Infinitely fast chemistry in a two-dimensional Navier-Stokes flow

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I. Introduction

Motivation and objectives We study an infinitely fast bimolecular chemical reaction in a two-dimensional closed Navier-Stokes flow. The reactants are initially segregated, separated by infinite gradients and well mixed in their respective domain. This research was motivated by the need to better understand the effect of resolution in Climate-Chemistry models in the stratosphere ([1,2]). Particular attention is given to the effect of the reactants' diffusion κ (or equivalently to the Prandtl number $Pr = \frac{\nu}{\kappa}$ since the viscosity ν will be taken constant). We focus on:

- The length of the contact line between the reactants
- The gradients of the reactants along the contact line (probability distribution)
- The probability distribution and the ensemble average of the reactants' concentrations

Our objective is to relate them to the Lagrangian stretching properties (LSP) of the chaotic trajectories of the flow.

We focus on the initial regime of the reaction characterized by a well defined one dimensional contact line. The duration of this regime can be roughly approximated by the mix-down time scale from the largest scale of the flow L to the diffusive cutoff: $T_{mix} \approx \frac{T}{2}\ln Pe = \frac{T}{2}\ln RePr$, where Re, Pe and Pr are respectively the Reynolds number, the Peclet number and the Prandtl number. T is the integral time scale of the flow

Infinitely fast chemistry We consider the bimolecular chemical reaction $A + B \longrightarrow C$ in stoichiometric quantities. The field $\phi = C_A - C_B$, defined as the difference between the reactants' concentration fields C_A and C_B is a passive tracer:

$$\frac{\partial \phi}{\partial t} + \mathbf{u}\cdot\nabla\phi = \kappa\nabla^2\phi, \tag{1}$$

The reaction is instantaneous: A and B cannot coexist at the same location. Denoting with an over-bar the space average over the domain, we have:

$$\begin{cases} C_A(\mathbf{x},t) = \phi(\mathbf{x},t) & \text{and } C_B(\mathbf{x},t) = 0 \quad \text{if } \phi(\mathbf{x},t) > 0 \\ C_B(\mathbf{x},t) = -\phi(\mathbf{x},t) & \text{and } C_A(\mathbf{x},t) = 0 \quad \text{if } \phi(\mathbf{x},t) < 0 \end{cases} \tag{2}$$

$$\overline{C_A} = \overline{C_B} = \frac{\overline{|\phi|}}{2} \tag{3}$$

If A and B are separated by a contact line $\mathcal{L} = \{\mathbf{x}|\phi(\mathbf{x}) = 0\}$ of dimension one and oriented in a counterclockwise direction such that it encloses reactant A (domain D_A), the time derivative of the reactants in an incompressible closed flow is:

$$\mathcal{A}\frac{\overline{dC_A}}{dt} = \mathcal{A}\frac{\overline{dC_B}}{dt} = \frac{1}{2}\mathcal{A}\frac{\overline{d|\phi|}}{dt} = -\kappa\int_{\mathcal{L}(t)}\nabla\phi\cdot\mathbf{n}dl, \tag{4}$$

where $\mathcal{A}$ is the total area of the domain and $\mathbf{n}$ a unit vector normal to $\mathcal{L}(t)$ pointing outward from D_A. We call $-\frac{d\overline{|\phi|}}{dt}$ the chemical speed.

Finite time Lyapunov exponents (FTLE) They are defined as the rate of exponential increase of the distance between the trajectories of two fluid parcels that are initially infinitely close. If $\delta\mathbf{l}(t)$ is the distance between two parcels that start at $\mathbf{x}$ and $\mathbf{x} + \delta\mathbf{l_0}$, then the FTLE $\lambda(\mathbf{x},t)$ at $\mathbf{x}$ over the time interval t is

$$\lambda(\mathbf{x},t) = \frac{1}{t}\max_{\psi}\left\{\ln\frac{|\delta\mathbf{l}|}{|\delta\mathbf{l_0}|}\right\}, \tag{5}$$

where the maximum is calculated over all the possible orientations ψ of $\delta\mathbf{l_0}$. The corresponding $\psi \equiv \psi_+(\mathbf{x},t)$ defines the orientation of a "singular vector" that converges asymptotically in time toward the forward Lyapunov exponent, whose orientation is $\Psi_+(\mathbf{x})$. The FTLE converges to λ_∞, the infinite time Lypunov exponent who is independent of $\mathbf{x}$ ([3]).

We can calculate them in an incompressible flow using the velocity gradient tensor $\mathbf{S} \equiv \nabla\mathbf{u}(\mathbf{X},t)$ along a trajectory $\mathbf{X}(\mathbf{x},t)$: $\delta\mathbf{l}$ is solution of $\frac{d\delta\mathbf{l}}{dt} - \mathbf{S}(t).\delta\mathbf{l} = 0$ and is given by $\delta\mathbf{l} = \mathbf{M}\delta\mathbf{l}(\mathbf{t}=\mathbf{0})$ where the resolvent matrix $\mathbf{M}$ is solution of $\frac{d\mathbf{M}}{dt} - \mathbf{S}(t)\mathbf{M} = 0$. The finite time Lyapunov exponent $\lambda(t)$ is given by the largest eigenvalue of $[\mathbf{M}^T\mathbf{M}]^{\frac{1}{2t}}$ with $(\cos\psi_+, \sin\psi_+)$ the associated eigenvalue.

It can be shown with the incompressibility that the FTLE is also the maximum exponential growth rate of a wave number $\mathbf{k}$ (or equivalently of a passive tracer gradient in the absence of diffusion), solution of $\frac{d\mathbf{k}}{dt} + \mathbf{S}^T(t).\mathbf{k} = 0$. Considering the resolvent matrix $\mathbf{N}$ such that $\mathbf{k} = \mathbf{N}\mathbf{k}(\mathbf{t}=\mathbf{0})$, the finite time Lyapunov exponent $\lambda(t)$ is the largest eigenvalue of $[\mathbf{N}^T\mathbf{N}]^{\frac{1}{2t}}$ with $(-\sin\psi_+, \cos\psi_+)$ the associated eigenvalue.

II. Theory

Contact line lengthening An element $\delta\mathbf{l_0} = |\delta\mathbf{l_0}|(\cos\alpha, \sin\alpha)$ of the contact line at the initial time is advected at time t into an element $\delta\mathbf{l}$ whose squared norm is

$$|\delta\mathbf{l}|^2 = \delta\mathbf{l_0}^T\mathbf{M}^T\mathbf{M}\delta\mathbf{l_0} = |\delta\mathbf{l_0}|^2\left[e^{2\lambda t}\cos^2(\psi_+ - \alpha) + e^{-2\lambda t}\sin^2(\psi_+ - \alpha)\right] \tag{6}$$

Noting that the angle α is random, we can show that the total ensemble average length of the contact line is (brackets are for an ensemble average):

$$\langle L\rangle(t) = L_0\int_0^\pi\int_0^\infty\frac{d\gamma}{\pi}dlP_\lambda(t,l)\sqrt{e^{2lt}\cos^2\gamma + e^{-2lt}\sin^2\gamma}, \tag{7}$$

where we have introduced the probability density function (pdf) P_λ of the FTLE.

Gradients along the contact line We define the coordinate $\mathbf{r}$ corresponding to the co-moving frame with a Lagrangian parcel trajectory $\mathbf{X}$. Assuming that the tracer varies only in the direction perpendicular to the contact line we write:

$$\phi(\mathbf{x},t) \equiv \chi(\mathbf{r},t) = \widetilde{\chi}(\mathbf{k}\cdot\mathbf{r},t) \equiv \widetilde{\chi}(\eta,t) \tag{8}$$

where $\mathbf{k}$ is a vector perpendicular to the contact line. Assuming a locally smooth and derivable velocity field, we can show from (1) and (8) (see e.g. [4]):

$$\begin{aligned} &\tfrac{d\mathbf{k}}{dt} + \mathbf{S}^T(t).\mathbf{k} = 0 \\ &\tfrac{\partial\widetilde{\chi}}{\partial t} = \kappa|\mathbf{k}|^2\tfrac{\partial^2\widetilde{\chi}}{\partial\eta^2} \end{aligned} \tag{9}$$

We can solve this equation noting that it is a heat equation with the rescaled time $\Theta \equiv \int_0^t du\,|\mathbf{k}(u)|^2$. The initial condition is $\frac{\partial\widetilde{\chi}}{\partial\eta}(t=0) = A_0\delta(\eta)$ (infinite initial gradient). We assume that the "singular vector" $(\cos\psi_+, \sin\psi_+)$ is constant and equal to the forward lyapunov vector $(\cos\Psi_+, \sin\Psi_+)$. We get the norm of the advected gradient $|\nabla\phi_\mathcal{L}|$ with the contact line:

$$\begin{aligned} &|\nabla\phi_\mathcal{L}| = \tfrac{A_0}{\sqrt{\pi\kappa}}G \\ &\text{with } G = \sqrt{\tfrac{e^{2\lambda t}\cos^2(\Psi_+ - \alpha) + e^{-2\lambda t}\sin^2(\Psi_+ - \alpha)}{\tau e^{2\lambda t}\cos^2(\Psi_+ - \alpha) + \widetilde{\tau}\sin^2(\Psi_+ - \alpha)}}. \end{aligned} \tag{10}$$

We introduce two equivalent times τ and $\widetilde{\tau}$:

$$\tau = \frac{\int_0^t e^{2u\lambda(u)}du}{e^{2t\lambda(t)}} \text{ and } \widetilde{\tau} = \int_0^t e^{-2u\lambda(u)}du. \tag{11}$$

The equivalent time τ measures the stretching time of a Lagrangian parcel in the recent past. The pdf $P_{G,\mathcal{L}}(t,g)$ of G along the contact line is:

$$P_{G,\mathcal{L}}(t,g) = \frac{\int\int\frac{d\gamma}{\pi}dlP_{G,\lambda}(t,g,l)\sqrt{e^{2lt}\cos^2\gamma + e^{-2lt}\sin^2\gamma}}{\int\int\frac{d\gamma}{\pi}dlP_\lambda(t,l)\sqrt{e^{2lt}\cos^2\gamma + e^{-2lt}\sin^2\gamma}}, \tag{12}$$

where we have introduced the joint pdf $P_{G,\lambda}(t,g,l)$ of G and λ. $P_{G,\mathcal{L}}(t,g)$ is asymptotically equivalent to $P_{G,\mathcal{L},\infty}(t,g)$ at large times:

$$P_{G,\mathcal{L}}(t,g) \sim P_{G,\mathcal{L},\infty}(t,g) = \frac{\int dlP_{\frac{1}{\sqrt{\tau}},\lambda}(t,g,l)e^{lt}}{\int dlP_\lambda(t,l)e^{lt}}, \tag{13}$$

where $P_{\frac{1}{\sqrt{\tau}},\lambda}$ is the joint pdf of $\frac{1}{\sqrt{\tau}}$ and λ.

Chemical speed The chemical speed can be written as the production of the diffusion with the mean contact line length $\langle L\rangle$ and the mean gradient along it ($\langle|\nabla\phi_\mathcal{L}|\rangle$):

$$-\langle\frac{d\overline{|\phi|}}{dt}\rangle = \frac{2A_0}{\sqrt{\pi\mathcal{A}}}\sqrt{\kappa}\langle L\rangle\langle G\rangle \tag{14}$$

Reactants density function It is possible to show that we can find $\epsilon \ll 1$ such that the pdf P_Φ of $|\phi|$ is:

$$P_\Phi(\phi) = \frac{4}{\mathcal{A}A_0}\sqrt{\kappa}\langle L\rangle\langle\frac{1}{G}\rangle erf^{-1'}\left(\frac{\phi}{A_0}\right) \text{ for } \phi\in[0, A_0(1-\epsilon)]. \tag{15}$$

The term $erf^{-1'}$ is the derivative of the inverse of the Gauss error function, defined for a real x as follows: $x \longmapsto \frac{2}{\sqrt{\pi}}\int_0^{x'}e^{-t^2}dt$. The denisty P_Φ is proportional to $\sqrt{\kappa}\langle L\rangle$ because the area where the field ϕ takes non-trivial values (i.e significantly different from the initial value A_0) is proportional to $\sqrt{\kappa}\langle L\rangle$: its length is $\langle L\rangle$ while its width is controlled by diffusive processes. Finally the term $\langle\frac{1}{G}\rangle$ depicts the effect of the mean gradient, with a decrease of the gradient along the contact line explaining an increase in the probability of small values of $|\phi|$.

III. A two-dimensional Navier Stokes flow

The vorticity equation, integrated with the pseudo-spectral method, is: $\frac{\partial\omega}{\partial t} + \mathbf{u}\cdot\boldsymbol{\nabla}\omega = F - R_0\omega + \nu\nabla^2\omega$. F is a forcing term at wave number 3, R_0 the Rayleigh friction and ν the viscosity. The equation is integrated in a doubly periodic box $[-\pi,\pi]\times[-\pi,\pi]$ on a 512×512 grid. The integral time scale of the flow $T \equiv \sqrt{\frac{2}{\langle\omega^2\rangle}}$ will be used to normalize the time axis. The Reynolds number is of the order of 10^4.

Finite time Lyapunov exponents maps

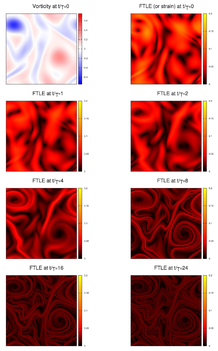

Figure 1: FTLE maps at different times and plotted at the starting locations of the trajectories. At the top are plotted the vorticity (left) and the strain (right) at $t = 0$.

Statistics of the Lagrangian stretching properties (LSP) .

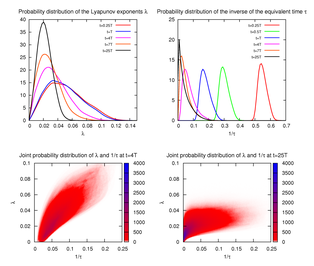

Figure 2: Top: probability density of the Lyapunov exponents (left) and of the inverse of the equivalent time τ (right) for $0 < t \leq 25T$. We note that the density of λ at $t = 0.25T$ is roughly the density of the strain. Bottom: their joint density at $t = 4T$ (left) and $t = 25T$ (right).

We define $G_e(l,t) = -\frac{\ln(P_\lambda(t,l))}{t} + \frac{\ln t}{2t} + \frac{A_e(t)}{t}$, where $A_e(t)$ is chosen to have $\min_\lambda G_e(l,t) = 0$. Large deviation theory predicts that A_e has a limit at infinity and that G_e converges to the Cramer function ([5]). With $P_\lambda(t,l) \propto \exp(-tG_e(l,t))$ we have for $t \ll \frac{T}{4}$ (from (7)):

$$\begin{aligned} \langle L\rangle \sim L_E \equiv\ & L_0\int\int\frac{d\gamma}{\pi}dlP_\lambda(t,l)|\cos\gamma|e^{lt} \\ & \propto e^{t\max_l(l - G_e(l,t))} \end{aligned} \tag{16}$$

The lengthening of the contact line is dominated by rare events for times that are not too small.

From our simulations $\max_l(l - G_e(l,t))$ saturates at ≈ 0.027.

Noting that $\langle G\rangle$ is asymptotically equivalent to $\langle\frac{1}{\tau}\rangle$ (assuming that τ and λ become independent), it has a time limit at infinity and we should have, for sufficiently large times,

$$-\langle\frac{d\overline{|\phi|}}{dt}\rangle \propto e^{t\max_\lambda(\lambda - G_e(\lambda,t))}. \tag{17}$$

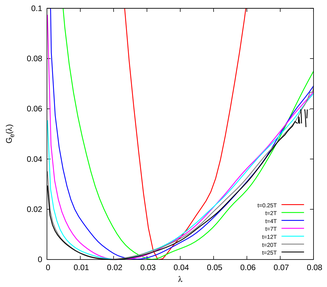

Figure 3: Function $G_e(\lambda)$ at different times $0.25 < t/T < 25$. We note the asymmetry of G_e and the faster convergence for large FTLE

IV. Numerical results

The numerical simulations are performed for eight different Prandtl numbers $Pr \equiv \frac{\kappa}{\nu} = 2^i$ for $0 \leq i \leq 7$ (Peclet number between 10^4 and 10^6). For each one we run an ensemble of 34 simulations integrating the vorticity and the passive tracer equations in the periodic box. Each member is defined by its initial condition on the flow, taken as the vorticity field every turnover time of a long time run of the flow. For each member, we use the following initial condition on the tracer: $\phi(x,y,t=0) = 2A_0(H(x) - \frac{1}{2})$ for $(x,y)\in[-\pi,\pi]^2$, , where H is the Heaviside step function.

Contact line

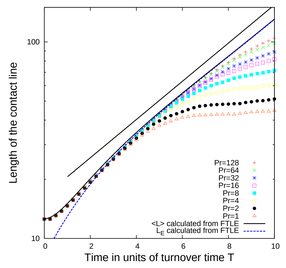

Figure 4: Ensemble average of the length of the contact line. The dotted lines correspond to the DNS, $\langle L\rangle$ and L_E are calculated using the FTLE pdf. The shifted line correspond to an exponential increase at the rate 0.027.

Chemical speed

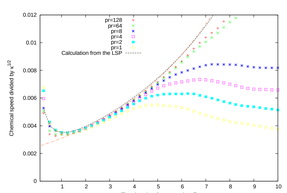

Figure 5: Chemical speed, rescaled by $\sqrt{\kappa}$, from the DNS, and calculated using the LSP. We also plot the curve corresponding to an exponential increase at the rate 0.027.

Gradients along the contact line pdf

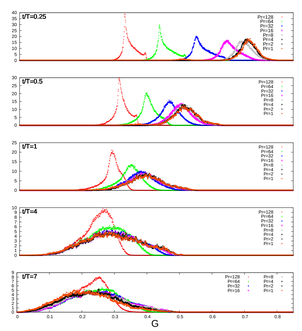

Figure 6: Pdf of $G \equiv \frac{\sqrt{\pi\kappa}}{A_0}|\nabla\phi_\mathcal{L}|$ calculated from the DNS at different times and different Prandtl numbers.

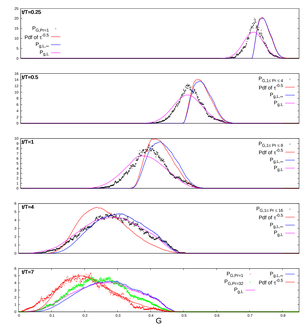

Figure 7: Comparison, in the limit of inifinite initial gradients, between the pdf of $G \equiv \frac{\sqrt{\pi\kappa}}{A_0}|\nabla\phi_\mathcal{L}|$ calculated from the DNS and from LSP.

Pdf of the reactants

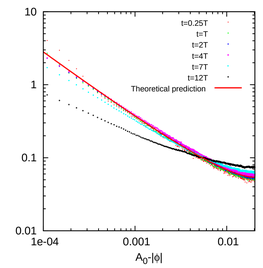

Figure 8: Probability density function of $A_0 - |\phi|$ multiplied by $\frac{\sqrt{\kappa}}{\langle L\rangle\langle\frac{1}{G}\rangle}$. The red curve (theoretical prediction) corresponds to $\frac{4}{\mathcal{A}A_0}erf^{-1'}\left(\frac{\phi}{A_0}\right)$, where erf is the Gauss error function. Log-log scale.

V. Conclusions

For an infinitely fast chemical reaction in a chaotic two-dimensional Navier-Stokes flow, at small and intermediate times, our study based on a Lagrangian stretching theory approach explains the lengthening of the contact line between the reactants, links the gradients of the reactants on this line to the Lagrangian stretching properties of the flow (specifically to the joint distribution of $(\lambda,\tau,\widetilde{\tau})$) and explains the effect of diffusion on theses quantities. In particular, we have highlighted the importance of rare events (large stretching) in the evolution of the mean reactants concentrations. This paves the way to the development of sub-grid parametrizations for fast chemistry in turbulent and chaotic flows.

Open questions and future work (some in progress) .
- Extension to fractal interfaces, to other initial conditions, to finite chemistry.
- What mechanisms drive the time evolution of the pdf of λ, τ and $\widetilde{\tau}$?
- What is the dependence between λ, τ and $\widetilde{\tau}$?

References [1] D. Tan, P. Haynes, A. MacKenzie, and J. Pyle, Journal of Geophysical Research-Atmospheres 103, 1585 (1998). [2] S. Edouard, B. Legras, F. Lefevre, and R. Eymard, Nature 384, 444 (1996). [3] G. Lapeyre, Chaos 12, 688 (2002). [4] M. Balluch and P. Haynes, Journal of Geophysical Research-Atmospheres 102, 23487 (1997). [5] R. Ott, Chaos in Dynamical Systems (Cambridge, England, 2002).