Fast Chemical Reactions in Chaotic Flows: Reaction Rate and Mixdown Time

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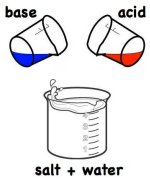
Fast Second Order Chemical Reactions

We consider infinitely fast bimolecular reactions in fluid flows:

$$A + B \to 2P$$

e.g. $\mathrm{NaOH}(aq) + \mathrm{HCl}(aq) \to \mathrm{NaCl}(aq) + \mathrm{H_2O}(\ell)$

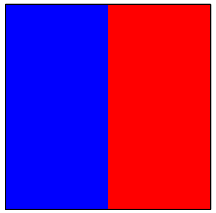


Advection-Diffusion-Reaction Equations

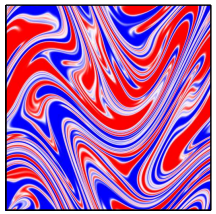
$$\frac{\partial a}{\partial t} + \mathbf{u}\cdot\nabla a = \kappa\nabla^2 a - \gamma ab$$
$$\frac{\partial b}{\partial t} + \mathbf{u}\cdot\nabla b = \kappa\nabla^2 b - \gamma ab$$
$$\frac{\partial p}{\partial t} + \mathbf{u}\cdot\nabla p = \kappa\nabla^2 a + 2\gamma ab$$

- **Fast reactions:**
  reaction time $\ll$ advection time $\ll$ diffusion time
- **Goal:** time dependence of product concentration

$$\langle p\rangle = 1 - 2\langle a\rangle$$



$\langle a(t=0)\rangle = \langle b(t=0)\rangle = 0.5$



$\langle a(t)\rangle = \langle b(t)\rangle$ for all t

A Model of Chaotic Flow

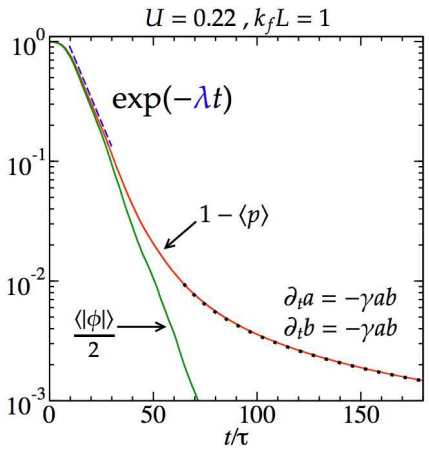
$$\boldsymbol{u}(\boldsymbol{x},t) = \begin{cases} \sqrt{2}U\cos[k_f y + \theta_1(n)]\,\hat{i}\,, & n\tau < t \leqslant (n+\frac{1}{2})\tau \\ \sqrt{2}U\cos[k_f x + \theta_2(n)]\,\hat{j}\,, & (n+\frac{1}{2})\tau < t \leqslant (n+1)\tau \end{cases}$$

where θ_1 and θ_2 are random numbers.

Domain size: $2\pi L \times 2\pi L$

Scale separation parameter $\sim k_f L$

Progress of Reaction



1. initial slow phase ($t < 10\tau$): very little fine structure in the concentration fields a and b
2. exponential phase ($10\tau < t < 40\tau$): filamentary structure developed, $\langle p\rangle$ reaches 90% of its ultimate value
3. classical chemical kinetics ($t > 60\tau$): system is fairly homogeneous, advection and diffusion become unimportant

- transition from phase 2 to phase 3 occurs at the crossover time

$$t_X \sim \frac{1}{\lambda}\ln\frac{\gamma\langle p\rangle_{t=\infty}}{\bar{h}} \quad (\sim 40\tau)$$

Relation to Decaying Passive Scalars

Consider the quantity:

$$\phi = a - b$$

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

$\Rightarrow$ $\phi \sim$ decaying passive scalar

For infinitely fast reactions: the fields $a(\boldsymbol{x},t)$ and $b(\boldsymbol{x},t)$ never overlap

$$\therefore \quad |\phi| = |a-b| = a+b$$

$$\langle a\rangle = \langle b\rangle = \frac{\langle|\phi|\rangle}{2}$$

Theory of Decaying Passive Scalar

Strange Eigenmodes

$$\phi(\boldsymbol{x},t) = \hat{\phi}(\boldsymbol{x},t)\,e^{-(s/2)t}$$

where $\hat{\phi}(\boldsymbol{x},t)$ is statistically stationary, hence

$$\langle|\phi|^n\rangle \sim e^{-n(s/2)t}$$

Decay of Scalar Variance

$$\langle\phi^2\rangle \sim e^{-st} \text{ as } \kappa \to 0$$

A. With Scale Separation, $k_f L \gg 1$

Eddy diffusion of the large-scale ϕ_L dominates,

$$\frac{\partial\phi_\mathrm{L}}{\partial t} = \kappa_\mathrm{eff}\nabla^2\phi_\mathrm{L}$$

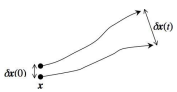
$$\langle\phi^2\rangle \sim e^{-st} \sim \exp(-\,2\frac{\kappa_\mathrm{eff}}{L^2}\,t)$$

B. Without Scale Separation, $k_f L \approx 1$

- *Finite-time Lyapunov Exponent*, h

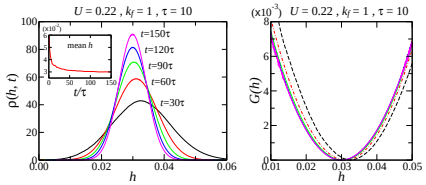
$$h(\boldsymbol{x},t) = \frac{1}{t}\log\frac{|\delta\boldsymbol{x}(t)|}{|\delta\boldsymbol{x}(0)|}$$

$$\bar{h} = \lim_{t\to\infty} h(\boldsymbol{x},t)$$



- *Probability density function* of h, $\rho(h,t)$ with *large time* asymptotic form:

$$\rho(h,t) \sim \exp[-tG(h)]$$



- Local stretching theory predicts

$$s = \min_h[h + G(h)]$$

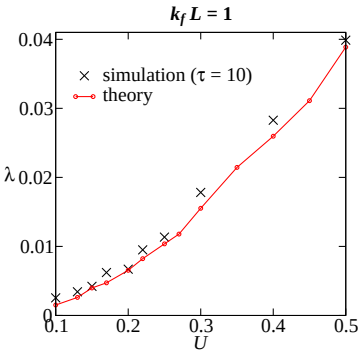
Predicting λ

$$1 - \langle p\rangle = 2\langle a\rangle \sim e^{-\lambda t}$$

$$\langle a\rangle \sim \langle|\phi|\rangle \sim e^{-(s/2)t}$$

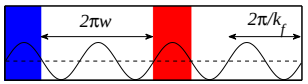
$$\boxed{\lambda = \frac{s}{2}}$$

Theory vs. Simulations



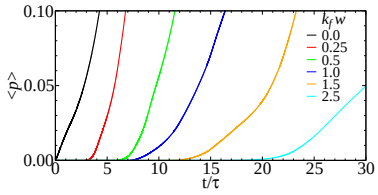
For $k_f L = 5$, using $\kappa_\mathrm{eff} = U^2\tau/8$ with $U = 0.25$ and $\tau = 10$, we get $\lambda_{theory} = 0.0031$. Numerical simulation gives $\lambda = 0.0033$.

Initially Isolated Reactants



- Broadcast spawning (Crimaldi, Cadwell and Weiss 2008)
- Parameterization in atmospheric chemical transport models (Thuburn and Tan 1997)

Reaction does not start until the separation $2\pi w$ is reduced to the diffusion length scale l_d by the action of the fluid. The time taken to do so is the **mixdown time**, τ_mix .



A crude model of τ_mix in terms of a typical stretching rate h_* :

$$l_d \sim w\exp(-h_*\tau_\mathrm{mix})$$

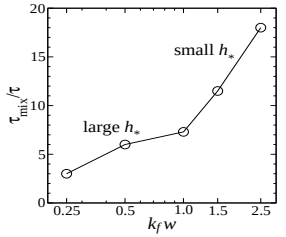


Table 1:

Fig. 1.—

Fig. 2.—

Fig. 3.—