Fast Chemical Reactions in Chaotic Flows: Predicting the Product Growth Rate

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Advanced Oxidation Processes

water treatment process to remove pharmaceutical contaminants using ozone and other reagents

Fluid flow (mixing) affects progress of reactions
Irreversible Bimolecular Reactions

\[ A + B \rightarrow P \]

Example: acid-base reaction (neutralization)

\[ \text{HCl}(aq) + \text{NaOH}(aq) \rightarrow \text{NaCl}(aq) + \text{H}_2\text{O}(l) \]
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Advection-Diffusion-Reaction Equation

Concentration fields: $a(x, t)$, $b(x, t)$ and $p(x, t)$

\[
\frac{\partial a}{\partial t} + u \cdot \nabla a = \kappa \nabla^2 a - \gamma ab
\]

\[
\frac{\partial b}{\partial t} + u \cdot \nabla b = \kappa \nabla^2 b - \gamma ab
\]

\[
\frac{\partial p}{\partial t} + u \cdot \nabla p = \kappa \nabla^2 p + \gamma ab
\]

\[\langle a(x, 0) \rangle = \langle b(x, 0) \rangle = 1\]
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\]

⟨$a(x, 0)$⟩ = ⟨$b(x, 0)$⟩ = 1

Fast reactions:

reaction time $\ll$ advection time $\ll$ diffusion time

Goal: time dependence of mean product concentration

⟨$p$⟩ = 1 − ⟨$a$⟩
Flow Model and Simulations

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

Domain size: \( 2\pi L \times 2\pi L \) (scale separation \( \sim k_f L \))
Progress of Reaction

\[ \langle a \rangle = 1 - \langle p \rangle \]

\[ U = 0.22, \ k_fL = 1 \]

\[ \frac{1}{D_a} = 0.13 \]

\[ U = 0.17 \]

\[ \frac{1}{D_a} = 0.22 \]

\[ \frac{1}{D_a} = 0.50 \]
Progress of Reaction

\[ U = 0.22 \, , \, k_fL = 1 \]

\[ \langle a \rangle = 1 - \langle p \rangle \]

\[ \exp(-\lambda t) \]
\[ U = 0.22, \; k_f L = 1 \]

\[
\langle a \rangle = 1 - \langle p \rangle = \exp(-\lambda t)
\]

\[
\partial_t a = -\gamma a b \\
\partial_t b = -\gamma a b
\]
Relation to Decaying Passive Scalar

\[ \frac{\partial a}{\partial t} + u \cdot \nabla a = \kappa \nabla^2 a - \gamma ab \]

\[ \frac{\partial b}{\partial t} + u \cdot \nabla b = \kappa \nabla^2 b - \gamma ab \]

\[ \phi \equiv a - b \]

\[ \Rightarrow \quad \frac{\partial \phi}{\partial t} + u \cdot \nabla \phi = \kappa \nabla^2 \phi \]

For \textit{infinitely} fast reactions: \( a(x, t) \) and \( b(x, t) \) never overlap

\[ |\phi| = |a - b| = a + b \quad (a \geq 0, b \geq 0) \]

\[ \langle a \rangle = \langle b \rangle = \frac{\langle |\phi| \rangle}{2} \]
Verifying the Passive Scalar Approximation

$\frac{1}{D_a} = 0.13$
$U = 0.17$
$\frac{1}{D_a} = 0.22$
$\frac{1}{D_a} = 0.50$

$U = 0.22, k_fL = 1$

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

$\langle |\phi| \rangle = \frac{1}{2}$
Literature on Decaying Passive Scalar

“Strange eigenmode”
- B. J. Bayly, in *Nonlinear Phenomena in Atmospheric and Oceanic Sciences* (1992)

Variance decay rate from finite-time Lyapunov exponent (local stretching)

Validity of local stretching theory, decay rate based on effective diffusivity

Experimental studies

Other: KAM surface, Kraichnan model, forced scalar, boundary effects,...etc
Finite-time Lyapunov Exponent

Finite-time Lyapunov exponent, $h$

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

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

probability density function of $h$, $\rho(h, t)$ at large time:

$$\rho(h, t) \sim \exp[-tG(h)] \quad \text{as} \quad t \to \infty$$
Theory of Decaying Passive Scalar

Strange eigenmodes:

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

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

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

Decay of scalar variance, \( \langle \phi^2 \rangle \sim e^{-st} \) as \( \kappa \to 0 \):

For \( k_f L \approx 1 \),

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

For \( k_f L \gg 1 \),

\[ s = \frac{\kappa_{\text{eff}}}{L^2} \]

where \( \kappa_{\text{eff}} \gg \kappa \) is the effective (eddy) diffusivity of the flow
**Predicting \( \lambda \)**

Recall for infinitely fast reactions,

\[
\langle a \rangle = \frac{\langle |\phi| \rangle}{2}
\]

and from the theory of passive scalar decay,

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

Hence, \( 1 - \langle p \rangle = \langle a \rangle \sim e^{-\lambda t} \) gives \( \lambda = s/2 \).

For \( k_fL \approx 1 \),

\[
\lambda \approx \frac{1}{2} \min_h [h + G(h)]
\]

For \( k_fL \gg 1 \),

\[
\lambda \approx \frac{\kappa_{\text{eff}}}{2L^2}
\]
assumptions: (1) infinitely fast reaction
(2) \( \kappa \to 0 \) (more restrictive)

an optimal velocity correlation time, \( \tau \approx \frac{2\pi/k_f}{U} \)
Theory vs. Simulations: $k_fL = 5$

For our flow model, $\kappa_{\text{eff}} = \frac{U^2\tau}{8}$.

So the theoretical prediction is $\lambda = \frac{\kappa_{\text{eff}}}{2L^2} = 0.0031$. 
Summary

- investigate the progress of fast bimolecular reactions in chaotic flows
- majority of product is formed during the exponential phase
- make prediction on the reactant decay (product creation) rate using decaying passive scalar theory

\[
\langle a \rangle = 1 - \langle p \rangle
\]

\[
d_t a = -\gamma_{ab}
\]

\[
d_t b = -\gamma_{ab}
\]

\[
\exp(-\lambda t)
\]

\[
U = 0.22, \ k_f L = 1
\]

\[
\frac{1}{Da} = 0.13
\]

\[
\frac{1}{Da} = 0.22
\]

\[
\frac{1}{Da} = 0.50
\]

\[
\tau = 10
\]

\[
\lambda
\]

\[
U
\]