# Simulation of Bi-molecular Reaction with Diffusion

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Bimolecular reaction between substances A and B

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Let $[X]$ denote the concentration of substance $X$. We want to study the reaction in a **macroscopic** way.

How will $[A]$, $[B]$, $[AB]$ evolve?

# Problem & equations: Well-mixed

In class, we discuss the simplest case: A and B are **well-mixed**

**Well-mixed**: $[X] = [X](t)$ is a function of time. Fix time $t$, $[X]$ is the same at every location $v$ in space.

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The equations for $[A]$ and $[B]$:

$$\begin{cases} \frac{d[A]}{dt}(t) = \underbrace{-k_1[A](t)[B](t) + k_2[AB](t)}_{\text{Reaction}} \\ \frac{d[B]}{dt}(t) = -k_1[A](t)[B](t) + k_2[AB](t) \\ \frac{d[AB]}{dt}(t) = k_1[A](t)[B](t) - k_2[AB](t) \end{cases}$$

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- Shape of the container

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Contribution of diffusion of $X$ to $\frac{\partial[X]}{\partial t}$ is characterized by the diffusion equation

$$\frac{\partial[X]}{\partial t} = D_X \triangle[X]$$

where $D_X \sim m^2/s$ is the diffusion coefficient of $X$ (constant), and $\triangle[X]$ is the Laplacian of $[X]$ w.r.t location $v$.

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Laplacian is in a sense "the average of concentration difference around $v$". This is characterized by an interesting property of Laplacian

$$\triangle f(v) = \lim_{r \to 0} \frac{2n}{r^2} \frac{1}{\omega(S^{n-1})} \int_{S^{n-1}} f(v+h) - f(v)\, dh$$

# Problem & equations: Bi-molecular Reaction with Diffusion

We can now fully characterize the evolution of substance concentration by computing the contribution of **reaction** and **diffusion**

$$\begin{cases} \frac{\partial [A]}{\partial t}(v,t) = \underbrace{-k_1[A](v,t)[B](v,t) + k_2[AB](v,t)}_{\text{Reaction}} + \underbrace{D_A \triangle [A]}_{\text{Diffusion}} \\ \frac{\partial [B]}{\partial t}(v,t) = -k_1[A](v,t)[B](v,t) + k_2[AB](v,t) + D_B \triangle [B] \\ \frac{\partial [AB]}{\partial t}(v,t) = k_1[A](v,t)[B](v,t) - k_2[AB](v,t) + D_{AB} \triangle [AB] \end{cases}$$

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*This doesn't violate the conservation of quantities $[A^*]$ and $[B^*]$. We integrate $\frac{\partial [A^*]}{\partial t} = \frac{\partial [A]}{\partial t} + \frac{\partial [B]}{\partial t}$ over space. The integral is still a constant.

# Problem & equations: Shape of Container

The reaction takes place on a 2d torus $\mathbb{T}$, which is formed by "gluing opposite sides of a 1m*1m square".

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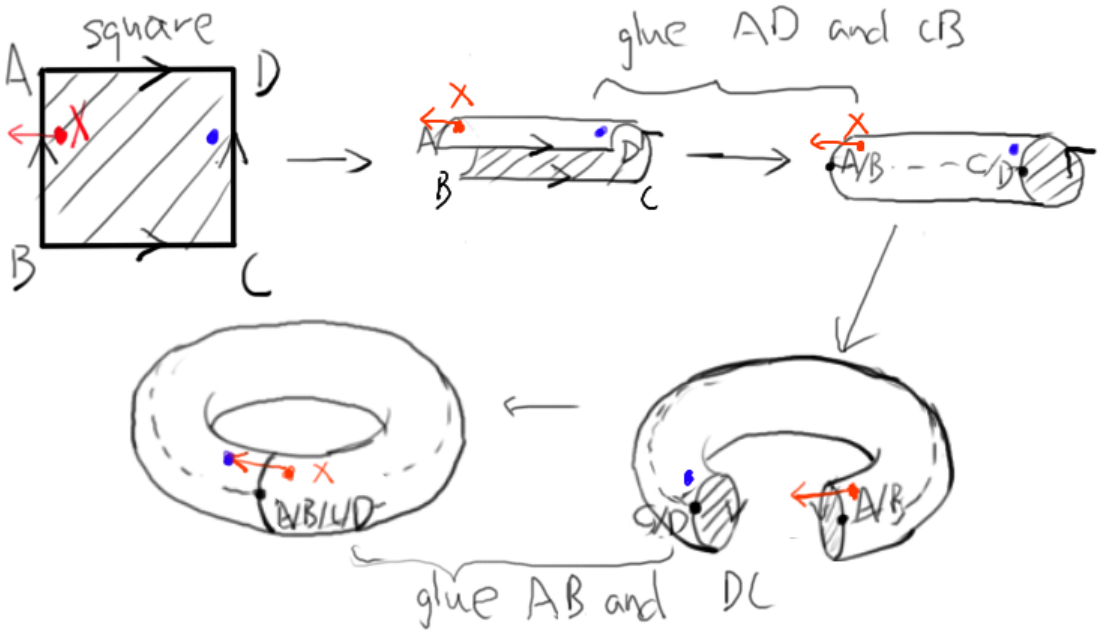

# Numerical Method: Discretize the torus $\mathbb{T}$

We discretize the square into grids of h m * h m blocks, and only consider the concentration on the vertices of the grid. $h \sim m$ is the side length of each small block.

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By discretize the square, we automatically discretize the torus.

# Numerical Method: Discretize the differential euqations

We adopt Euler method and obtain the system of difference equation

$$\begin{cases} [A](v,t+\Delta t) &= [A](v,t) + (-k_1[A](v,t)[B](v,t) + k_2[AB](v,t) \\ &\quad + D_A\tilde{\triangle}[A](v,t))\Delta t \\ [B](v,t+\Delta t) &= [B](v,t) + (-k_1[A](v,t)[B](v,t) + k_2[AB](v,t) \\ &\quad + D_B\tilde{\triangle}[B](v,t))\Delta t \\ [AB](v,t+\Delta t) &= [AB](v,t) + (k_1[A](v,t)[B](v,t) - k_2[AB](v,t) \\ &\quad + D_{AB}\tilde{\triangle}[AB](v,t))\Delta t \end{cases}$$

where $\tilde{\triangle}u$ is the discrete version of Laplacian $\triangle u$.

# Numerical Method: Discrete Laplacian

Using Taylor series, we can find a nice approximation of Laplacian by finite difference

$$\tilde{\triangle} u(x, y, t) = \frac{u(x+h, y, t) + u(x-h, y, t) + u(x, y+h, t) + u(x, y-h, t) - 4u(x, y, t)}{h^2}$$

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*Some version of discretization of Laplaician also involves diagonal neighbors of $v$, but this one is the simplest to work with in theory and in practive

# Numerical Method: Validation

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Numerically, it means the standard deviation of $[A^*]$ and $[B^*]$ over time should be small during a valid simulation.

The quantities are conserved for different parameters under which the simulation is **numerically stable** (we will come back to this in the experiment later).

# Numerical Method: Validation

The parameters are $D_A = D_B = D_{AB} = 0.0002m^2/s$, $k1 = k2 = 0.23$, $h = 0.005m$, $dt = 0.01s$. The experiment lasts for $400s$ and the reaction reaches an equilibrium.

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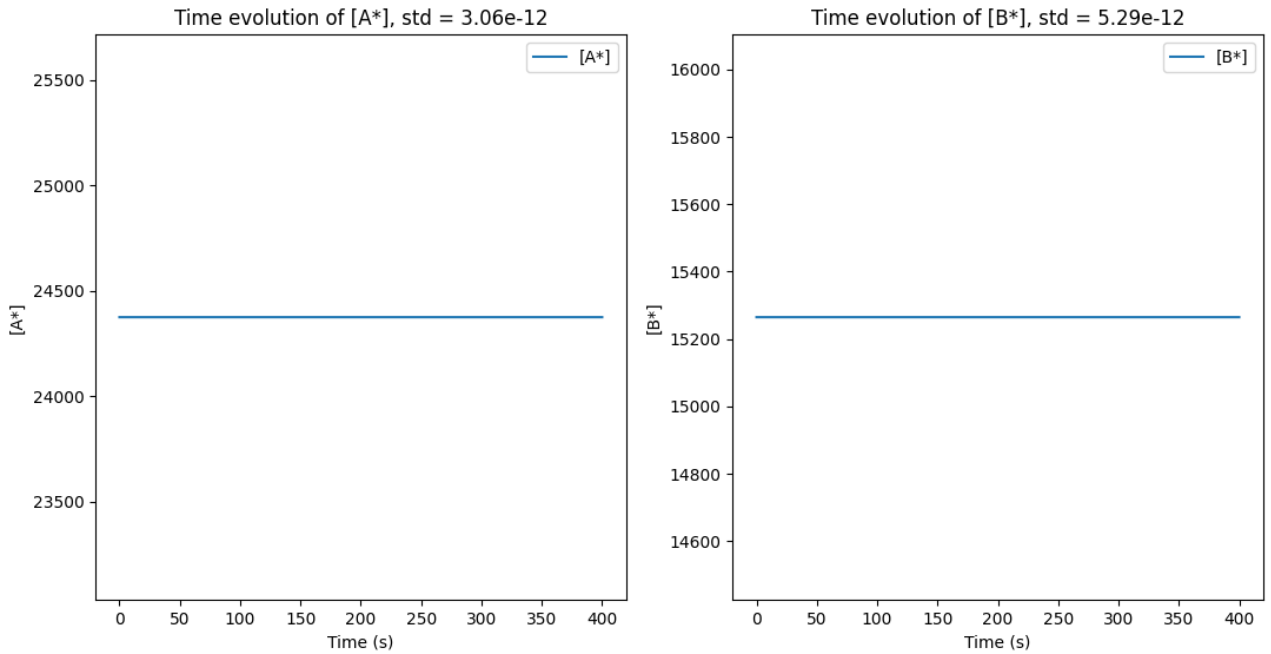
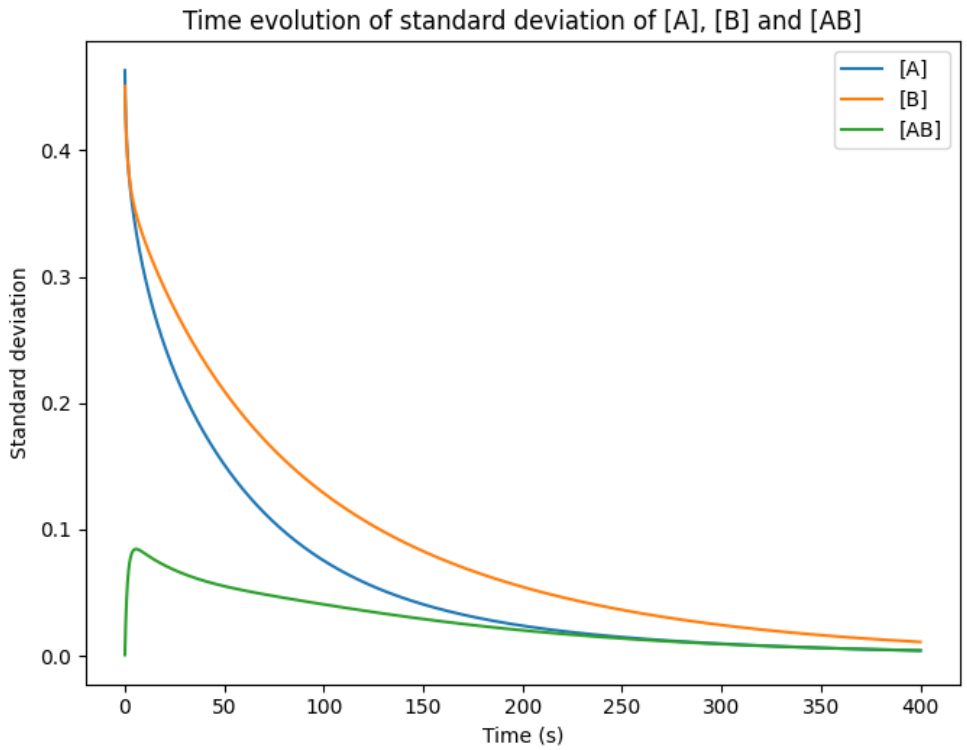


# Numerical Method: Validation

standard deviation over space of each species $\approx 0$ <=> equilibrium



# Exp 1. Numerical Stability

**Experiment 1**: How to choose parameters so that the simulation is numerically stable?

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**Answer**:

- For species $X$, $D_X$, $h$, $\Delta t$ satisfy

$$\mu := \frac{D_X \Delta t}{h^2} \leq 0.25$$

# Exp 1. Numerical Stability

## Signs of Numerical Instability

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- Negative Concentration

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- NaN caused by negative infinity

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From experiment, $C = 0.25$

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Fix $D_A = D_B = D_{AB} = 0.0002 m^2/s$, $k1 = k2 = 0.23$, run simulation for different pairs of $(\Delta t, h)$

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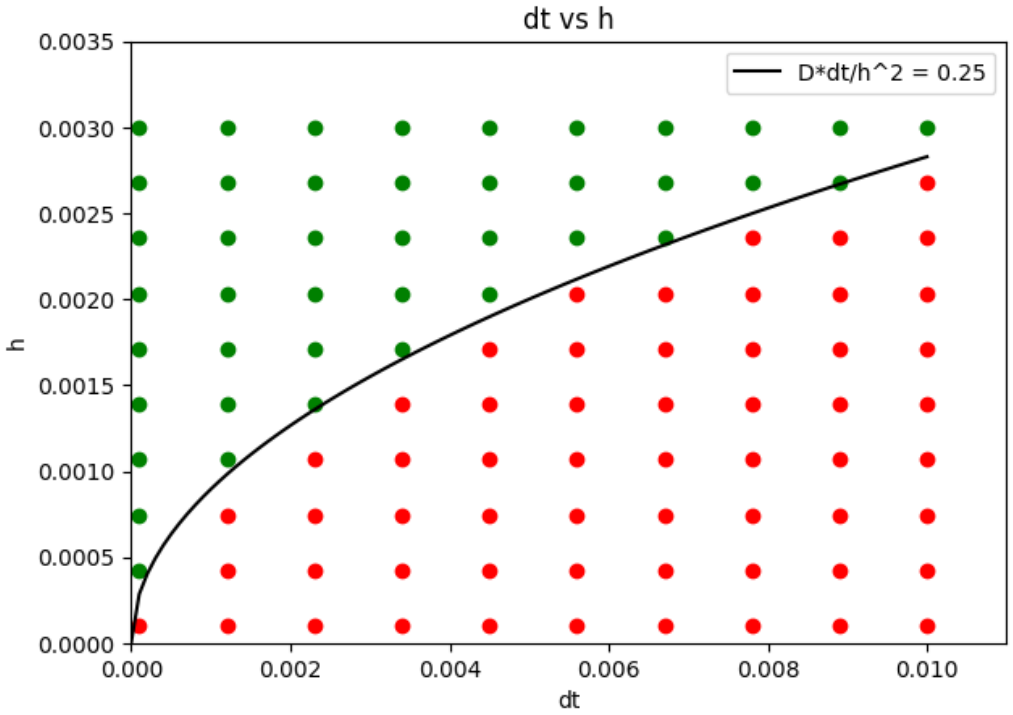

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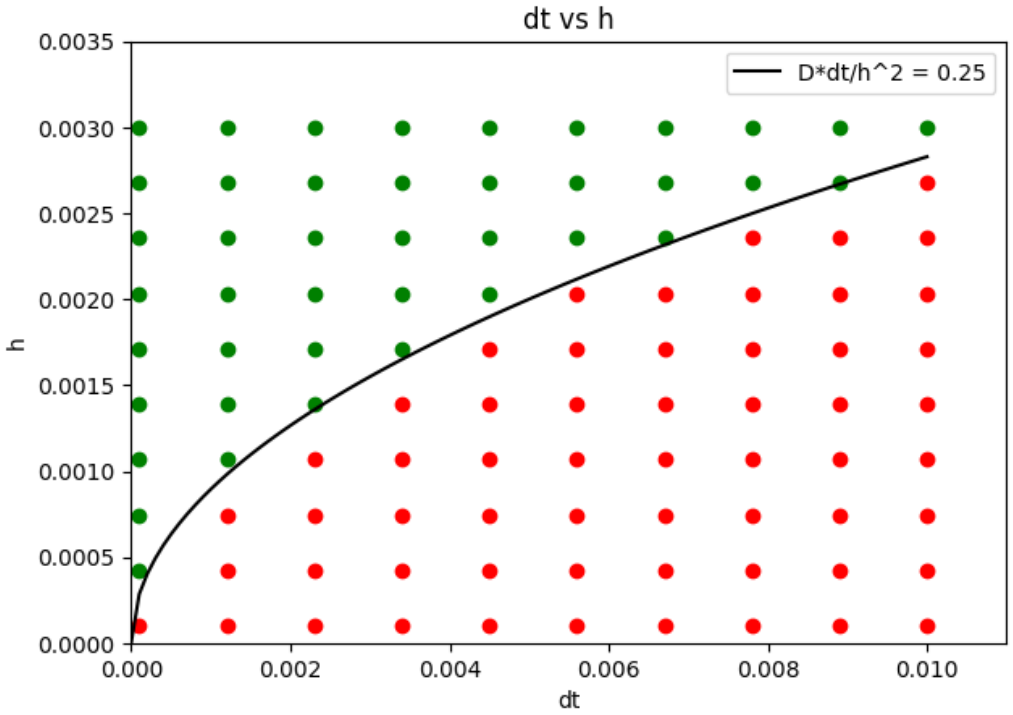


Pairs above $D\Delta t/h^2 = 0.25$ is numerically stable.

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*Reversible reaction have different dynamic: the substances are supplied by both diffusion and reaction, which breaks the boundary.

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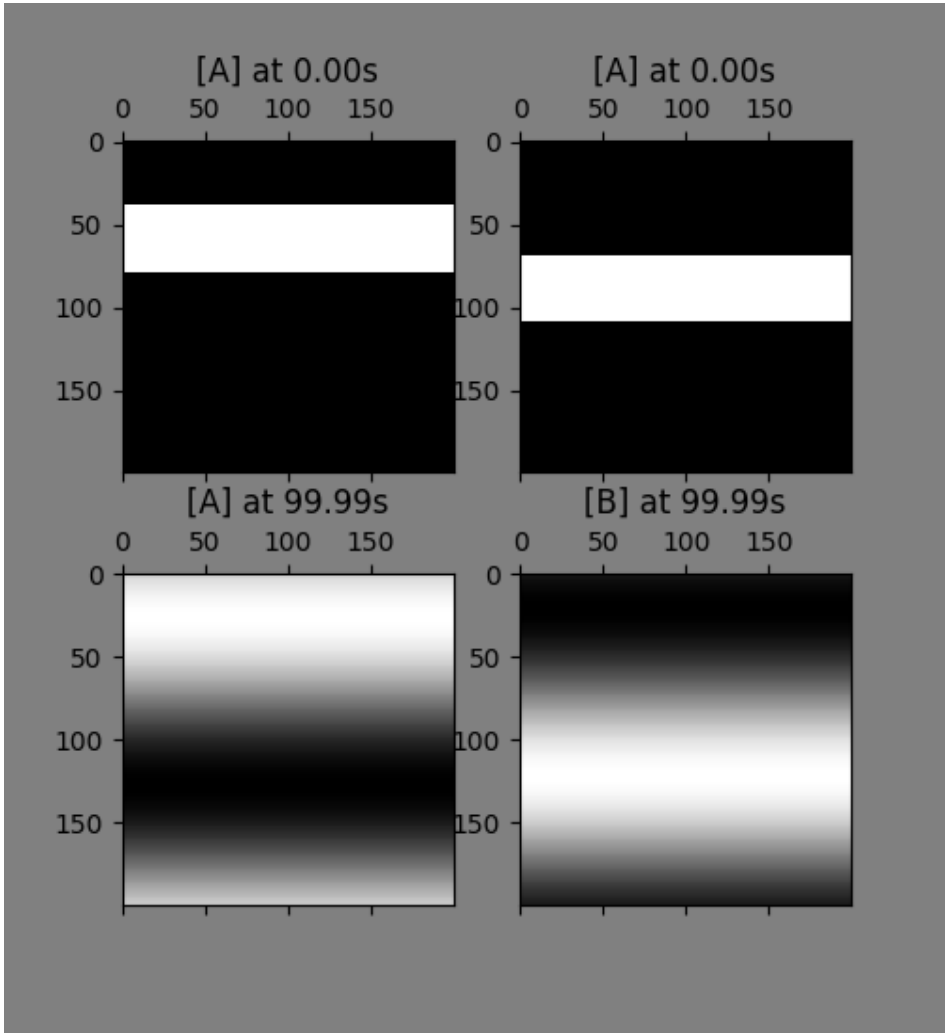
e.g. Overlapping strips



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A more involved example: Overlapping squares

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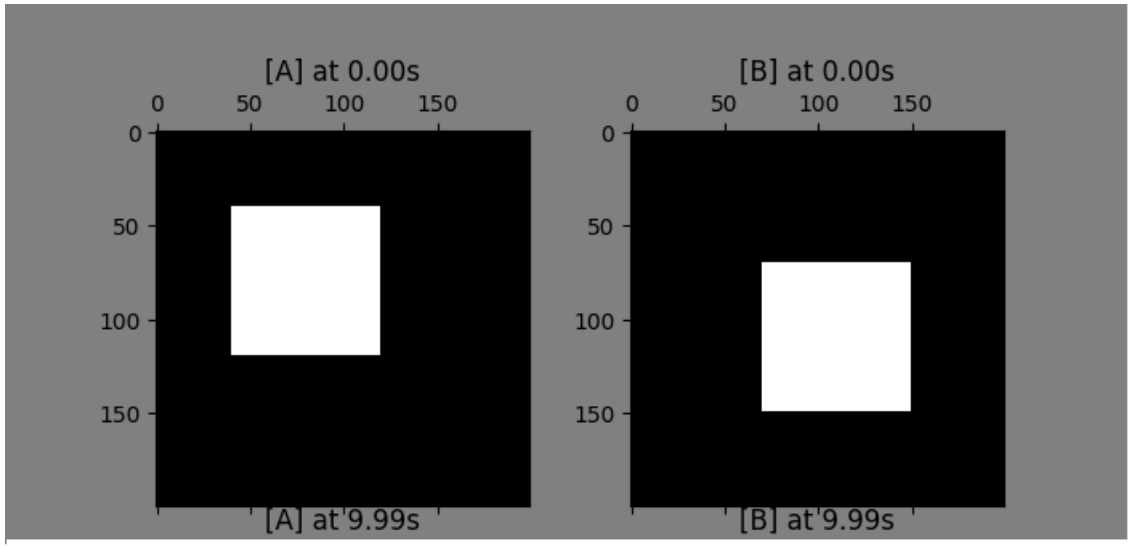
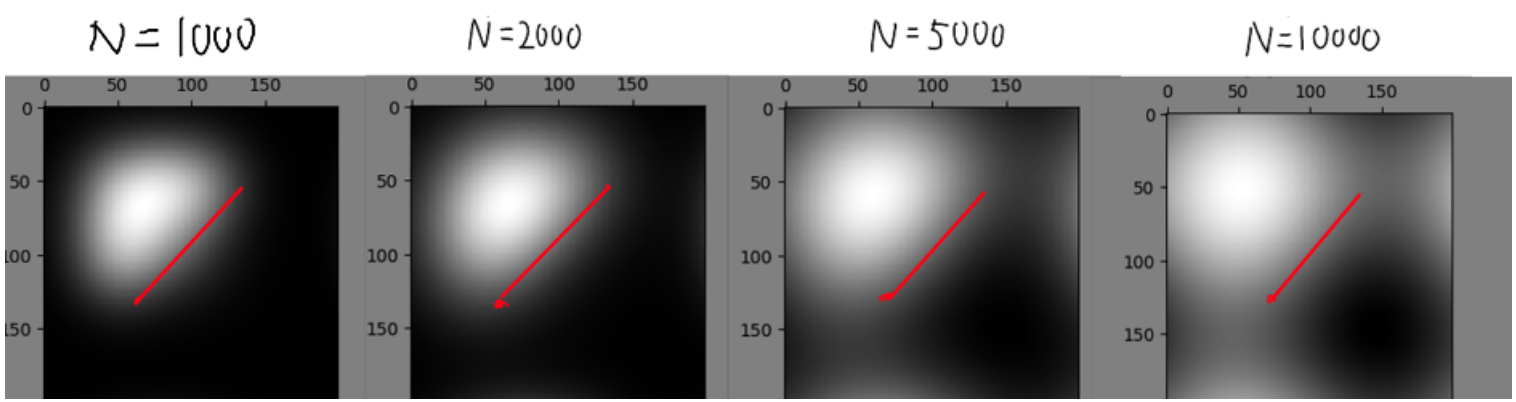


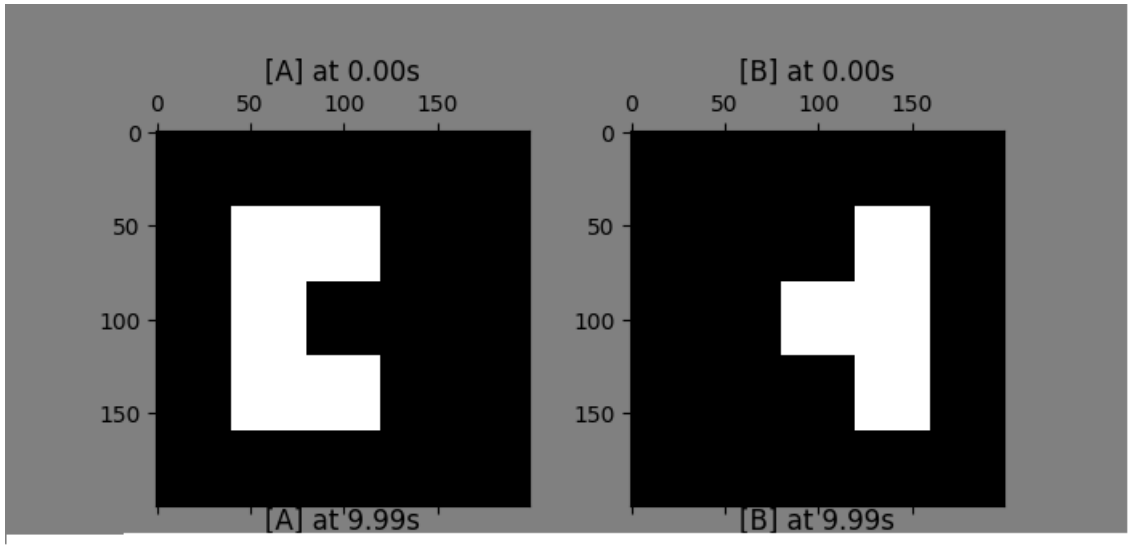
# Exp 2. Boundary of Reaction

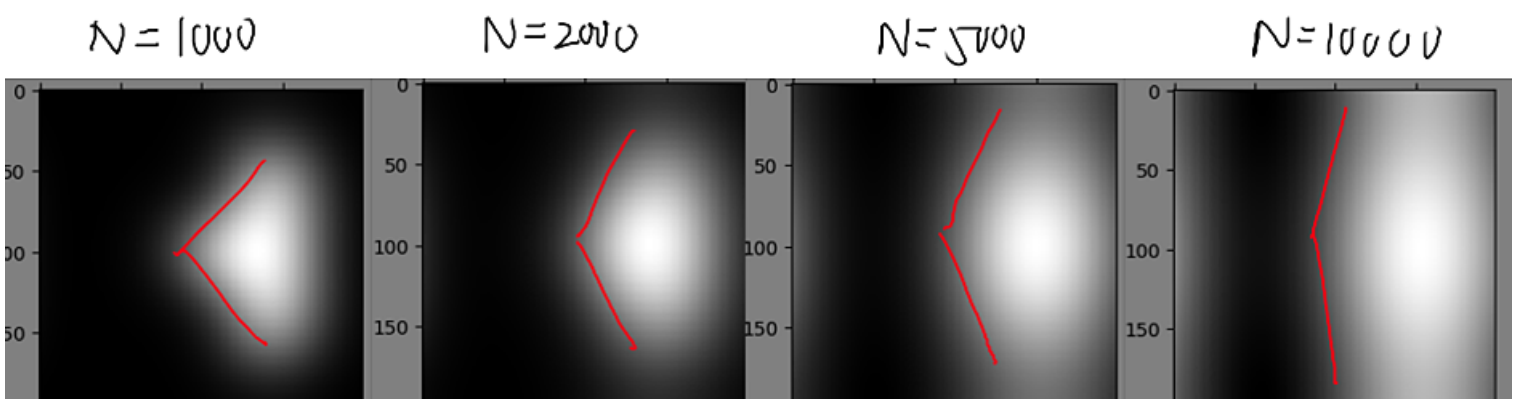
A more involved example: Overlapping squares

https://xinyu-li-123.github.io/images/1.mp4

# Exp 2. Boundary of Reaction

The boundary can be dynamic



# References I