



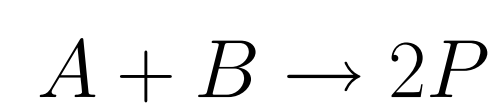
# Fast Chemical Reactions in Chaotic Flows: Reaction Rate and Mixdown Time

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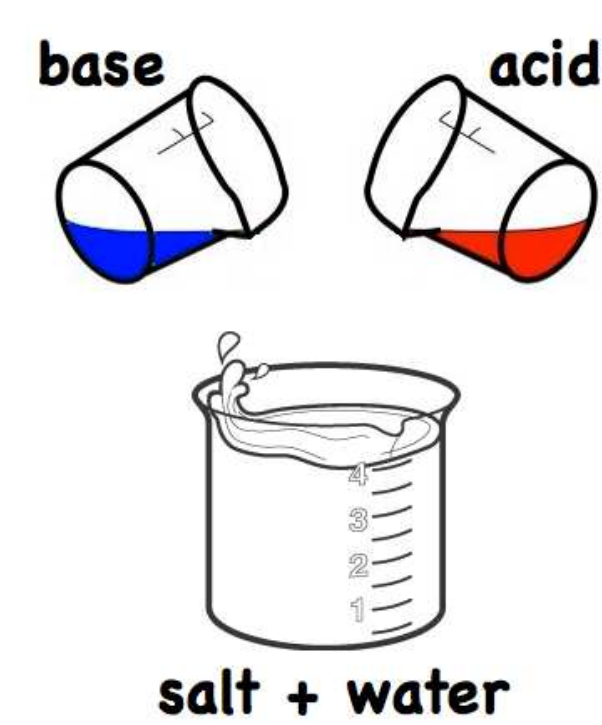
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## Fast Second Order Chemical Reactions

We consider **infinitely fast** bimolecular reactions in fluid flows:



e.g.  $\text{NaOH}(aq) + \text{HCl}(aq) \rightarrow \text{NaCl}(aq) + \text{H}_2\text{O}(\ell)$



## Advection-Diffusion-Reaction Equations

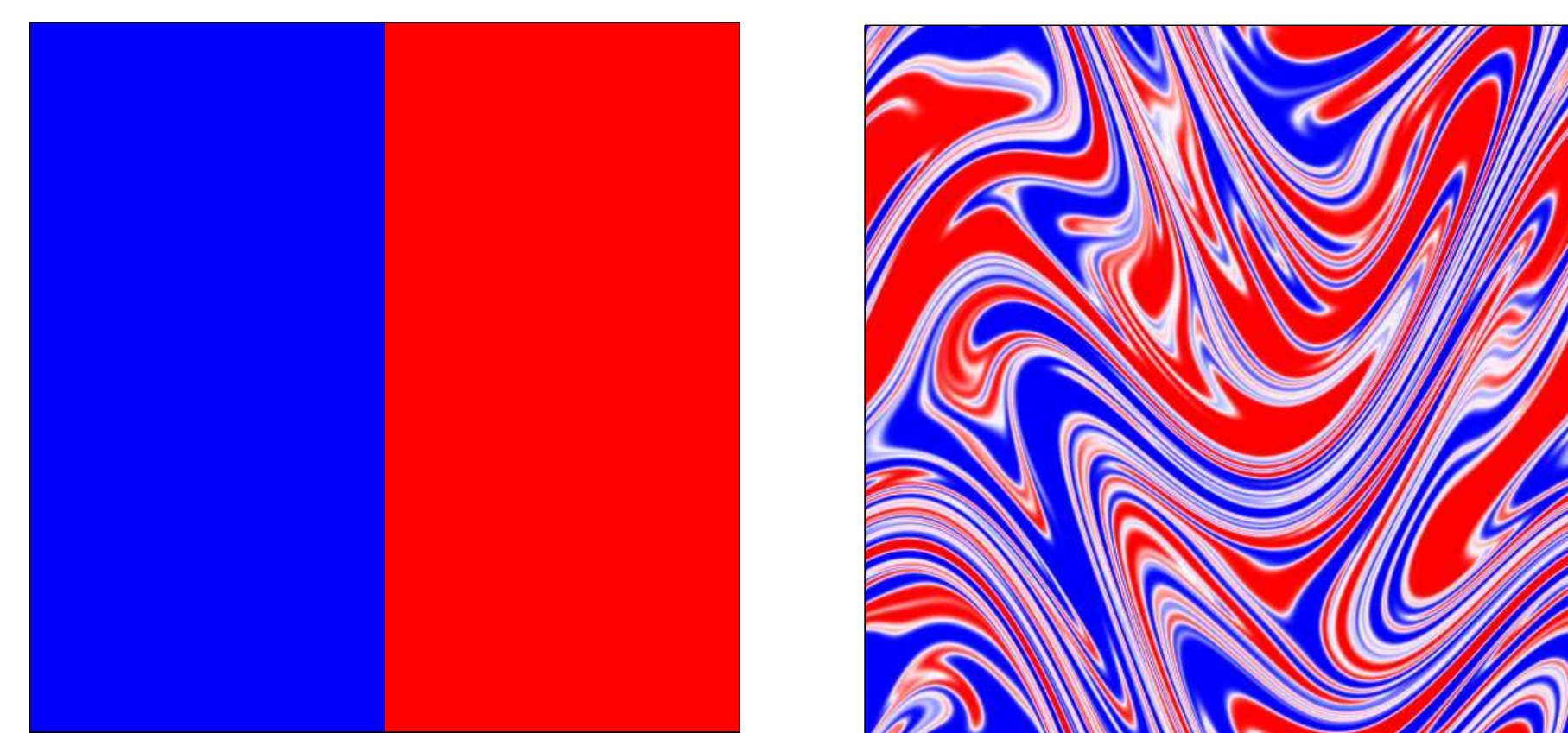
$$\begin{aligned} \frac{\partial a}{\partial t} + \mathbf{u} \cdot \nabla a &= \kappa \nabla^2 a - \gamma ab \\ \frac{\partial b}{\partial t} + \mathbf{u} \cdot \nabla b &= \kappa \nabla^2 b - \gamma ab \\ \frac{\partial p}{\partial t} + \mathbf{u} \cdot \nabla p &= \kappa \nabla^2 p + 2\gamma ab \end{aligned}$$

### 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

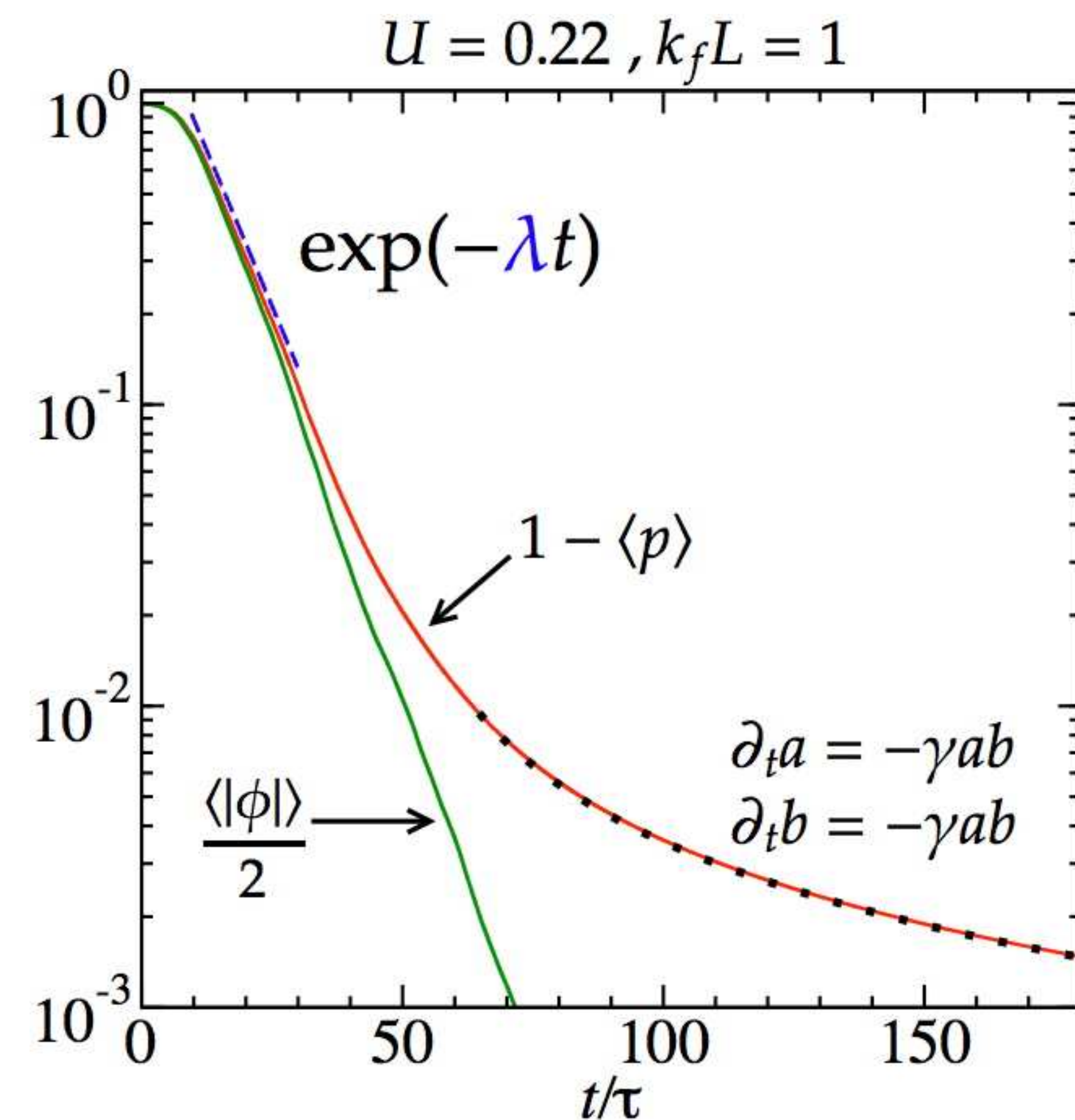
$$\mathbf{u}(\mathbf{x}, t) = \begin{cases} \sqrt{2}U \cos[k_f y + \theta_1(n)] \hat{i}, & n\tau < t \leq (n+\frac{1}{2})\tau \\ \sqrt{2}U \cos[k_f x + \theta_2(n)] \hat{j}, & (n+\frac{1}{2})\tau < t \leq (n+1)\tau \end{cases}$$

where  $\theta_1$  and  $\theta_2$  are random numbers.

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

Scale separation parameter  $\sim k_f L$

## Progress of Reaction



- initial slow phase** ( $t < 10\tau$ ): very little fine structure in the concentration fields  $a$  and  $b$
- exponential phase** ( $10\tau < t < 40\tau$ ): filamentary structure developed,  $\langle p \rangle$  reaches 90% of its ultimate value
- 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  $a(\mathbf{x}, t)$  and  $b(\mathbf{x}, t)$  never overlap

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

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

## Theory of Decaying Passive Scalar

### Strange Eigenmodes

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

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

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

### Decay of Scalar Variance

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

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

Eddy diffusion of the large-scale  $\phi_L$  dominates,

$$\frac{\partial \phi_L}{\partial t} = \kappa_{\text{eff}} \nabla^2 \phi_L$$

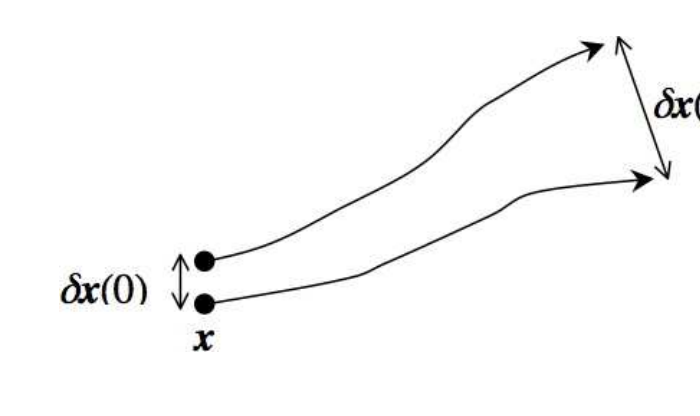
$$\langle \phi^2 \rangle \sim e^{-st} \sim \exp\left(-2 \frac{\kappa_{\text{eff}}}{L^2} t\right)$$

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

- Finite-time Lyapunov Exponent,  $h$

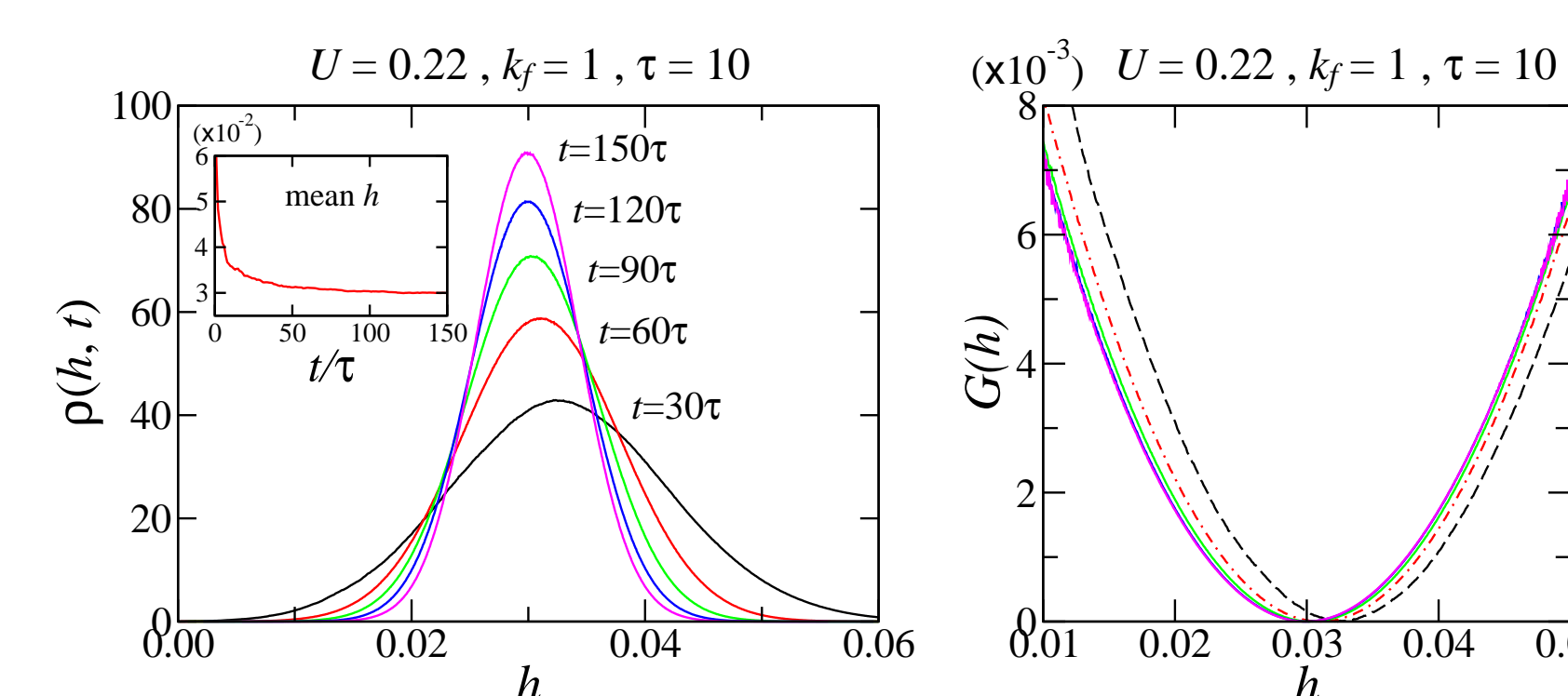
$$h(\mathbf{x}, t) = \frac{1}{t} \log \frac{|\delta \mathbf{x}(t)|}{|\delta \mathbf{x}(0)|}$$

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



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

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



- Local stretching theory predicts

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

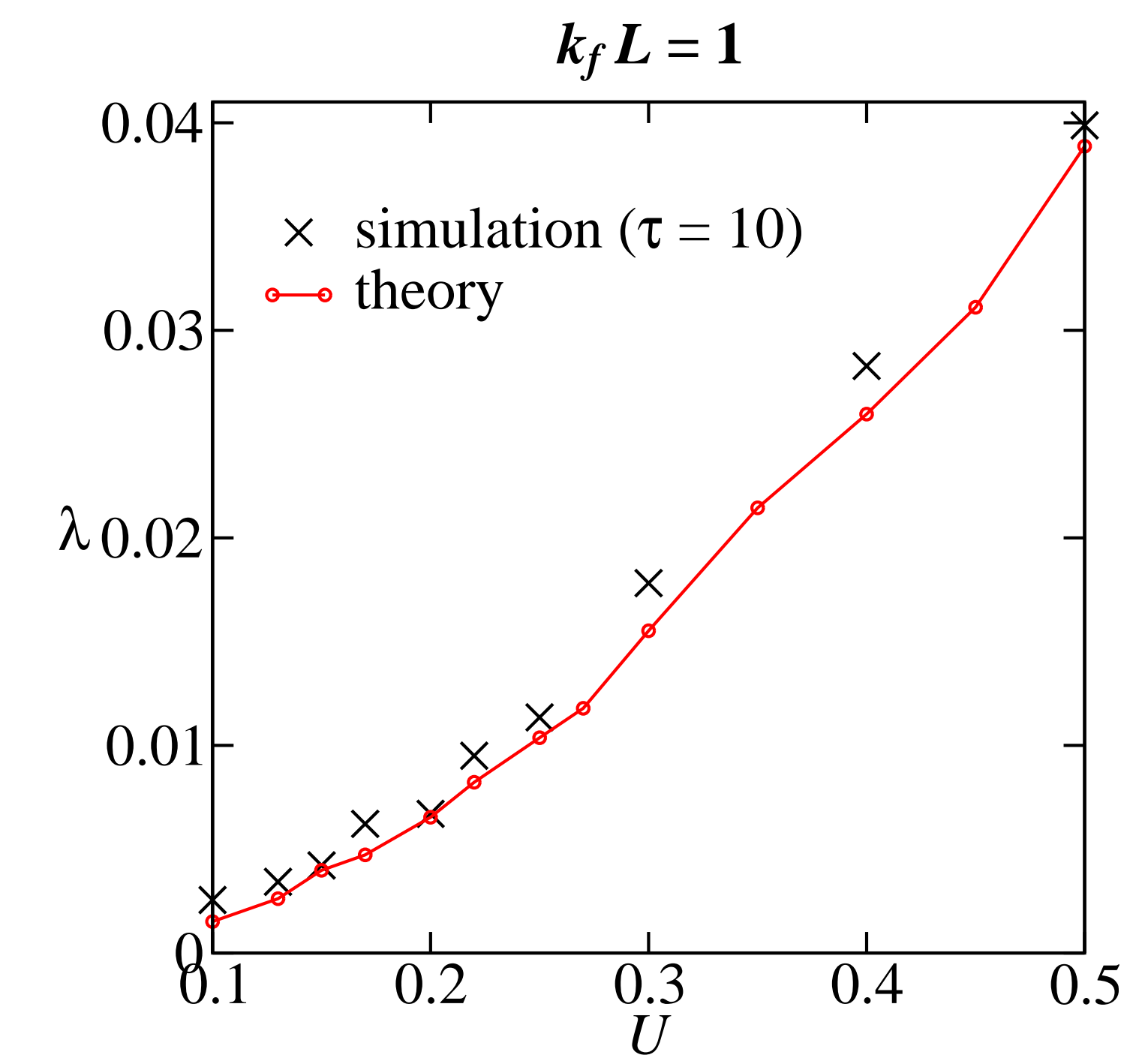
## Predicting $\lambda$

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

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

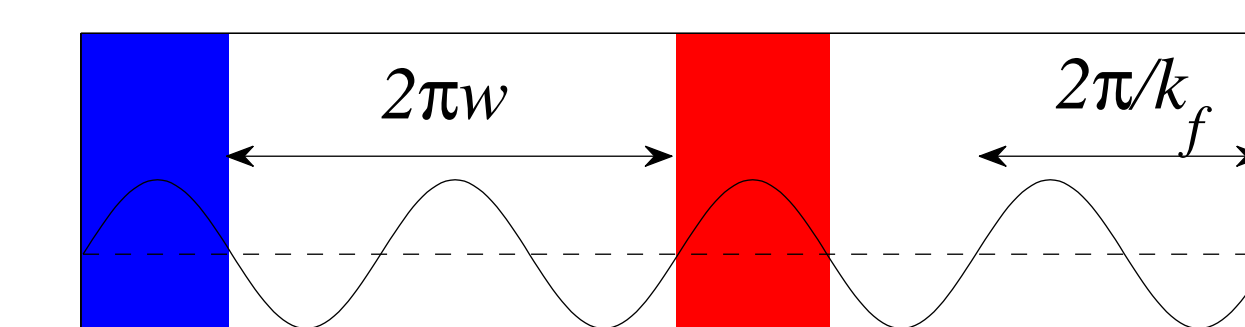
$$\lambda = \frac{s}{2}$$

## Theory vs. Simulations



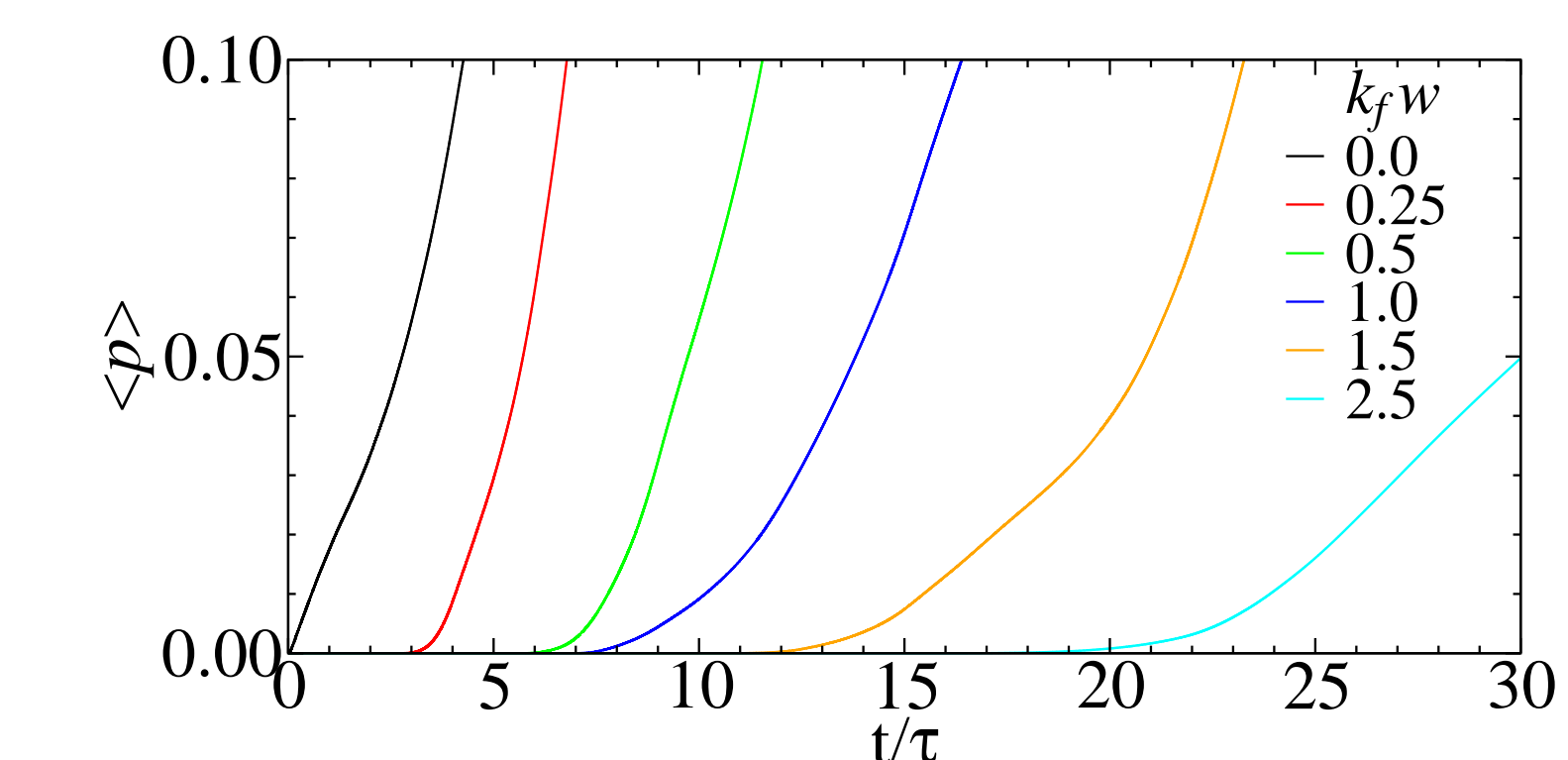
For  $k_f L = 5$ , using  $\kappa_{\text{eff}} = U^2 \tau / 8$  with  $U = 0.25$  and  $\tau = 10$ , we get  $\lambda_{\text{theory}} = 0.0031$ . Numerical simulation gives  $\lambda = 0.0033$ .

## 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**,  $\tau_{\text{mix}}$ .



A crude model of  $\tau_{\text{mix}}$  in terms of a typical stretching rate  $h_*$ :

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

