What Determines the Progress of Fast Chemical Reactions in Chaotic Flows?

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What is a fast chemical reaction?

We consider infinitely fast acid-base type reactions in solutions:

$$A + B \to 2P$$

For example,

$$\mathrm{NaOH} + \mathrm{HCl} \to \mathrm{NaCl} + \mathrm{H_2O}$$

Advection-Diffusion-Reaction Equations:

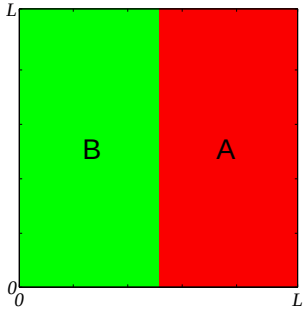
$$\frac{\partial A}{\partial t} + \mathbf{u}\cdot\nabla A = \kappa\nabla^2 A - \gamma AB$$
$$\frac{\partial B}{\partial t} + \mathbf{u}\cdot\nabla B = \kappa\nabla^2 B - \gamma AB$$
$$\frac{\partial P}{\partial t} + \mathbf{u}\cdot\nabla P = \kappa\nabla^2 A + 2\gamma AB$$

Conservation of mass:

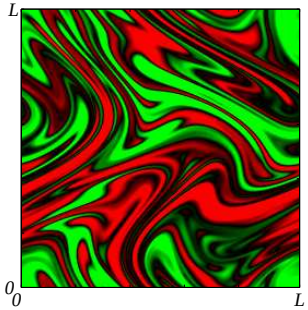
$$P_f = \langle P\rangle_{t=\infty} = 2\langle A\rangle_0 = 2\langle B\rangle_0$$
$$\langle P\rangle = P_f - \langle A+B\rangle$$

- reaction time $\ll$ advection time $\ll$ diffusion time
- overall reaction rate limited by diffusion
- diffusion can be enhanced by mixing

$t = 0$



$t = 20$



Goal: To determine the progress of the reaction,
i.e. $\langle P\rangle$ as a function of time t

How do we mix the reactants?

Chaotic Advection: nearby fluid elements separate exponentially in time:

A Chaotic Flow Model

$$\mathbf{u}(\mathbf{x},t) = \begin{cases} \sqrt{2}U\cos[k_f y + \theta_1(n)]\hat{i}, & n\tau < t \le (n+\frac{1}{2})\tau \\ \sqrt{2}U\cos[k_f x + \theta_2(n)]\hat{j}, & (n+\frac{1}{2})\tau < t \le (n+1)\tau \end{cases}$$

where θ_1 and θ_2 are random numbers.

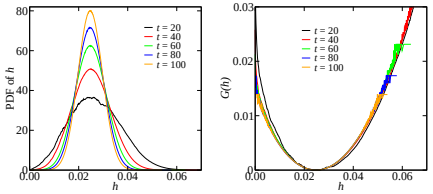
Characterizing Stretching in Chaotic Flows

- *Finite-time Lyapunov Exponent*, h

$$h(\vec{x},t) = \frac{1}{t}\log\frac{|\delta\vec{x}(t)|}{|\delta\vec{x}(0)|}$$
$$\bar{h} = \lim_{t\to\infty} h(\vec{x},t)$$

- probability density function of h, $\mathcal{P}(h,t)$ with *large time* asymptotic form:

$$\mathcal{P}(h,t) \sim \exp[-tG(h)]$$



How to relate reaction rate to stretching?

Consider the quantity

$$\phi = A - B$$

- equation of motion for ϕ:

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

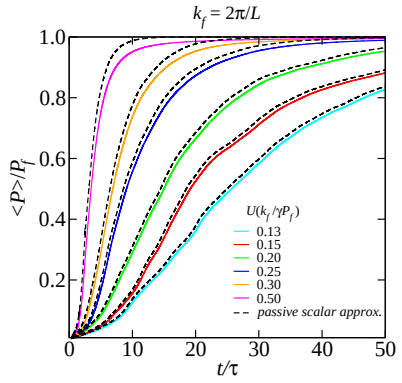
No reaction term $\Rightarrow$ $\phi \sim$ decaying passive scalar

- infinitely fast reaction $\Rightarrow$ no region where A and B coexist

i.e. it is either $\phi = A\,(B=0)$ or $\phi = -B\,(A=0)$

so $\langle|\phi|\rangle = \langle A+B\rangle$

$$\therefore \quad \boxed{\langle P\rangle \approx P_f - \langle|\phi|\rangle}$$



Theory of Decaying Passive Scalar

$$\langle\phi^2\rangle \sim \mathrm{e}^{-\lambda_2 t} \qquad \text{as} \qquad \kappa \to 0$$
$$\lambda_2 = \min_h [h + G(h)]$$

We conjecture that

$$\langle|\phi|\rangle \sim \mathrm{e}^{-\lambda_1 t} \qquad \text{as} \qquad \kappa \to 0$$
$$\lambda_1 = \lambda_2/2$$

(This may be justified by the notion of "strange eigenmode": $\phi(\mathbf{x},t) \sim \bar{\phi}(\mathbf{x},t)\exp(-\sigma t)$ where $\bar{\phi}$ is slowly varying in time, which is supported by our numerical simulations.)

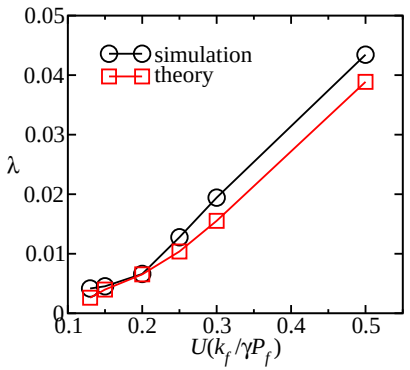
Predicting the Rate of Product Creation

Using results from passive scalar advection, it is straight forward to see that

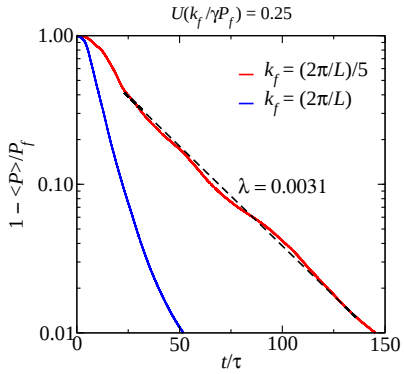
$$\frac{\langle P\rangle}{P_f} = 1 - \mathrm{e}^{-\lambda t}$$

where

$$\boxed{\lambda = \frac{\min_h [h + G(h)]}{2}}$$



Is local stretching always the determining factor?



When the domain size $\gg$ velocity scale, the overall reaction rate becomes slower.

Theory of Decaying Passive Scalar (once again)

- If $L \gg 1/k_f$, the large scale component of ϕ, which determines the decay rate, satisfies the diffusion equation with an effective diffusivity

$$D = \frac{U^2\tau}{8}$$

- Hence, in this case

$$\boxed{\lambda = \frac{4\pi^2}{L^2}D}$$

- For $k_f = (2\pi/L)/5$, $U(k_f/\lambda P_f) = 0.25$ and $\tau = 10$, this gives $\lambda = 0.003125$.

Summary

- The theory for a decaying passive scalar is used to predict the progress of an infinitely fast chemical reaction in a chaotic flow
- Depending on the relative length scales of the velocity field and the domain, the overall reaction rate is either related to the distribution of the finite-time Lyapunov exponent or an effective diffusivity
- These results are different to the common perception that the overall reaction rate is determined by a single mean Lyapunov exponent.