On the Modeling of Multi-component Inhibitory Systems

Chong Wang

Joint work with Xiaofeng Ren and Yanxiang Zhao

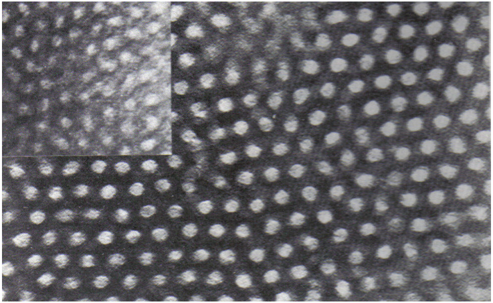
Young Researchers Workshop:
Stochastic and deterministic methods in kinetic theory

Outline

Disc Assemblies

Vampire Plecostomus (Image Credit: PlanetCatfish.com)

Disc Assemblies



A cross section of a diblock copolymer in the cylindrical phase
(Image Credit: Peter R. Lewis)

Diverse Patterns

Lamellar Patterns

Marbled Headstander (Image Credit: seriouslyfish.com)

Diverse Patterns

Core-shell assemblies

Blue Spotted Grouper (Image Credit: flickr.com)

Block Copolymers

When two or more different monomers unite together to polymerize, their result is called a **copolymer**.

Copolymers can be classified based on how the monomers are arranged along the chain. These include:

- **Alternating copolymers**
- **Random copolymers**
- **Block copolymers**

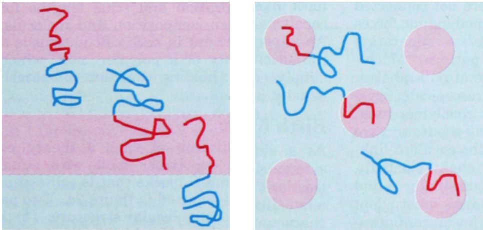
—A—B—A—B—A—B—A—B—A—B—

—A—B—B—B—A—B—A—B—A—A—

—B—B—B—B—B—A—A—A—A—A—

Block Copolymers

- a soft material, characterized by fluid-like disorder on the molecular scale and a high degree of order at a longer length scale
- a molecule: a linear sub-chain of A-monomers grafted covalently to another sub-chain of B-monomers



(Image Credit: Frank S. Bates and Glenn H. Fredrickson)

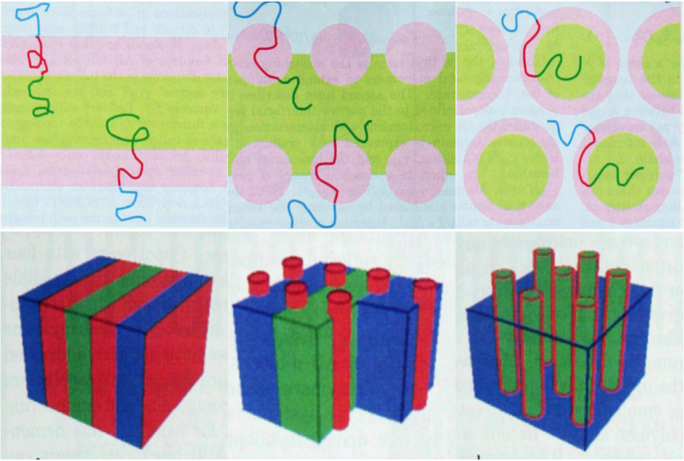
Block Copolymers

- the repulsion between the unlike monomers, the different type sub-chains tend to segregate
- chemical bond in chain molecules, the segregation of sub-chains cannot lead to a macroscopic phase separation

Micro-phase separation :
micro-domains rich in A monomers and micro-domains rich in B monomers emerge as a result.

Commercially used as thermoplastic elastomers:
Wine bottle stoppers, jelly candles, outdoor coverings for optical fibre cables, adhesives, bitumen modifiers, or in artificial organ technology.

Block Copolymers



(Image Credit: Frank S. Bates and Glenn H. Fredrickson)

Inhibitory Systems

An inhibitory system is a system characterized by two properties: growth and inhibition.
A deviation from homogeneity has a strong feedback on its future increase.
A longer ranging confinement mechanism prevents unlimited spreading.

- a diblock copolymer - a binary inhibitory system
- a triblock copolymer - a ternary inhibitory system
- a tetrablock copolymer - a quaternary inhibitory system

A Sharp Interface Model of a Binary Inhibitory System

The free energy functional of the binary inhibitory system takes the form

$$\mathcal{J}(\Omega) = \underbrace{\frac{1}{n-1}\mathcal{P}_D(\Omega)}_{\text{growth}} + \underbrace{\frac{\gamma}{2}\int_D \left|(-\triangle)^{-\frac{1}{2}}(\chi_\Omega - \omega)\right|^2 dx}_{\text{inhibition}}$$

for subsets Ω of D of prescribed measure. Namely Ω is in

$$\mathcal{A} = \{\Omega \subset D : \Omega \text{ is Lebesgue measurable and } |\Omega| = \omega|D|\}.$$

- $D \subset \mathbb{R}^n$: a bounded domain occupied by a block copolymer.
- Two parameters: $\omega \in (0,1)$ and $\gamma > 0$.
- Ω: the region of A-monomers; $D \setminus \Omega$: the region of B-monomers.

A Sharp Interface Model of a Binary Inhibitory System

$\mathcal{P}_D(\Omega)$: the perimeter of Ω in D.

$$\mathcal{P}_D(\Omega) = \sup\{\int_\Omega \operatorname{div} g(x)dx : g \in C_0^1(D;\mathbb{R}^n), |g(x)| \le 1 \ \forall x \in D\},$$

Ω is called a Caccioppoli set if $\mathcal{P}_D(\Omega) < \infty$.

The operator $(-\triangle)^{-1}$ is defined by the Poisson's equation,

$$-\triangle u = f \text{ in } D, \partial_n u = 0 \text{ on } \partial D, \int_D u(x)dx = 0.$$

$(-\triangle)^{-\frac{1}{2}}$ is its positive square root.

A Sharp Interface Model of a Binary Inhibitory System

Proposition. There exists a global minimizer of $\mathcal{J}$ in $\mathcal{A}$.

There are two main research directions.

- Study the exact shape of the global minimizers.
- Construct stable stationary sets.

Euler-Lagrange equation:

$$\mathcal{H}(\partial\Omega) + \gamma(-\triangle)^{-1}(\chi_\Omega - \omega) = \lambda \text{ on } \partial\Omega \cap D.$$

$\partial\Omega \cap D$: the interface separating A-monomers from B-monomers.
If Ω and D share boundary,

$$\partial\Omega \cap D \perp \partial D \text{ on } \overline{\partial\Omega \cap D} \cap \partial D.$$

Analytic Results of the Binary Problem

The binary problem has been studied intensively in recent years.

- All solutions to the Euler-Lagrange Equation in one dimension are known to be local minimizers of $\mathcal{J}$.
- Many solutions in two and three dimensions have been found that match the morphological phases in diblock copolymers.
- Global minimizers of $\mathcal{J}$ are studied for various parameter ranges.

Extensive literature:
Acerbi-Fusco-Morini, Alberti-Choksi-Otto, Bonacini-Cristoferi, Chen-Oshita, Choksi-Glasner, Choksi-Peletier, Choksi-Ren, Choksi-Sternberg, Fife-Hilhorst, Goldman-Muratov-Serfaty, Knüpfer-Muratov, Lu-Otto, Müller, Muratov, Nishiura-Ohnishi, Ren-Wei, Shirokoff-Choksi-Nave, Sternberg-Topalaglu.

The free energy of the ternary inhibitory system is given by

$$\mathcal{J}(\Omega_1, \Omega_2) = \underbrace{\frac{1}{2(n-1)} \sum_{i=1}^{3} \mathcal{P}_D(\Omega_i)}_{\text{growth}}$$

$$+ \underbrace{\sum_{i,j=1}^{2} \frac{\gamma_{ij}}{2} \int_D \left((-\triangle)^{-\frac{1}{2}} (\chi_{\Omega_i} - \omega_i) \right) \left((-\triangle)^{-\frac{1}{2}} (\chi_{\Omega_j} - \omega_j) \right) dx.}_{\text{inhibition}}$$

- Three regions: Ω_1, Ω_2, $\Omega_3 = D \setminus (\Omega_1 \cup \Omega_2)$, $|\Omega_1 \cap \Omega_2| = 0$.
- $|\Omega_i| = \omega_i |D|, i = 1, 2,\ \omega_1 + \omega_2 \in (0, 1)$.
- $[\gamma_{ij}]_{i,j=1}^{2} > 0$, $\gamma_{12} = \gamma_{21}$.

Extension to a Ternary Inhibitory System

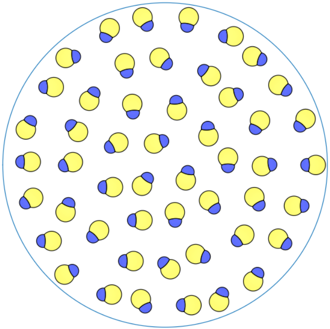
Euler-Lagrange equations:

$$\begin{aligned} \kappa_1 + \gamma_{11} I_{\Omega_1} + \gamma_{12} I_{\Omega_2} &= \lambda_1 \ \text{ on } \ \partial\Omega_1 \setminus \partial\Omega_2 \\ \kappa_2 + \gamma_{12} I_{\Omega_1} + \gamma_{22} I_{\Omega_2} &= \lambda_2 \ \text{ on } \ \partial\Omega_2 \setminus \partial\Omega_1 \\ \kappa_0 + (\gamma_{11} - \gamma_{12}) I_{\Omega_1} + (\gamma_{12} - \gamma_{22}) I_{\Omega_2} &= \lambda_1 - \lambda_2 \ \text{ on } \ \partial\Omega_1 \cap \partial\Omega_2 \\ \nu_1 + \nu_2 + \nu_0 &= \vec{0} \ \text{ at } \ \partial\Omega_1 \cap \partial\Omega_2 \cap \partial\Omega_3. \end{aligned}$$

- $\kappa_1, \kappa_2, \kappa_0$: curvatures
- $I_{\Omega_i} = (-\triangle)^{-1}(\chi_{\Omega_i} - \omega_i)$, $i = 1, 2$: inhibitors
- ν_1, ν_2, ν_3: unit tangent vectors

Analytic Results of the Ternary Problem

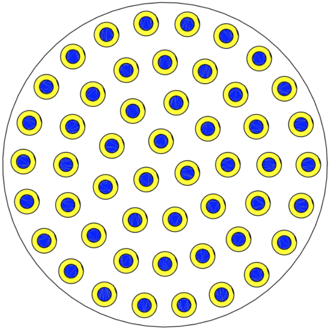
(X. Ren and J. Wei, 2015)



An illustration of the double bubble assembly of a ternary inhibitory system.

Analytic Results of the Ternary Problem

(X. Ren and C. Wang, 2017)



An illustration of the core-shell assembly of a ternary inhibitory system.

Analytic Results of the Ternary Problem

Theorem (Existence of the Core-shell Assembly)

Let D be a bounded, sufficiently smooth domain in $\mathbb{R}^2$, $m \in (0,1)$, $n \in \mathbb{N}$, and $\iota \in (0,1]$. For each compact subset $K \subset int(S)$, there exist positive numbers δ, σ depending on D, m, n, K, and ι only, such that if

1. $0 < \epsilon < \delta$,
2. $\frac{\sigma}{\epsilon^3 \log \frac{1}{\epsilon}} < \overline{\lambda}(\gamma)$ *in the case* $n \geq 2$,
3. $\epsilon^3 \gamma \in K$,
4. $\iota \overline{\overline{\lambda}}(\gamma) \leq \overline{\lambda}(\gamma)$,

then $\mathcal{J}$ admits a stationary assembly of n perturbed core-shells, satisfying the constraints.

Analytic Results of the Ternary Problem

Theorem (Locations and Radii of the Core-shells)

Let $\xi^{*,k}$ be the center of the $k-$th perturbed core-shell of the stationary assembly in Theorem 1, and $r_1^{*,k}$ and $r_2^{*,k}$ be the radii of the inner and outer interfaces, respectively.

1. *As $\epsilon \to 0$,*
$$\frac{r_1^{*,k}}{\epsilon} \to \sqrt{\frac{m}{n\pi}}, \frac{r_2^{*,k}}{\epsilon} \to \sqrt{\frac{1}{n\pi}}.$$
for all $k = 1, 2, \cdots, n$,
2. *If $\xi^{*,k} \to \xi^{\circ,k}$ for all $k = 1, 2, \cdots, n$, possibly along a subsequence, as $\epsilon \to 0$, then*
$$F\left(\xi^{\circ,1}, \xi^{\circ,2}, \cdots, \xi^{\circ,n}\right) =$$
$$\min\left\{F(\xi^1, \cdots, \xi^n), \xi^1, \cdots, \xi^n \in D, \xi^k \neq \xi^l \text{ if } k \neq l\right\}.$$

Analytic Results of the Ternary Problem

- $|\Omega_1| = \epsilon^2 m, |\Omega_2| = \epsilon^2(1-m)$.
- The fixed number m measures the relative size of $|\Omega_1|$ vs $|\Omega_2|$.
- $S = \left\{\Gamma \in \mathbb{S}^2 : \Gamma_{22} > \Gamma_{12}, \Gamma > 0, M_l(\Gamma) > 0, \forall l \geq 2\right\}$.
- $F(\xi^1, \cdots, \xi^n) = \sum_{k=1}^{n} R(\xi^k, \xi^k) + \sum_{k=1}^{n} \sum_{l=1, l\neq k}^{n} G(\xi^k, \xi^l)$.
- $G(x, y) = \frac{1}{2\pi} \log \frac{1}{|x-y|} + \frac{1}{2\pi}\left[\frac{|x|^2}{2} + \frac{|y|^2}{2} + \log \frac{1}{|x\bar{y}-1|}\right] - \frac{3}{8\pi}$ when D is the unit disc.

Extension to a Quaternary Inhibitory System

The free energy of the quaternary inhibitory system is given by

$$\mathcal{J}(\Omega_1, \Omega_2, \Omega_3) = \underbrace{\frac{1}{2(n-1)} \sum_{i=1}^{4} \mathcal{P}_D(\Omega_i)}_{\text{growth}}$$

$$+ \underbrace{\sum_{i,j=1}^{3} \frac{\gamma_{ij}}{2} \int_D \left((-\triangle)^{-\frac{1}{2}} (\chi_{\Omega_i} - \omega_i) \right) \left((-\triangle)^{-\frac{1}{2}} (\chi_{\Omega_j} - \omega_j) \right) dx.}_{\text{inhibition}}$$

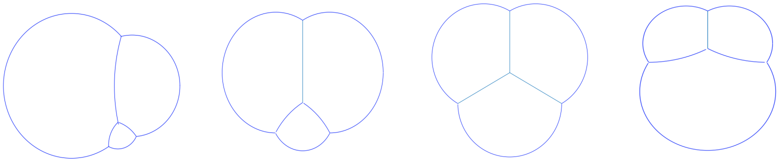
Extension to a Quaternary Inhibitory System

Euler-Lagrange equations:

$$
\begin{aligned}
\kappa_1 + (\gamma_{13} - \gamma_{12}) I_{\Omega_1} + (\gamma_{23} - \gamma_{22}) I_{\Omega_2} + (\gamma_{33} - \gamma_{23}) I_{\Omega_3} &= \lambda_3 - \lambda_2 \\
\kappa_2 + (\gamma_{11} - \gamma_{13}) I_{\Omega_1} + (\gamma_{12} - \gamma_{23}) I_{\Omega_2} + (\gamma_{13} - \gamma_{33}) I_{\Omega_3} &= \lambda_1 - \lambda_3 \\
\kappa_3 + (\gamma_{12} - \gamma_{11}) I_{\Omega_1} + (\gamma_{22} - \gamma_{12}) I_{\Omega_2} + (\gamma_{23} - \gamma_{13}) I_{\Omega_3} &= \lambda_2 - \lambda_1 \\
\kappa_4 + \gamma_{13} I_{\Omega_1} + \gamma_{23} I_{\Omega_2} + \gamma_{33} I_{\Omega_3} &= \lambda_3 \\
\kappa_5 + \gamma_{12} I_{\Omega_1} + \gamma_{22} I_{\Omega_2} + \gamma_{23} I_{\Omega_3} &= \lambda_2 \\
\kappa_6 + \gamma_{11} I_{\Omega_1} + \gamma_{12} I_{\Omega_2} + \gamma_{13} I_{\Omega_3} &= \lambda_1 \\
\nu_{1,O} + \nu_{4,O} + \nu_{5,O} &= \vec{0} \\
\nu_{1,R} + \nu_{2,R} + \nu_{3,R} &= \vec{0} \\
\nu_{2,P} + \nu_{4,P} + \nu_{6,P} &= \vec{0} \\
\nu_{3,Q} + \nu_{5,Q} + \nu_{6,Q} &= \vec{0}
\end{aligned}
$$

Analytic Results of the Quaternary Problem

(X. Ren and C. Wang)



- Asymmetric and symmetric triple bubbles
- The triple bubble assembly

A Diffusive Interface Model for the Binary Problem

$$\begin{aligned}\mathcal{I}_\epsilon(\phi) &= \int_D [\frac{\epsilon^2}{2}|\nabla\phi|^2 + W(\phi)]dx \\ &+\frac{\epsilon\gamma}{2}\int_D \left((-\triangle)^{-\frac{1}{2}}(\phi-\omega)\right)\left((-\triangle)^{-\frac{1}{2}}(\phi-\omega)\right)dx.\end{aligned}$$

ϕ, the concentration of one of the two components

- $\phi(x) = 1$, the point $x \in D$ is occupied by the first component
- $\phi(x) = 0$, the point $x \in D$ is occupied by the second component
- $0 < \phi(x) < 1$, the point $x \in D$ is taken by a mixture of the two components
- $W(\phi) = 18\phi^2(\phi-1)^2$.

A Diffusive Interface Model for the Binary Problem

Scheme I:

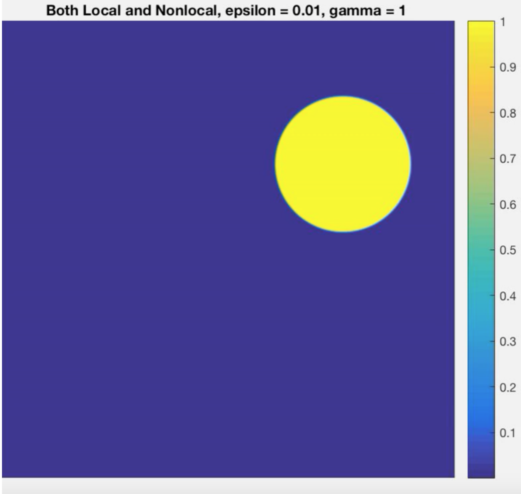
$$\frac{\partial \phi}{\partial t} = \epsilon^2 \triangle \phi - W'(\phi) + \overline{W'(\phi)} - \epsilon\gamma(-\triangle)^{-1}(\phi - \omega).$$

Scheme II:

$$\frac{\partial \phi}{\partial t} = \epsilon^2 \triangle \phi - W'(\phi) - \epsilon\gamma(-\triangle)^{-1}(\phi - \widetilde{\omega}) - M\left[\int_D \phi dx - \omega|D|\right].$$

Numerical Simulations

(C. Wang, Y. Zhao and X. Ren)



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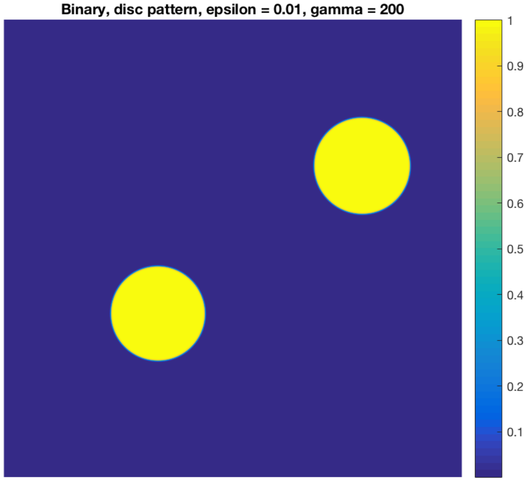

Numerical Simulations

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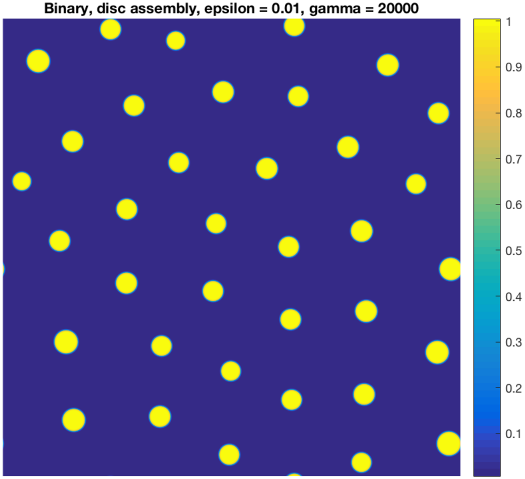
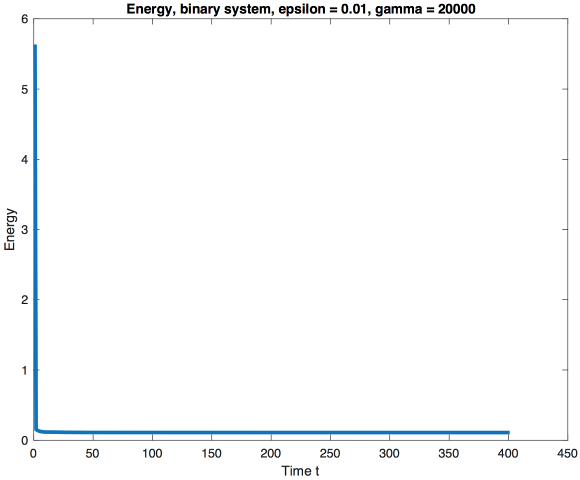


Energy Analysis



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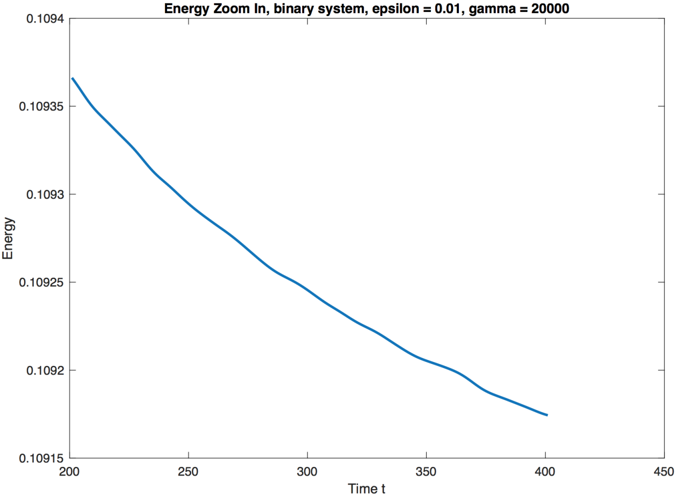

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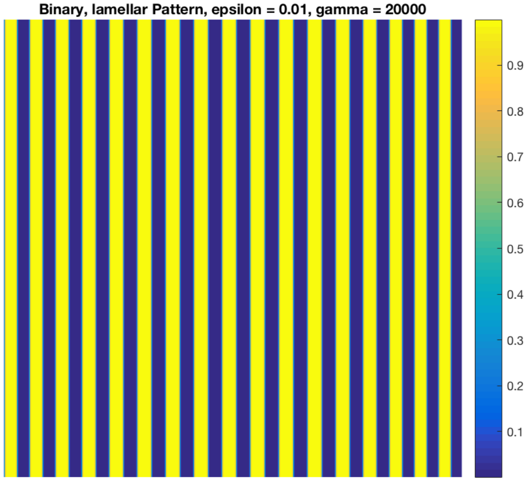

Remarks

De Giorgi's Gamma-convergence theory connects $\mathcal{I}_\epsilon$ and $\mathcal{J}$.

- As $\epsilon \to 0$, $\epsilon^{-1}\mathcal{I}_\epsilon$ Gamma converges to $\mathcal{J}$.
- As $\epsilon \to 0$, a global minimizer of $\mathcal{I}_\epsilon$ converges to a global minimizer of $\mathcal{J}$.
- If $\mathcal{J}$ has an isolated local minimizer Ω, then for small ϵ, $\mathcal{I}_\epsilon$ has a local minimizer ϕ_ϵ such that

$$\int_D |\phi_\epsilon - \chi_\Omega| dx \to 0 \text{ as } \epsilon \to 0.$$

Future Directions of the Numerical Simulation

- Ternary and quaternary inhibitory systems
- Boundary conditions
- Higher dimensions
- General domains
- New Patterns

Thank you!