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On the connection between reaction efficiency and interface structure in open laminar flows

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ABSTRACT

We investigate numerically the steady-state properties of a mixing-controlled reaction between segregated reactants continuously inflowing–outflowing the annular region between counter-rotating coaxial cylinders in the Stokes regime. This system provides a prototypical example of an open nonchaotic flow generating steady-state kinematic mixing structures of arbitrarily fine lengthscales which can be characterized analytically. The kinematic interface structure is compared and contrasted to that of the reaction interface associated with the presence of a small but finite diffusivity. Results of accurate numerical simulations show that reaction efficiency and mixing performance are only weakly correlated with the global measure of both the kinematic and the reaction interface. Relevant information on reaction regimes at low diffusivity can instead be obtained from the analysis of the spatial distribution of the kinematic interface, which controls the localization properties of unreacted species. The generality of the results is tested for several prototypical open and closed channel flows.

1. Introduction

In the last decade, the research focusing on fluid mixing and chemical reactions in laminar flows has been experiencing a second burst of activity owed to the swift development of microfluidic devices, which mainly operate in the laminar or even the Stokes regime (Ehrfeld, Hessel, & Löwe, 2001; Karniadakis, Beskok, & Aluru, 2005).

This line of investigation was initiated more than 20 years ago by Aref, who showed how a simple time-periodic incompressible flow can generate complex mixing structures characterized by arbitrarily fine lengthscales (see, e.g., Aref, 2002 for a historical perspective on the subject). Stemming from the deterministic nature of the convective process, the characterization of mixing and chemical reactions in laminar flows rests upon a direct analysis of kinematic motion and deformation based on classical tools of dynamical system theory, such as Poincaré sections, interface stretching dynamics, Lyapunov exponents, metric and topological entropy (the reader interested in the dynamical system approach to fluid mixing is referred to the work by Finn, Cox, and Byrne (2004), and to the references cited therein).

However powerful, the dynamical system approach suffers some limitations as regards its domain of application, namely (i) it cannot take into explicit account the presence of molecular transport (diffusion), and (ii) owing to the time-asymptotic nature of the approach, its tools are well-defined only in the context of closed (i.e. impermeable) bounded flows in that fluid particle trajectories are confined to the mixing space at all times, and therefore the Lagrangian quantities, that are defined as time-averages along typical orbits, can be computed in the large[1].

As regards the first shortcoming, theoretical arguments have been developed, starting from the mid eighties, in the framework of the so-called *lamellar models* for estimating the impact of diffusion and chemical reactions on the kinematics-based analysis of mixing processes (see, e.g., Clifford, Cox, & Roberts, 1998; Szalai, Kukura, Arratia, & Muzzio, 2003, and therein cited references). A direct comparison of lamellar model predictions with the actual behavior of the corresponding advecting–diffusing-reacting system showed that a successful implementation of the lamellar approach is sensible only in the case where the flow defines a globally chaotic kinematics, i.e. when the local deformation mechanisms induce sustained exponential stretching of line (or surface) fluid ele-

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[1] More formally, the impermeable nature of the finite-sized mixing domain implies the validity Poincaré's recurrence theorem, which constitutes the cornerstone of the ergodic theory of dynamical systems (Katok & Hasselblatt, 1995).

ments, independently of their specific location within the mixing domain.

Motivated by these results, a number of authors have considered the problem of defining optimal mixing conditions in a purely kinematic framework, where convective protocols yielding the fastest increase of Intermaterial Contact Area (henceforth referred to as ICA) were sought (Fourcade, Wadley, Hoefsloot, Green, & Iedema, 2001; Galaktionov, Anderson, & Peters, 2002; Hwu, Young, & Chen, 1997; Meleshko & Aref, 1996; Meleshko & Aref, 1998; Vikhansky (2002)). Quantitative tools have also been developed for addressing the nonuniform character of the spatial distribution of ICA in two- (Alvarez, Muzzio, Cerbelli, Adrover, & Giona, 1998) and three-dimensional (Giona & Adrover, 2001) chaotic flows.

In general terms, when molecular diffusion is active, selecting an optimal stirring protocol on the basis of the fastest increase of kinematic intermaterial contact area is based on the following argument. In incompressible flows, an exponential increase of ICA must occur along with the exponential shrinking of lengths in a direction transverse to that of ICA stretching. Therefore, the enhancement of mass transfer between the segregated mixing regions is associated with a twofold effect, namely the existence of an increased interfacial area available for the mass transfer, and the amplification of concentration gradients which enhances the Fickian flux of the concentration of the transported entity across the interface. In point of fact, this seemingly indisputable conclusion overlooks an important effect associated with the bounded nature of the mixing space, namely the nonlocal character of the mixing process, whose ultimate origin is to be ascribed to the folding of partially mixed structures which repeatedly brings into close contact fluid portions that were originally apart from each other. In partially chaotic flows where large islands of regular motion are present, or, *a fortiori*, in nonchaotic flows, this nonlocal effect might control the mixing rate and overshadow chaotic transport (Giona, Adrover, Cerbelli, & Vitacolonna, 2004; Cerbelli, Vitacolonna, Adrover, & Giona, 2004). The breakdown of the advection-dominated regime and the onset of the asymptotic regime is discussed in Thiffeault (2003).

Besides, even in kinematically regular bounded closed flows, the interaction between advection and diffusion can still result in enhanced mixing and reaction regimes with respect to the case where molecular transport is the only mixing mechanism (Giona, Cerbelli, & Vitacolonna, 2004; Gleeson, Roche, West, & Gelb, 2004). Exploiting this effect can become crucial in microflow devices, where globally chaotic conditions are often unattainable due to fabrication and/or pressure drop constraints (Squires & Quake, 2005). The necessity of achieving convection-enhanced mixing regimes is particularly felt in biological applications of microfluidics, where the small diffusivity associated with biomolecules (DNA strands, globular proteins, etc.) results in high values of the Peclet number (up to order 10^5 to 10^6, see, e.g., Nguyen & Wu, 2005) even at such small lengthscales.

A different conceptual issue, that concerns both micro- and ordinary lengthscale inflow–outflow devices, is the open nature of the flow domain, which suggests a careful attitude when applying to this situation strategies and techniques developed in the context of closed (i.e. impermeable) bounded flows. An indication that such an approach can be deceiving, even in the purely kinematic context of topological mixing, has been recently offered by Finn and coworkers, who analyzed the mixing performance of a braided pipe mixer (Finn, Cox, & Byrne, 2003). To quote the authors "... in contrast to the case of (two-dimensional) batch mixers, there is no corresponding three-dimensional theory for topological chaos in static mixers. So the expectation that nontrivial braids mix best is based on an analogy rather than on any theoretical foundation ...".

Along the same line of thinking, in this article we undertake an analysis of closed vs. open flow systems in yet a different physical context, namely the steady-state performance of an instantaneous reaction in an open bounded flow. As a case study we consider two segregated reactant streams entering an inflow–outflow Couette device that operates in the Stokes regime. The system is constituted by two coaxial cylinders of radii κR and R ($\kappa < 1$), and length L that can rotate independently at constant angular speed. A three-dimensional Stokes flow is defined as the superposition of the cross-sectional Couette flow associated with the rotation of the two cylinders, and an axial, pressure-driven, Poiseuille flow.

As in the case of closed bounded flow (Giona, Cerbelli, & Adrover, 2002), the instantaneous character of the reaction permits us to define and identify the interface separating the reactants (reaction interface) even in the presence of molecular diffusion. Therefore, the reaction interface provides a well-defined means to establish a comparison between the geometric properties of the partially mixed structures in the presence and in the absence of molecular diffusion.

Due to the rotating walls and to the nonuniform axial velocity profile which vanishes at the cylinder surfaces, the inflow–outflow Couette device exhibits a peculiar feature, namely the existence of flow trajectories whose length increases unboundedly when the inlet condition approaches the system boundaries. Specifically, flow orbits can readily be computed analytically and consist of helices with vanishing pitch in the near-wall regions. As a result, the kinematic interface separating the reactant streams at steady state in the diffusionless limit possesses infinite measure.

Thus, if one were to compare the mixing performance of this apparatus with respect to classical inflow–outflow static mixers (see, e.g., Szalai & Muzzio, 2003) on the basis of ICA generation efficiency, an immediate paradox would arise, namely that a completely regular (i.e. nonchaotic flow) would yield an incomparably better performance than a chaotic stirring field. In fact, in classical static mixers as well as in micromixers exploiting chaotic advection, the steady-state kinematic interface is typically exponentially stretched along the axial direction, but always possesses a finite measure (for an example of ICA stretching computation in a micromixer see Jiang, Drese, Hardt, Küpper, & Schönfeld, 2004).

However, when finer details of the kinematic interface structure are considered, such as its spatial density distribution, important information regarding reaction and mixing regimes in the limit of vanishing diffusivity can be recovered.

By using a generalized version of the the Couette–Poiseuille model, that includes a wider class of physically realizable flows, we show that the low-diffusivity regimes arise as a consequence of the localization of unreacted species at points where the interface density vanishes. This observation, which brings in new physical insight in the existing theory of eigenfunction localization developed in the specific context of parallel flows and based on the concept of effective potential, is apt to provide fruitful generalizations which could be exploited to infer mixing properties of more general classes of flows.

The article is conceptually organized into two main parts. The first part (Sections 2–5) is focused on the analysis of the reaction interface in the three-dimensional Couette device and of its relationship with the kinematic interface and reaction efficiency. The lack of a straightforward connection between these quantities is linked to the nonuniform spatial distribution of the kinematic interface and to the localization of reactant gradients. In the second part (developed in Section 6), a Cartesian model system, that encompasses a variety of channel flows, is used as a benchmark prototypical system to assess the validity and the limits of the results discussed for the open Couette device.