Multi-scale Modeling of Polymeric Mixtures

Anna C. Balazs
Jae Youn Lee
Gavin A. Buxton
Olga Kuksenok
Kevin Good
Valeriy V. Ginzburg*

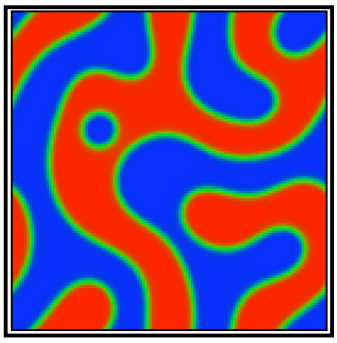
Chemical Engineering Department
University of Pittsburgh
Pittsburgh, PA

*Dow Chemical Company
Midlland, MI

• Use Multi-scale Modeling to Examine:

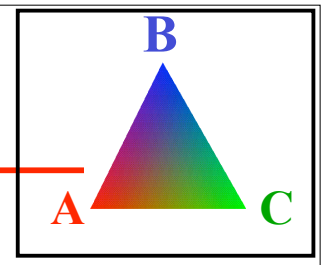
- **Reactive A/B/C ternary mixture**
  - A and B form C at the A/B interface

$$A + B \underset{\Gamma_-}{\overset{\Gamma_+}{\Leftrightarrow}} C$$



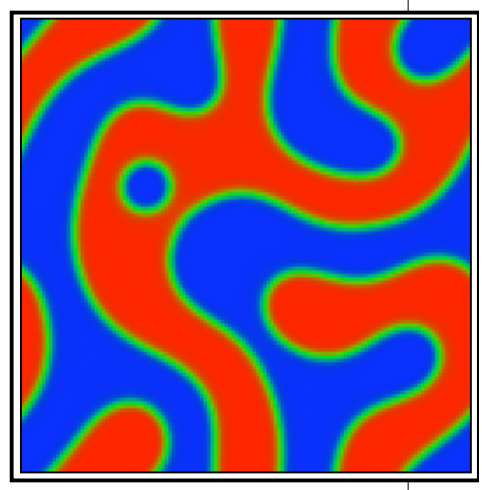
- **Critical step in many polymerization processes**
- **Challenges in modeling system:**
  - Incorporate reaction
  - Include hydrodynamics
  - Capture structural evolutional and domain growth
  - Predict macroscopic properties of mixture
- **Results yield guidelines for controlling morphology and properties**

• **System** $A + B \underset{\Gamma_-}{\overset{\Gamma_+}{\Leftrightarrow}} C$



θ **A and B are immiscible**

Φ Fluids undergo phase separation



θ **C forms at A/B interface**

Φ Alters phase-separation

θ **Examples:**

Φ Interfacial polymerization

Φ Reactive compatibilization

θ **Two order parameters model:**

Φ $\varphi = \rho_A - \rho_B$

Φ $\psi = \rho_c$

here $\rho_i \quad i = A, B, C$ is density

θ **Challenges:**

Φ Modeling hydrodynamic interactions

Φ Predicting morphology & formation of C

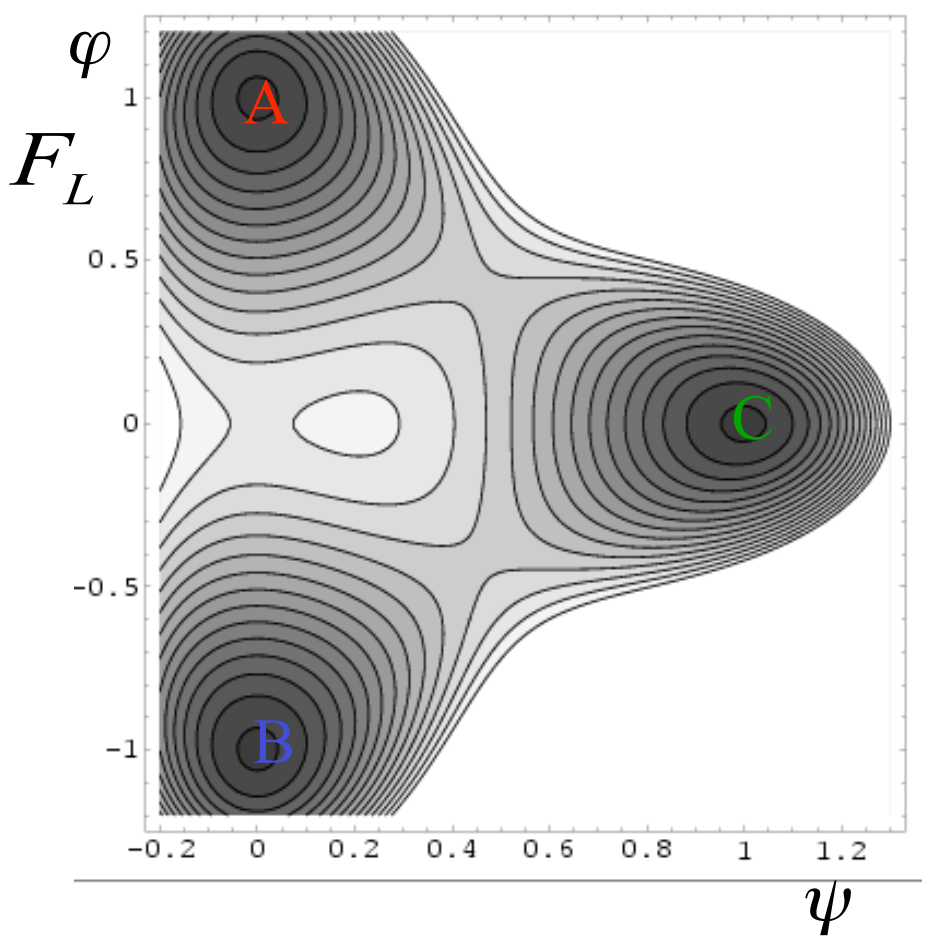
- **Free Energy for Ternary Mixture: F_L**

θ **Free energy $F = F_L + F_{NL}$**

Φ

$$F_L = \int d\vec{r} \begin{bmatrix} -A_{20}\varphi^2 + A_{40}\varphi^4 \\ + A_{02}\psi^2 - A_{03}\psi^3 + A_{04}\psi^4 \\ + A_{22}\psi^2\varphi^2 \end{bmatrix}$$

Φ **Coefficients for F_L yield 3 minima**



$A_{20} = 1/4$

$A_{40} = 1/8$

$A_{02} = 1/4$

$A_{03} = 1$

$A_{04} = 5/8$

$A_{22} = 1$

Φ Three phase coexistence

• Free Energy : Non-local part, F_{NL}

θ **Free energy** $F = F_L + F_{NL}$

$$F_{NL} = \int d\vec{r} \left[\begin{array}{l} k_\varphi \left|\vec{\nabla}\varphi\right|^2 - s\psi^2 \left|\vec{\nabla}\varphi\right|^2 + w\left|\vec{\nabla}^2\varphi\right|^2 \\ + k_\psi \left|\vec{\nabla}\psi\right|^2 \end{array} \right]$$

Φ Reduction of A/B interfacial tension by C:

Φ $(k_\varphi - s\psi^2)\,|\vec{\nabla}\varphi|^2$

Φ No formation of C in absence of chemical reactions ($\delta F / \delta\psi = 0$)

Φ Cost of forming C interface: $k_\psi \left|\vec{\nabla}\psi\right|^2$.

θ **For** $\psi \to 0$ (no reactions & no C)

$$F = \int d\vec{r} \left[-\tfrac{1}{4}\varphi^2 + \tfrac{1}{8}\varphi^4 + k_\varphi \left|\vec{\nabla}\varphi\right|^2 \right]$$

Φ Standard phase-separating binary fluid in two-phase coexistence region

•Evolution Equations*

$$A + B \underset{\Gamma_-}{\overset{\Gamma_+}{\Leftrightarrow}} C$$

θ **Order parameters evolution:**

Φ Cahn –Hilliard equations

$$\frac{\partial \varphi}{\partial t} + \vec{u}\vec{\nabla}\varphi = M\vec{\nabla}^2\mu$$

$$\frac{\partial \psi}{\partial t} + \vec{u}\cdot\vec{\nabla}\psi = M_\psi \nabla^2 \mu_\psi +$$

$$1/2\cdot\Gamma_+(\rho - \psi + \varphi)(\rho - \psi - \varphi) - \Gamma_-\psi$$

Φ $\mu = \delta F/\delta\varphi, \quad \mu_\psi = \delta F/\delta\psi$

Φ $\rho_A = \frac{1}{2}\left[\rho - \varphi - \psi\right] \quad \rho_B = \frac{1}{2}\left[\rho + \varphi - \psi\right]$

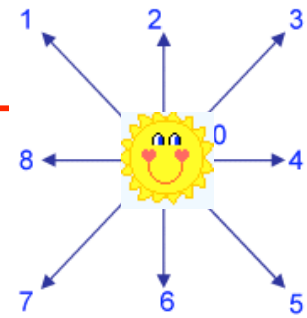
Φ $M_w(A) = M_w(B);\ M_w(C) = 2^* M_w(A)$

θ **Navier-Stokes equation**

$$\rho\partial_t\vec{u} + \rho(\vec{u}\cdot\vec{\nabla})\vec{u} = -\vec{\nabla}P_0 + \eta\nabla^2\vec{u} - \psi\vec{\nabla}\mu_\psi - \varphi\vec{\nabla}\mu$$

C. Tong, H. Zhang, Y.Yang, J.Phys.Chem B, 2002

• Lattice-Boltzmann Method



θ **D2Q9 scheme**

Φ 3 distribution functions

$$f_i(\mathbf{r}+\mathbf{e}_i\delta, t+\delta) = f_i(\mathbf{r},t) - \varpi_f(f_i^{eq} - f_i)$$

$$g_i(\mathbf{r}+\mathbf{e}_i\delta, t+\delta) = g_i(\mathbf{r},t) - \varpi_g(g_i^{eq} - g_i)$$

$$h_i(\mathbf{r}+\mathbf{e}_i\delta, t+\delta) = h_i(\mathbf{r},t) - \varpi_h(h_i^{eq} - h_i) + F_i$$

Φ Macroscopic variables:

$$\sum_i f_i = \rho; \quad \sum_i g_i = \varphi; \quad \sum_i h_i = \psi; \quad \sum_i f_i \mathbf{e}_i = \rho\mathbf{u};$$

Φ Constrains & Conservation Laws

$$\sum_i f_i^{eq} = \rho; \quad \sum_i g_i^{eq} = \varphi; \quad \sum_i h_i^{eq} = \psi;$$

$$\sum_i f_i^{eq}\mathbf{e}_i = \rho\mathbf{u}; \quad \sum_i f_i^{eq}\mathbf{e}_\alpha\mathbf{e}_\beta = P_{\alpha\beta} + \rho\mathbf{u}_\alpha\mathbf{u}_\beta$$

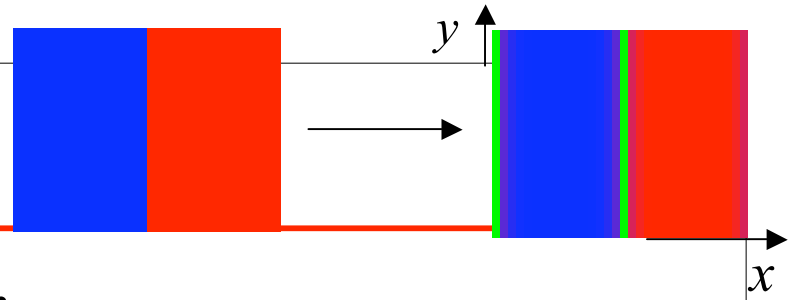
$$\sum_i g_i^{eq}\mathbf{e}_\alpha\mathbf{e}_\beta = M_\varphi^{/}\mu_\varphi\delta_{\alpha\beta} + \varphi\mathbf{u}_\alpha\mathbf{u}_\beta$$

$$\sum_i h_i^{eq}\mathbf{e}_\alpha\mathbf{e}_\beta = M_\psi^{/}\mu_\psi\delta_{\alpha\beta} + \varphi\mathbf{u}_\alpha\mathbf{u}_\beta$$

Φ Governing equations in continuum limit are:

- Φ Cahn –Hilliard equations
- Φ Navier-Stokes equation

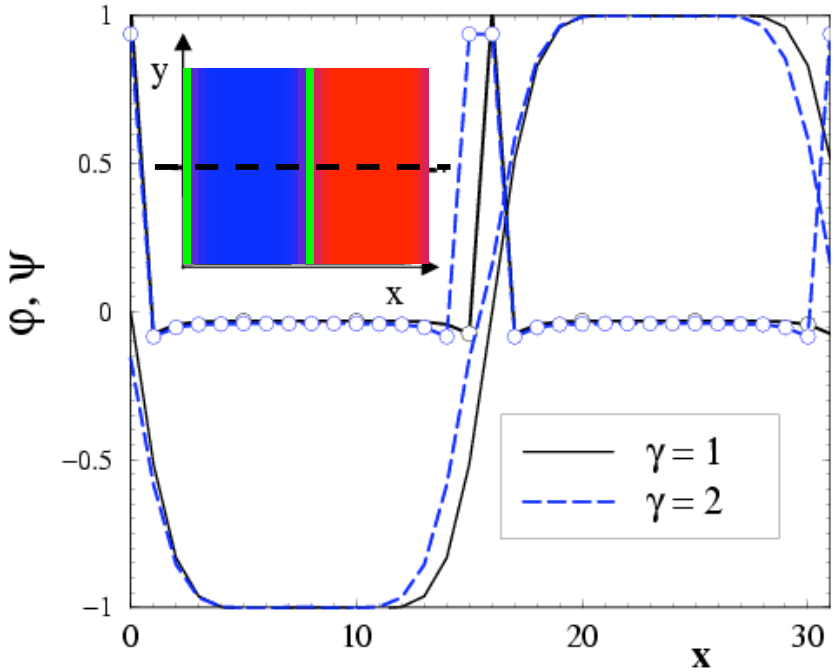
- $A + B \underset{\Gamma_-}{\overset{\Gamma_+}{\Leftrightarrow}} C$



θ **Single Interface:**

Φ System behavior vs $\gamma = \dfrac{\Gamma_+}{\Gamma_-}$, $(\Gamma_- = 10^{-4})$

- Steady-state distributions:

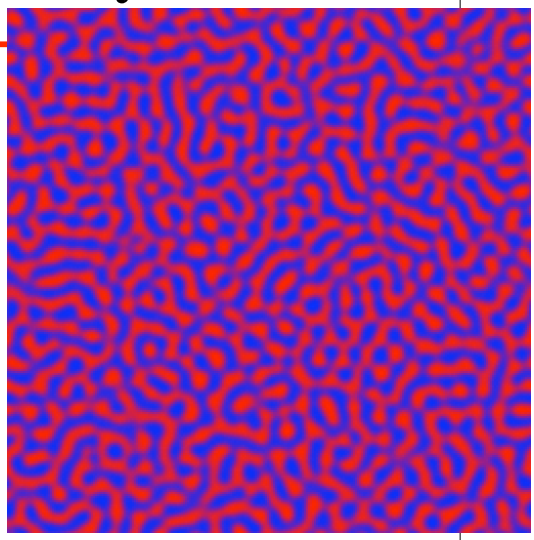


Φ Higher γ leads to wider C layer

Φ Choose parameters to have narrow interface

Φ Need other parameters and additional non-local terms to model wide interfaces.

• Diffusive Limit: No Effects of Hydro



θ **Initial state:**

Φ 256 x 256 sites

Φ High visc. $\omega_f = 3 \cdot 10^{-3}$

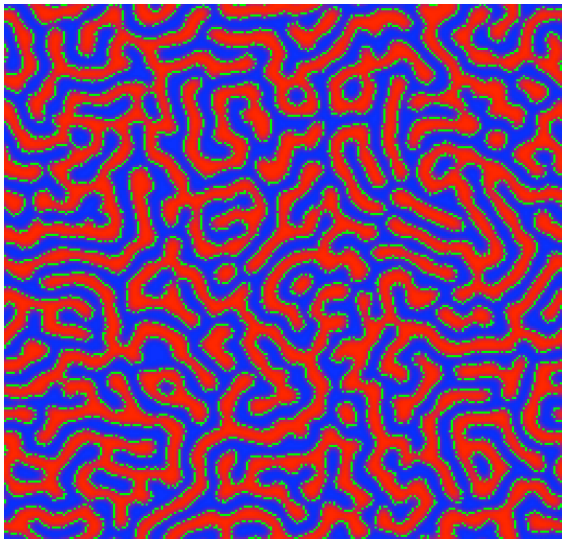
θ **No reaction** $\Gamma_- = \Gamma_+ = 0$

Φ Domain growth $R \sim t^{1/3}$

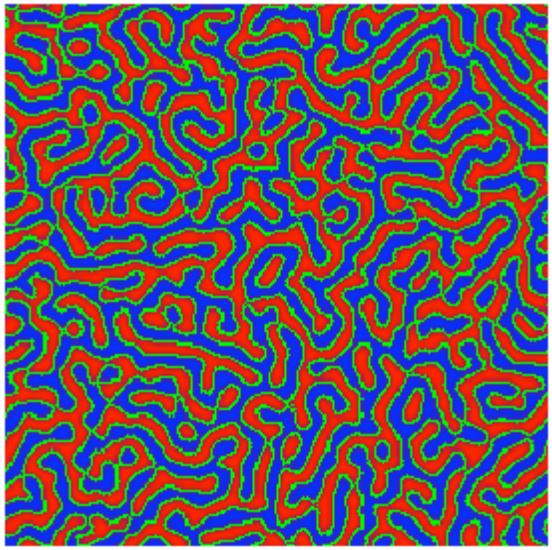
θ **Turn on reaction when *R* =4**

θ **W/reactions: steady-states** $(\Gamma_- = 10^{-4})$ $\gamma = \dfrac{\Gamma_+}{\Gamma_-}$

$\gamma = 1$



$\gamma = 2$



Φ Reactions arrest domain growth

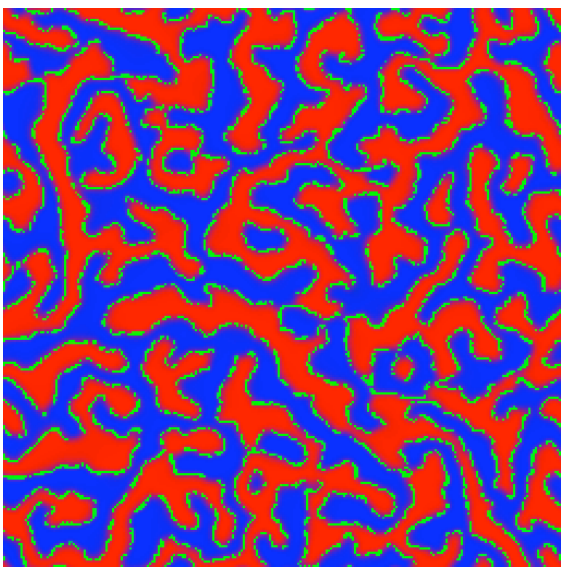
• Viscous Limit: Effect of Hydrodynamics

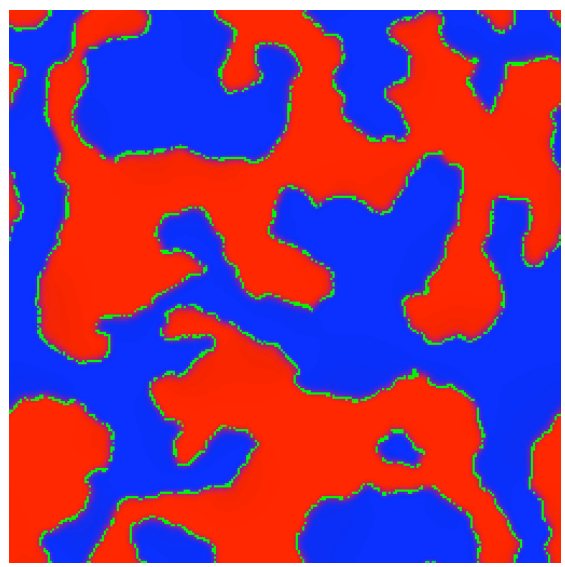
θ **No reaction** $\Gamma_- = \Gamma_+ = 0 \qquad \omega_f = 3 \cdot 10^{-4}$

Φ Domain growth $R \sim t^{1/2}$

θ **Evolution w/reactions:** $\Gamma_- = 10^{-4}$, $\gamma = 1$

$t = 4 \cdot 10^4$ $\qquad$ $t = 4 \cdot 10^5$





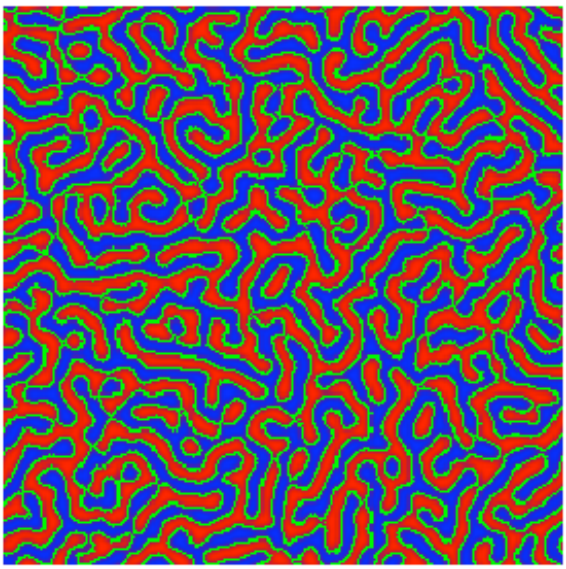
Φ Domain growth slows down but does not stop

θ **Velocities due to** $\vec{\nabla}\mu_\psi, \vec{\nabla}\mu$

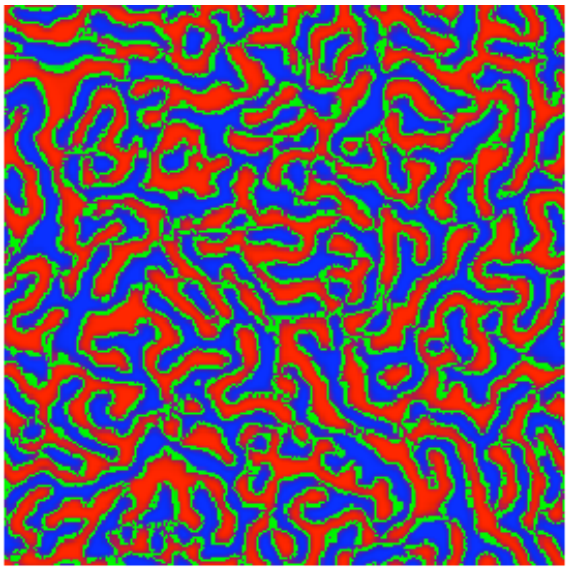
Φ Advect interfaces and prevent equilibrium between reaction & diffusion

- **Compare Morphologies** $\gamma = 2$

Diffusive regime:
Steady-state $(t = 10^5)$

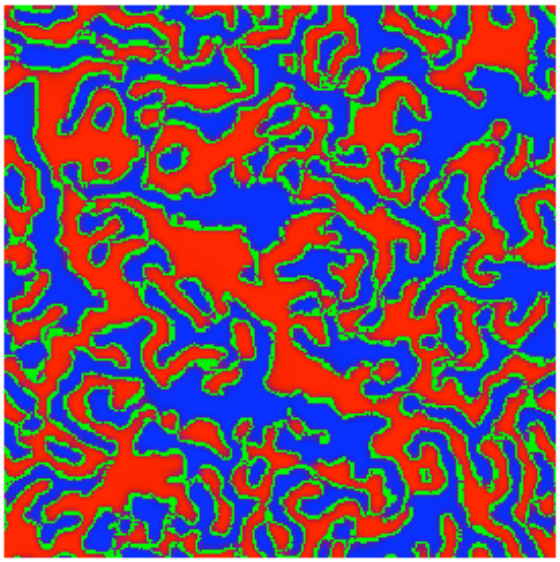


Viscous regime:
Early time $(t = 4 \cdot 10^4)$

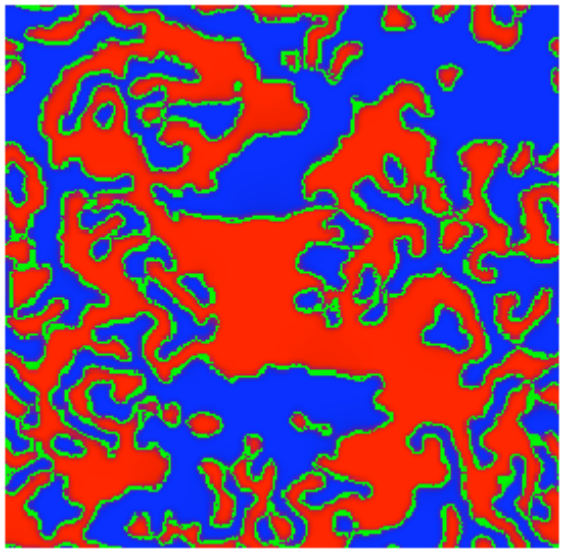


Viscous regime: Late times

$(t = 4 \cdot 10^5)$

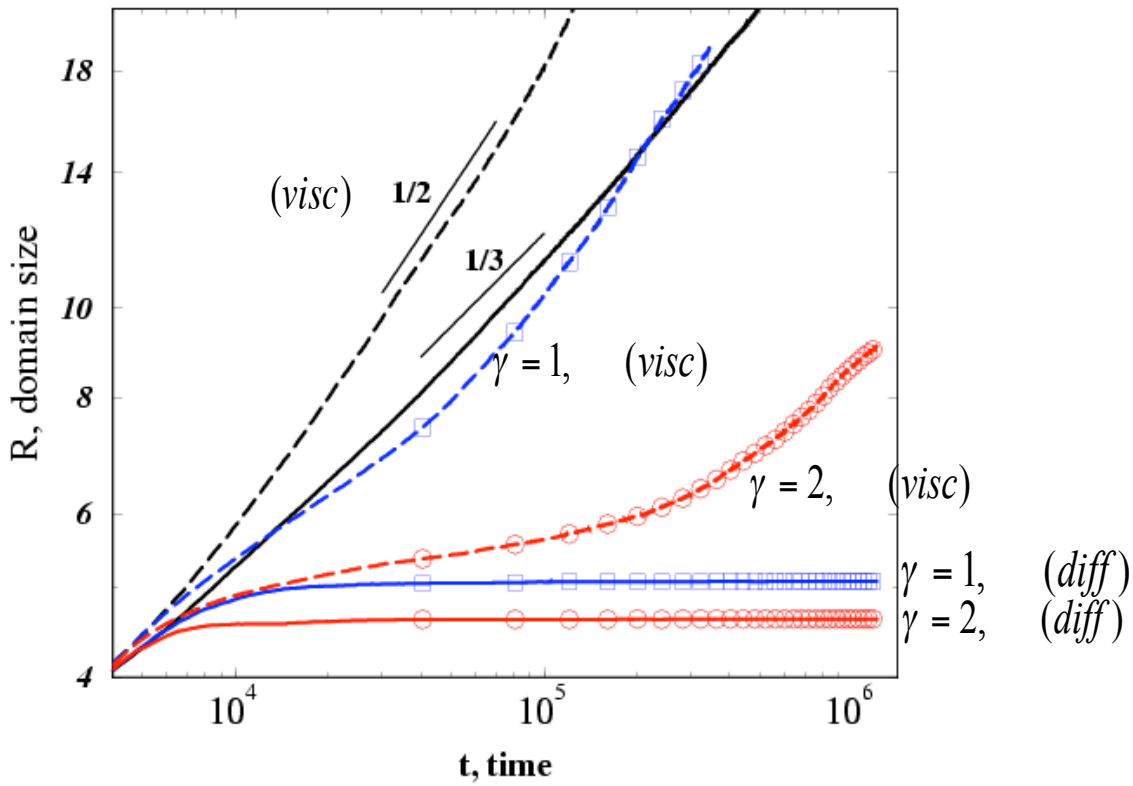


$(t = 1.4 \cdot 10^6)$



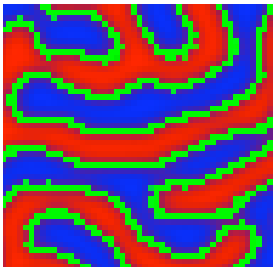
•Domain Growth vs. Reaction Rate Ratio, γ

θ ***R(t)*** **vs. time for different** γ



θ **Diffusive limit:**

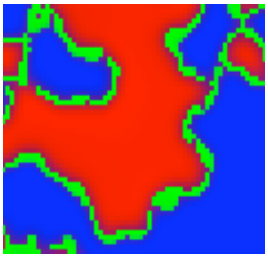
Φ Freezing of *R* due to interfacial reactions



θ **Viscous limit:**

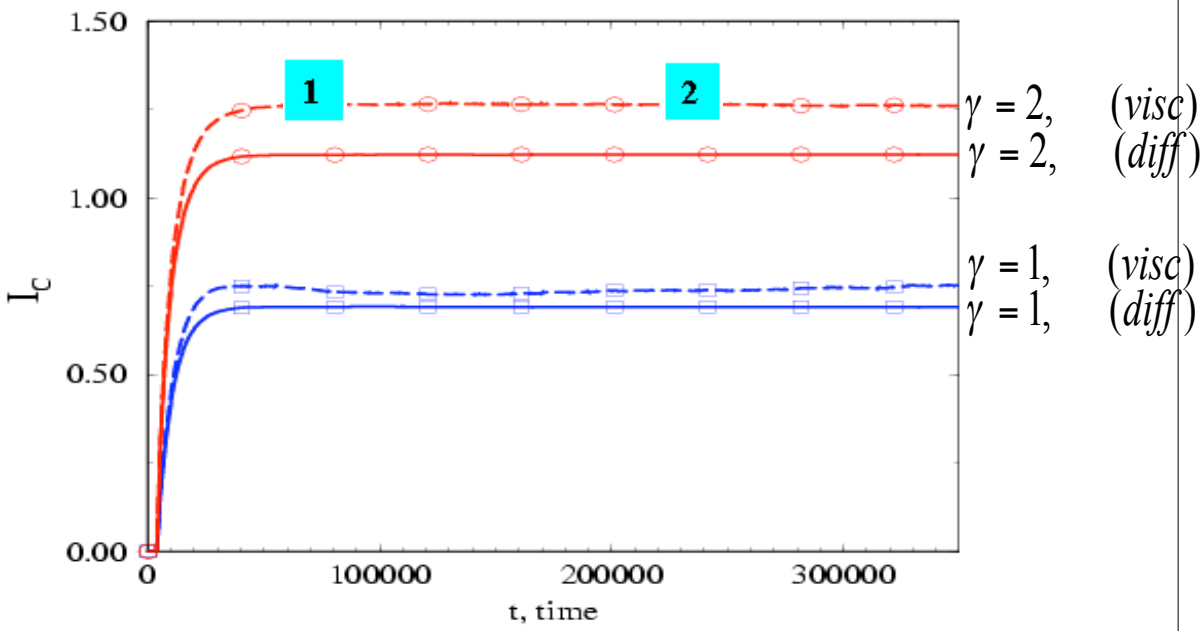
Φ Growth of *R* slows down, especially at early times

Φ *R* smaller for greater γ



•Viscous Limit: Evolution of Average Interface Coverage, I_C .

θ $I_c = \overline{\psi}\,(L^2 / L_{AB}) = \overline{\psi} \cdot R$

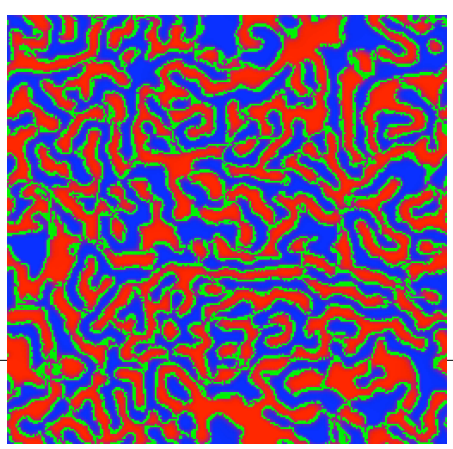


Φ I_C saturates quickly; value similar in diffusive and viscous limits

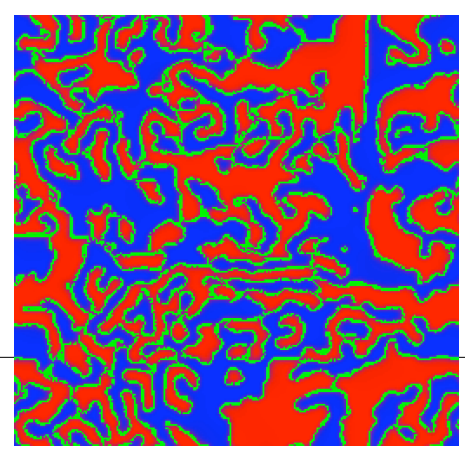
Φ Domain growth freezes in diffusive limit

Φ I_C = const for different R in viscous regimes

1

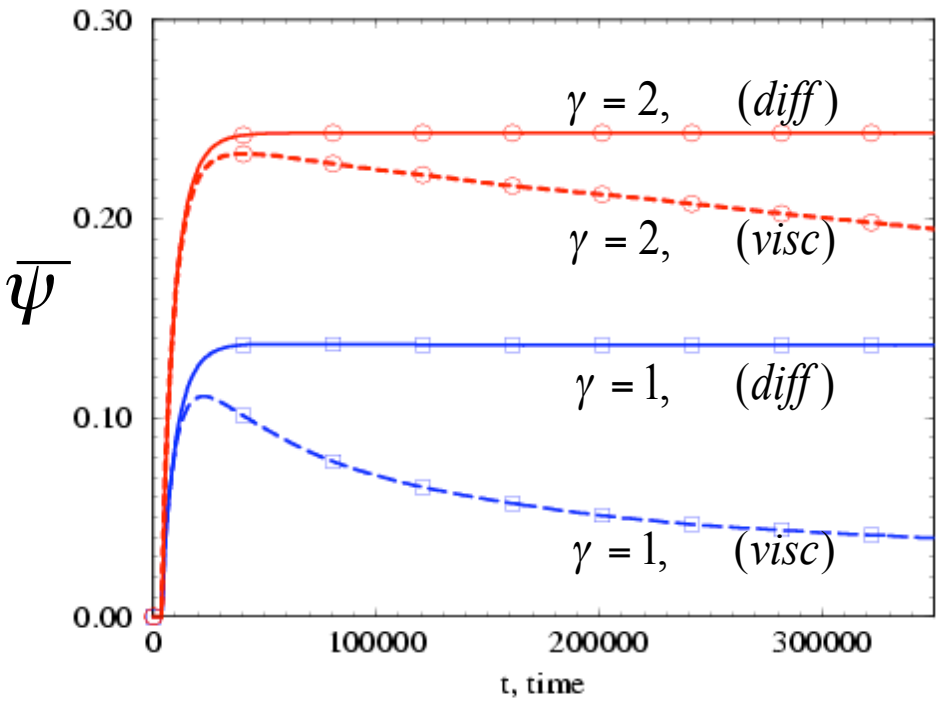


2

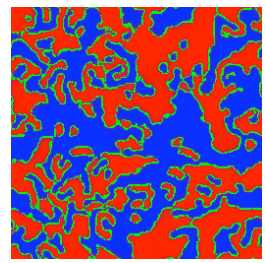


•Viscous Limit: Evolution of $\overline{\psi}$

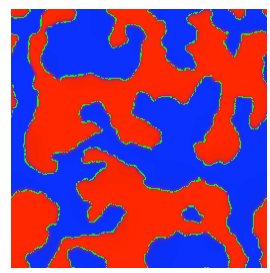
θ **Avg. Amount of C:** $\overline{\psi} = \frac{1}{I_c^2}\int \psi(\mathbf{r})d\mathbf{r}$



$\gamma = 2, \quad (visc)$



$\gamma = 1, \quad (visc)$



Φ At early times, $\overline{\psi}$ is the similar in both cases until I_C saturates

Φ At late times, $\overline{\psi} = I_c / R$ is smaller in viscous regime than in diffusive

Φ Velocity advects interfaces

Φ $\overline{\psi}$ larger for greater γ

• Dependence on Reaction Rates: Diffusive Regime, $\gamma = 2$

θ **Reaction rates:**

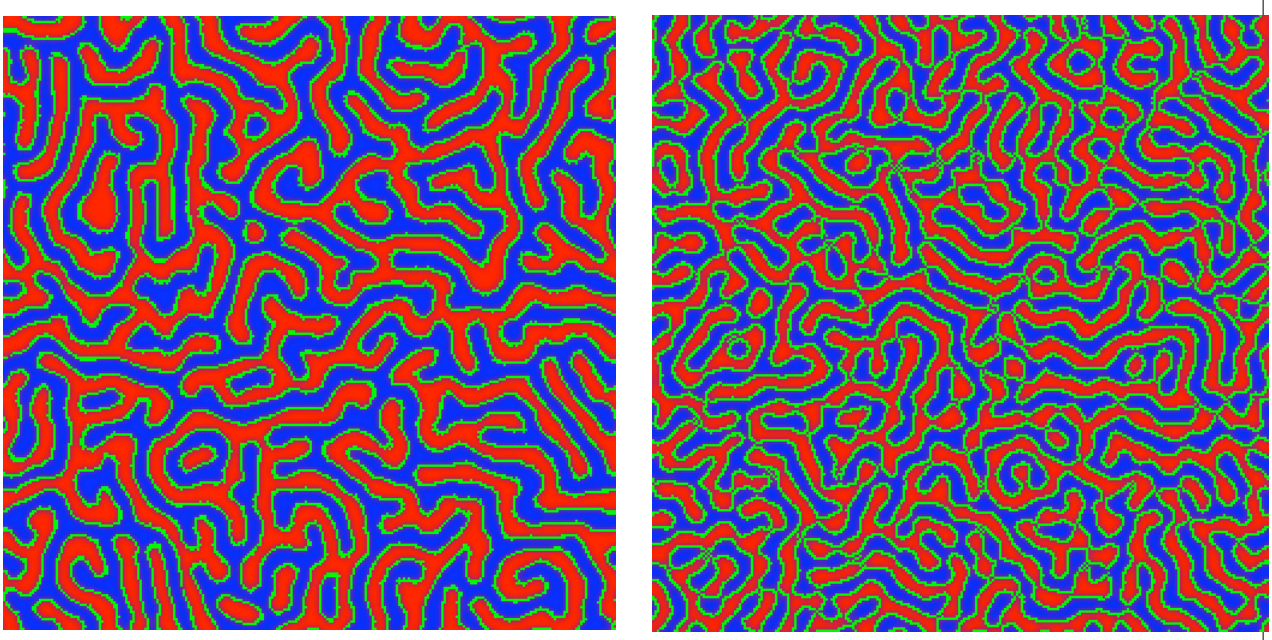
a) ($\Gamma_- = 10^{-4}; \Gamma_+ = 2 \cdot 10^{-4}$)

b) ($\Gamma_- = 2.5 \cdot 10^{-5}; \Gamma_+ = 5 \cdot 10^{-5}$)

c) ($\Gamma_- = 4 \cdot 10^{-4}; \Gamma_+ = 8 \cdot 10^{-4}$)

θ **Steady-state :**

(b) **(c)**



Φ The higher the reaction rates, the faster the interface saturates

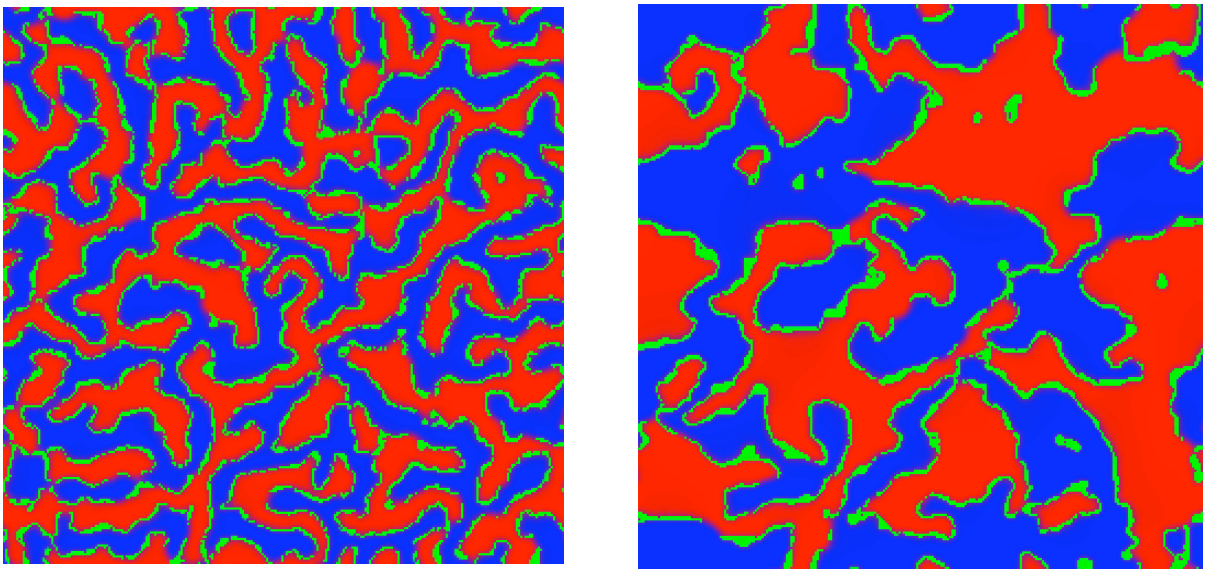
Φ The lower the saturated value of R

- **Dependence on Reaction Rates:**
  Viscous Regime, $\gamma = 2$

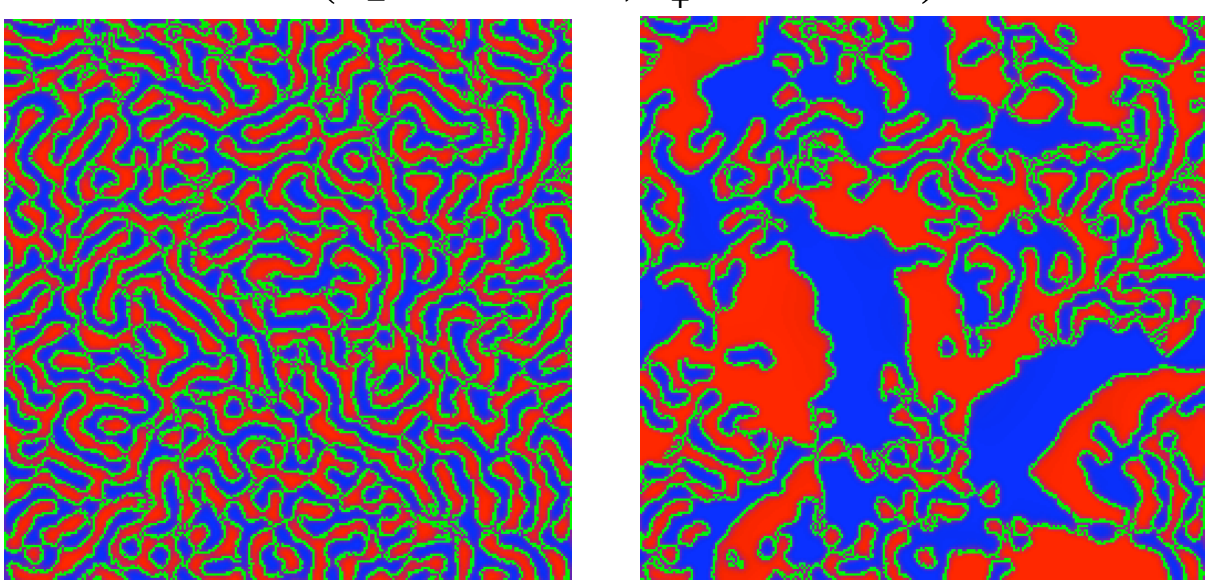
$t = 4 \cdot 10^4$

$t = 7 \cdot 10^5$

$(\Gamma_- = 2.5 \cdot 10^{-5}; \Gamma_+ = 5 \cdot 10^{-5})$



$(\Gamma_- = 4 \cdot 10^{-4}; \Gamma_+ = 8 \cdot 10^{-4})$

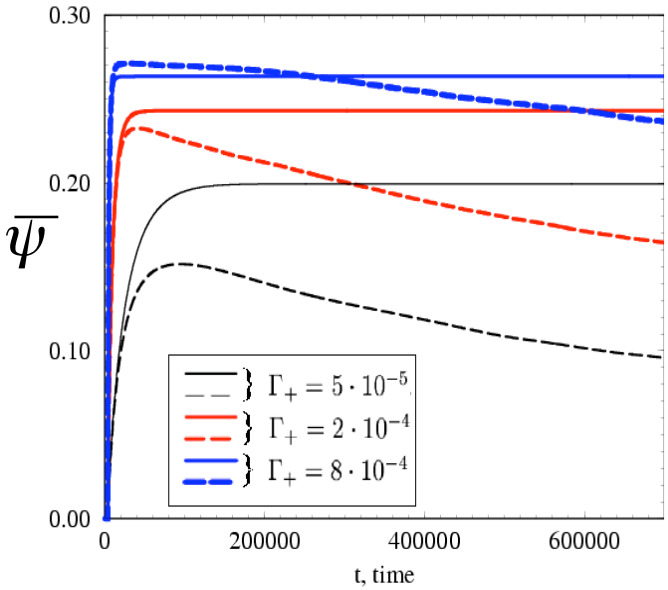


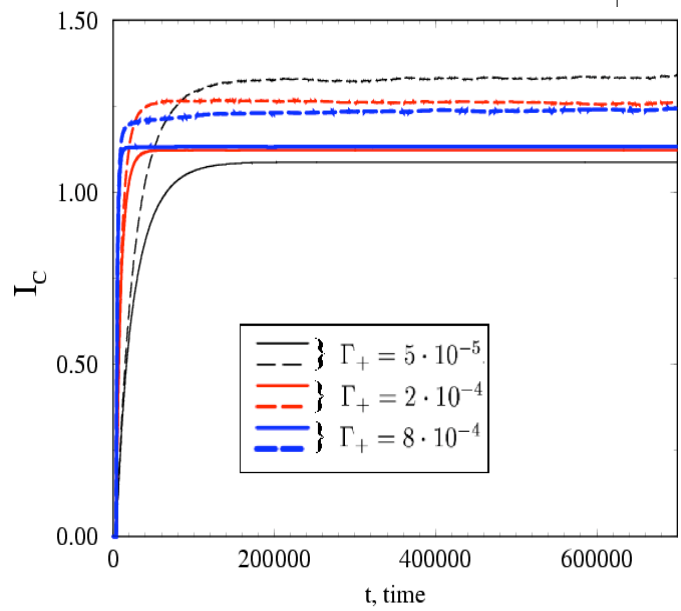
Φ No saturation of R

Φ R(t) smaller for higher reaction rates

• Dependence on Reaction Rates, $\gamma = 2$

θ $\overline{\psi}$ & Interface Coverage, I_C





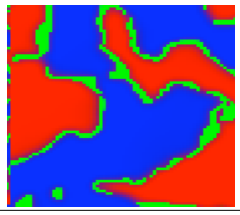
Φ Value of $\overline{\psi}$ depends on values of reaction rates

Φ Higher reaction rates yield greater $\overline{\psi}$

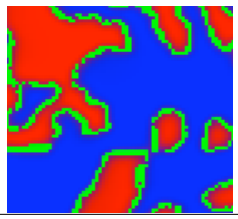
Φ Sat. of I_C faster for higher reaction rates

Φ Values similar for different cases

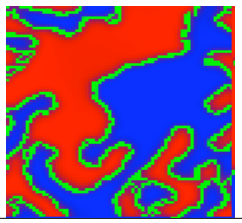
$m = 1/4$



$m = 1$

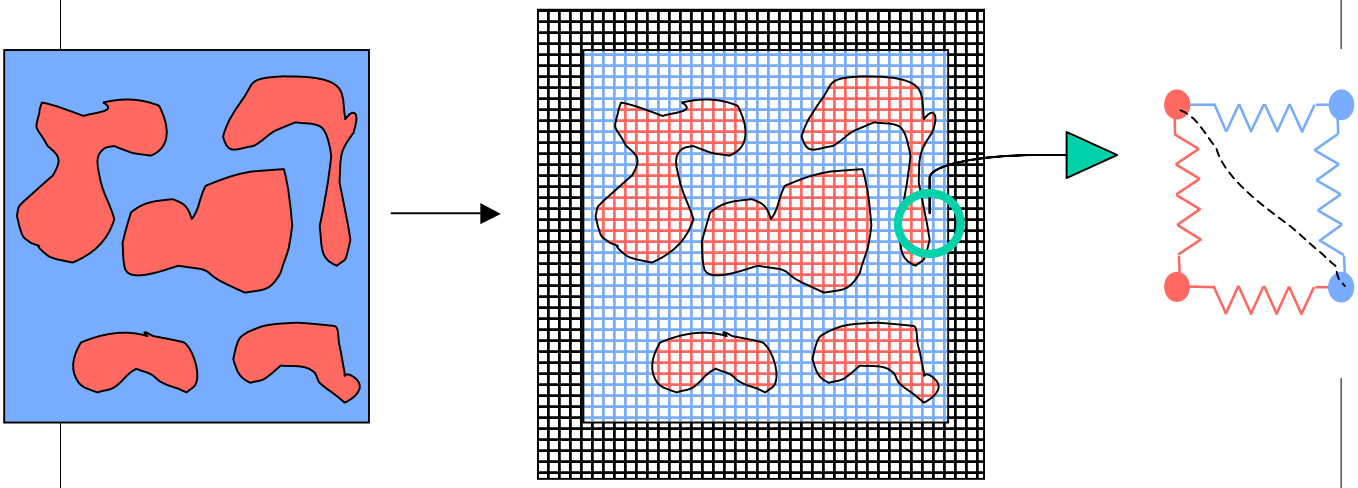


$m = 4$



•Morphology ⟶ Mechanical Properties

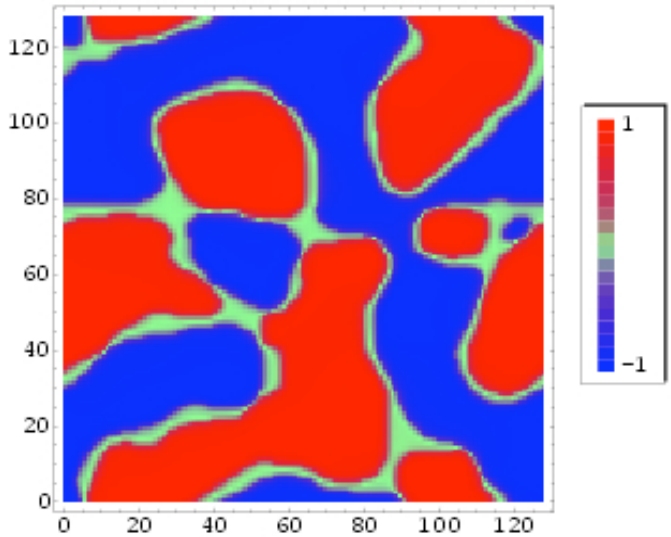
- **Output from morphology study is input to Lattice Spring Model (LSM)**



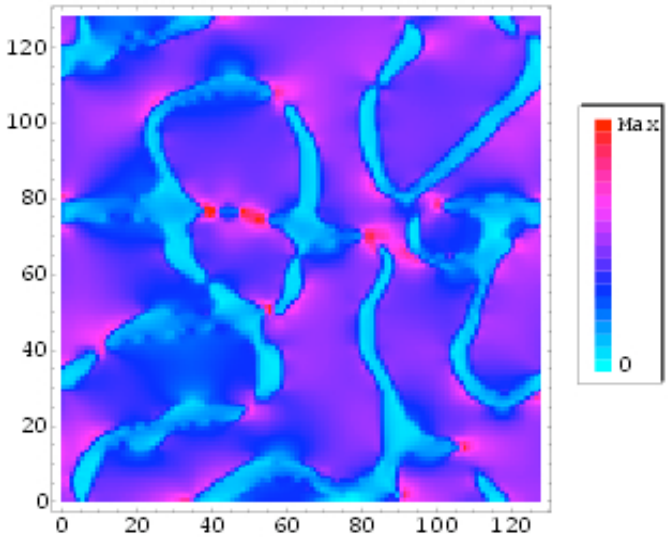
- **LSM: 3D network of springs**
  - Consider springs between nearest and next-nearest neighbors
  - Model obeys elasticity theory
  - Different domains incorporated via local variations in spring constants
- **Apply deformation at boundaries**
  - Calculate local elastic fields

• Determine Mechanical Properties

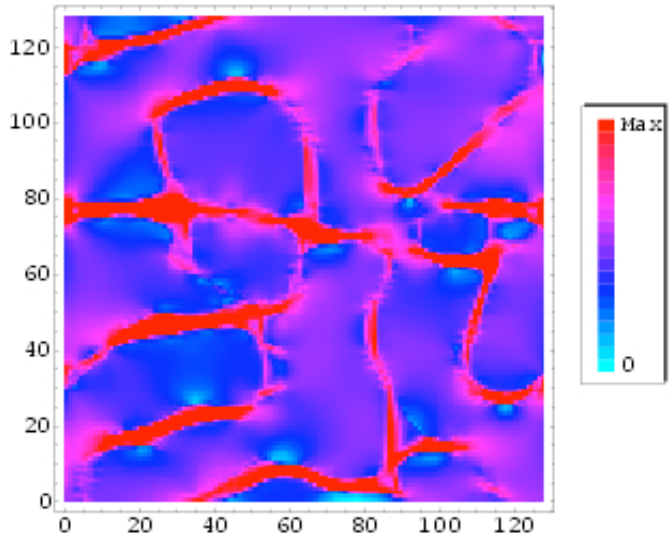
- θ Use output from LB as input to LSM
- θ Morphology



- θ Strain



Stress



• **Symmetric Ternary Fluid;** $A + B \underset{\Gamma_-}{\overset{\Gamma_+}{\Leftrightarrow}} C$

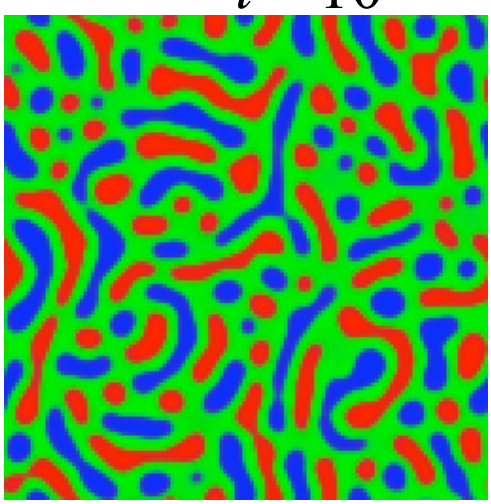
θ $$F = F_L + \int d\vec{r}\left[k_\varphi\left|\vec{\nabla}\varphi\right|^2 + k_\psi\left|\vec{\nabla}\psi\right|^2\right]$$

Φ Local F_L in 3 phase coexistence;

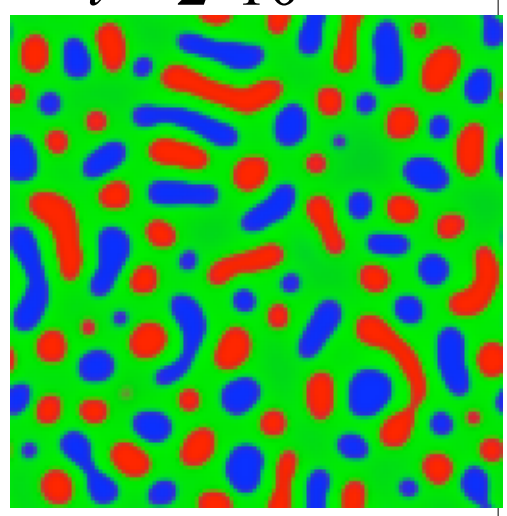
Φ Cost of A/C and B/C interfaces ($\vec{\nabla}\psi$)

θ **Viscous limit,** $\gamma = 20$

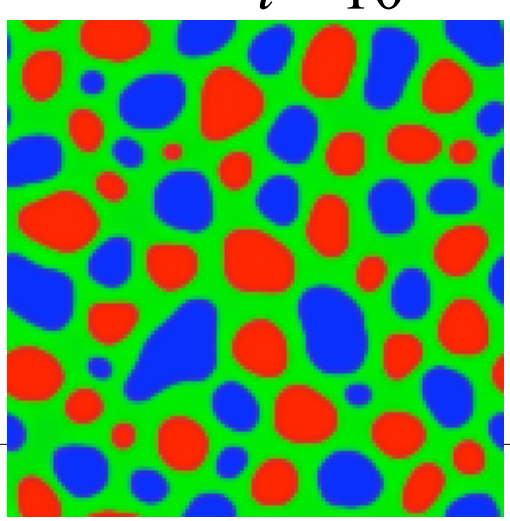
$t = 10^4$



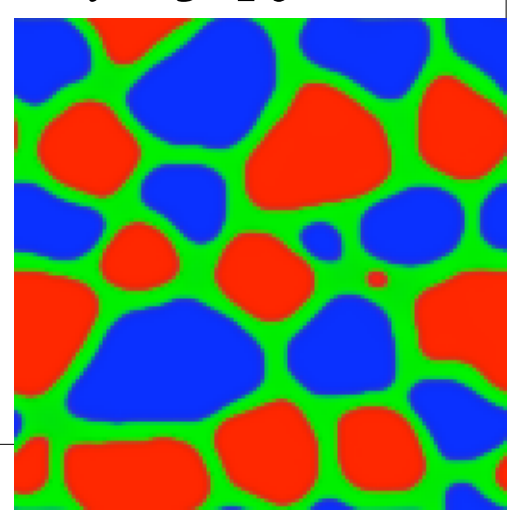
$t = 2 \cdot 10^4$



$t = 10^5$



$t = 3 \cdot 10^5$



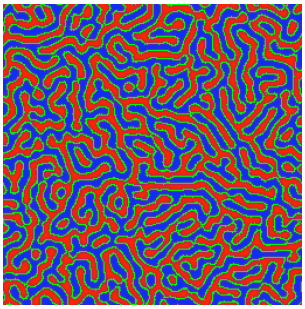
• Conclusions

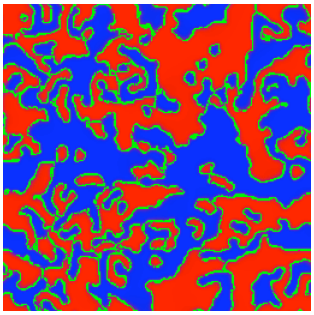
θ **Developed model for reactive ternary mixture** $A + B \Leftrightarrow C$ **with hydrodynamics**

Φ Lattice Boltzmann model

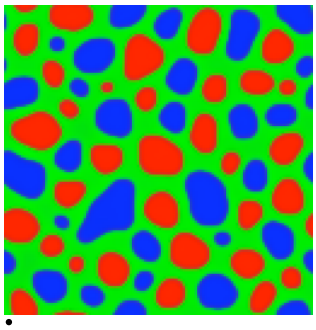
θ **Compared viscous and diffusive regimes**

Φ Freezing of domain growth in diffusive limit and slowing down in viscous limit

diffusive : 

viscous : 

θ ***R(t)*** **depends on γ and specific values of reaction rates**



θ **Future work: "Symmetric" ternary fluids**

Φ A & B & C domain formation

Φ Determine mechanical properties