account that $c^{1+\beta} \equiv d$ and $c^{-\beta} d^* \equiv cd^*/d$, and linearize Eqs. (4), (9), and (11), as

$$\dot{d} = -b\bar{\lambda}d^*(d - d^*), \quad (15)$$

$$\dot{c} = -a\bar{\lambda}(c - 1) - \bar{\lambda}(b - a/d^*)(d - d^*), \quad (16)$$

$$\dot{D}_{\text{eff}} = \frac{a\bar{\lambda}}{\ln d^*}(c - 1) + \frac{\bar{\lambda}}{\ln d^*}(b - a/d^*)(d - d^*), \quad (17)$$

respectively, where D_{eff} is used instead of β , and notations $a \equiv f'(1)$ and $b \equiv g'(d^*)$ have been introduced. We immediately observe that the dynamics of the effective dimension D_{eff} simply follows the dynamics of the average concentration c as we approach the steady state: comparing (16) and (17) we see that $\dot{D}_{\text{eff}} = -\dot{c}/\ln d^*$. The exponential convergence $c \rightarrow 1$ is governed by the largest of the eigenvalues of the Jacobian in Eqs. (15) and (16). The eigenvalues turn out to be $-a\bar{\lambda}$ and $-bd^*\bar{\lambda}$, hence we have

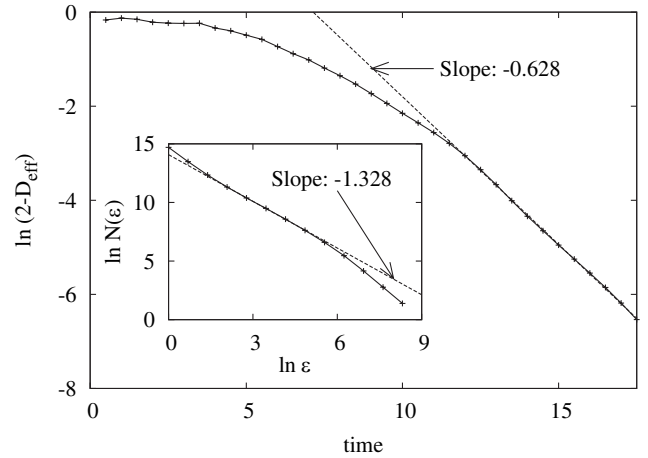


FIG. 2. Time dependence of the effective dimension, in the same numerical experiment as in Fig. 1. Crosses represent the measured D_{eff} values, while the straight line is predicted by (18). The relaxation exponent is $\sigma = 0.628 \pm 0.01$. Exponent D_{eff} is obtained from a box-counting algorithm carried out by counting the number $N(\epsilon)$ of squares of linear size ϵ [over a range $\epsilon > d(t)$] needed to cover the product-occupied region at different times. An example is shown in the inset, where the data correspond to time $t = 8$.

$$c - 1 \sim \exp(-\sigma t), \quad D_{\text{eff}} - 2 \sim \exp(-\sigma t), \quad (18)$$

with

$$\sigma = \min\{a\bar{\lambda}, bd^*\bar{\lambda}\}. \quad (19)$$

It is easy to check from the definition of $g(d)$ that for autocatalytic reactions $bd^* = 1$ ($\sigma = \min\{a\bar{\lambda}, \bar{\lambda}\}$), while for acid-base reactions $bd^* = 2$ ($\sigma = \min\{a\bar{\lambda}, 2\bar{\lambda}\}$).

The exponential convergence (18) has been verified in numerical experiments. The flow we used is a sinusoidal shear flow in alternating directions in a unit square with periodic boundary conditions [22]. The unit square was covered with a grid. Initially, one reacting particle was placed in each grid cell of a narrow band across the fluid. Autocatalytic reaction events occurred after each half time period of the flow, when the flow changes direction. At these instances all occupied grid cells “infected” all their neighbors. The average concentration of the autocatalytic particles as a function of time is well predicted by (18), as illustrated in Fig. 1. The inset shows a snapshot of the active particles. In Fig. 2 the prediction (18) for the effective dimension is verified in the large t regime, and $\sigma \approx \bar{\lambda}$ was obtained. The inset illustrates how the instantaneous effective dimension was estimated. For very large times we observed a deviation from (18) which might be interpreted as a result of numerical diffusion. Similar results have been obtained for the acid-base reaction in the same flow with $\sigma = 1.34\bar{\lambda}$. This is an example where the relaxation exponent is different from the Lyapunov exponent.

We mention briefly what the theory predicts for a dye droplet in a closed container when both diffusion and reaction are absent. In this case, $g \equiv 1$ and $f \equiv 0$, since there is no saturation in filament length. From (9) $\dot{c} \equiv 0$ follows, as it should in a closed container. From (11) we find that $\dot{\beta} = -\bar{\lambda}/\text{Inc} = \text{const}$, consequently $\beta = \beta_0 - (\bar{\lambda}/\text{Inc})t$. From (10) $D_{\text{eff}} = (1 + 2\beta)/(1 + \beta)$, i.e.,

$$D_{\text{eff}}(t) = 2 - \frac{2 - D_{\text{eff},0}}{1 - (2 - D_{\text{eff},0})\bar{\lambda}t/\text{Inc}}. \quad (20)$$

The time evolution of the effective dimension is much slower in passive advection than in reacting cases since it is governed by a power law.

We note that Eqs. (9) and (11) also contain the equation obtained previously for autocatalytic reactions in open flows. In that case, the effective dimension is the time-independent information dimension D of the unstable manifold, $D_{\text{eff}} \equiv D$, $\dot{D}_{\text{eff}} \equiv 0$, implying $\dot{\beta} \equiv 0$. From (11) $f \equiv 1 - (D - 1)g$ must hold. With this, (9) yields

$$\dot{c} = -c\bar{\lambda}(2 - D)g(c^{1+\beta}). \quad (21)$$

For frontal reactions $g(c^{1+\beta}) = 1 - 2U/c^{1+\beta}$, and by introducing the escape rate $\kappa \equiv (2 - D)\bar{\lambda}$ we find

$$\dot{c} = -c\kappa + 2U\kappa c^{-\beta}, \quad (22)$$

the result of [6,13].

In conclusion, the predicted asymptotic behavior and the initial nonexponential growth of the chemical product in closed containers can directly be checked in experiments. An extension of the theory towards including the distribution of the local Lyapunov exponents might lead to further details without changing the features obtained here for the average behavior.

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