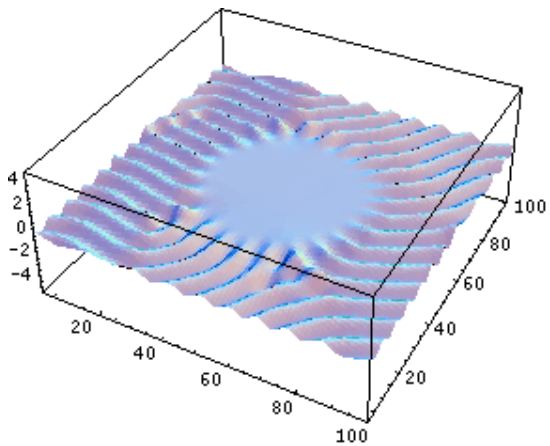
# *Multi-Component Reactive Membranes: A Computer Simulation Study*

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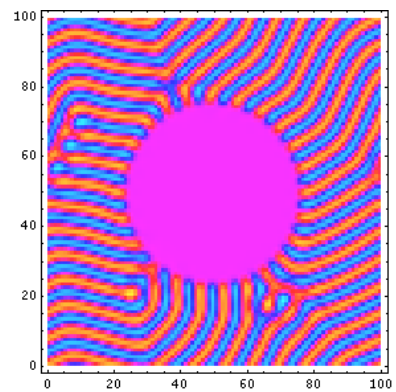


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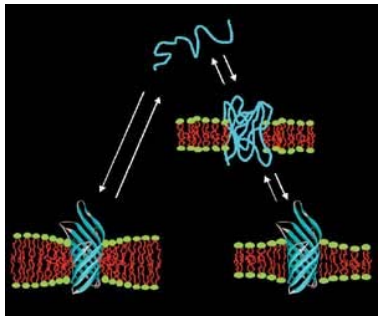
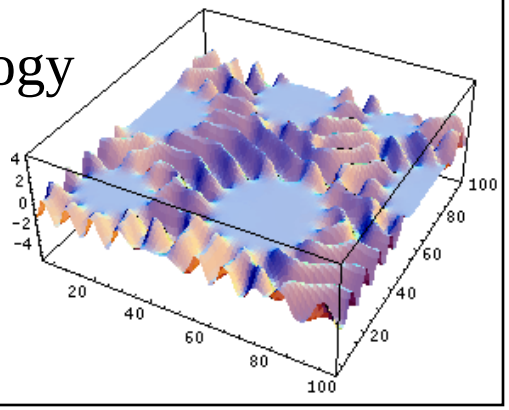
# Introduction

- **Inspiration: non-equilibrium dynamical behavior of bio-membranes**
  - Diverse reactivity
  - Perform biological functions (signaling, molecular recognition, transport)



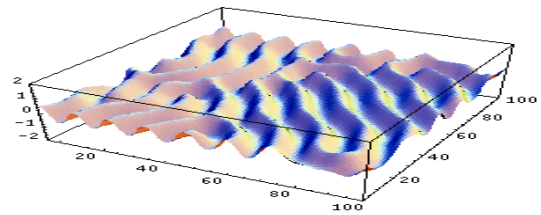
*Membrane protein: reaction in lipid bilayers*
*http://www.pnas.org/misc/Archive022304.shtml*
*PNAS News Archive (2004)*

- **Goal: design synthetic responsive surfaces**
  - Dynamically controlled composition & topology
    - Reactive three component membrane
      - Exhibit rich dynamical behavior
      - Perform "gradient sensing"



# Model : Reactive Membrane

- **Three components (A,B,C)**
  - Local composition $\varphi(x,y)=\rho_A-\rho_B, \quad \psi(x,y)=\rho_C; \quad \sum \rho_i = 1.$
- **Surface height** $h(x,y)$
  - Measured with respect to flat surface



- **Free energy:** $F(\varphi,\psi,h)=\frac{1}{V}\int d\mathbf{r}\left[f_0(\varphi,\psi)+f_1(\varphi,h)\right]$

Phase separation between A,B and C

$$f_{local}(\varphi,\psi)+\frac{\gamma_\varphi}{2}(\nabla\varphi)^2+\frac{\gamma_\psi}{2}(\nabla\psi)^2$$

Energy due to height variation

$$\frac{\sigma}{2}(\nabla h)^2+\frac{\kappa}{2}\left(\nabla^2 h-H_{eq}(\varphi)\right)^2$$

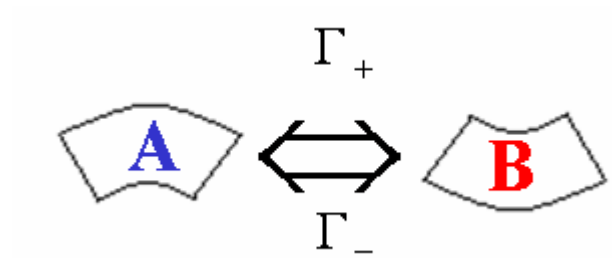
- $\kappa$ is bending rigidity, $\sigma$ is lateral surface tension
- $H_{eq}(\varphi)=\varphi H_0$ is spontaneous curvature


  - In equilibrium, A & B will take their spontaneous curvatures

# Model: Evolution Equations

- **Externally controlled reaction between A and B**
  - ☞ Affects composition and shape of *AB*

*As introduced in: R.Reigada, J.Buceta, K.Lindenberg,PRE 72, 051921 (2005)*




- **Evolution equations**

$$\frac{\partial \varphi}{\partial t} = M_\varphi \nabla^2 \frac{\delta F}{\delta \varphi} - \Gamma \varphi$$

evolution of AB composition

$$\frac{\partial \psi}{\partial t} = M_\psi \nabla^2 \frac{\delta F}{\delta \psi}$$

evolution of C

$$\frac{\partial h}{\partial t} = -M_h \frac{\delta F}{\delta h} + \Gamma \varphi \xi$$

evolution of height

- ☞ $M_i$ is mobility of *i*-th order parameter; $\Gamma_+ \equiv \Gamma_- \equiv \frac{1}{2}\Gamma$
- ☞ Reactive term $\Gamma \varphi \xi$ was introduced by *R.Reigada et. al., PRE (2005)*

  $\xi$ is strength of effect of reaction on shape

## Linear Stability Analysis in Binary Case

- **Evolution of AB mixture:**

$$\frac{\partial \varphi}{\partial t} = M_\varphi \nabla^2 \left[ \frac{\partial f_{local}(\varphi, \psi)}{\partial \varphi} - \gamma_\varphi \nabla^2 \varphi + \kappa H_0^2 \varphi - \kappa H_0 \nabla^2 h \right] - \Gamma \varphi$$

$$\frac{\partial h}{\partial t} = M_h \nabla^2 \left[ \sigma h + \kappa \varphi H_0 - \kappa \nabla^2 h \right] + \Gamma \varphi \xi$$

- Uniform state (fixed point) $\varphi_0 = 0, h_0 = 0.$

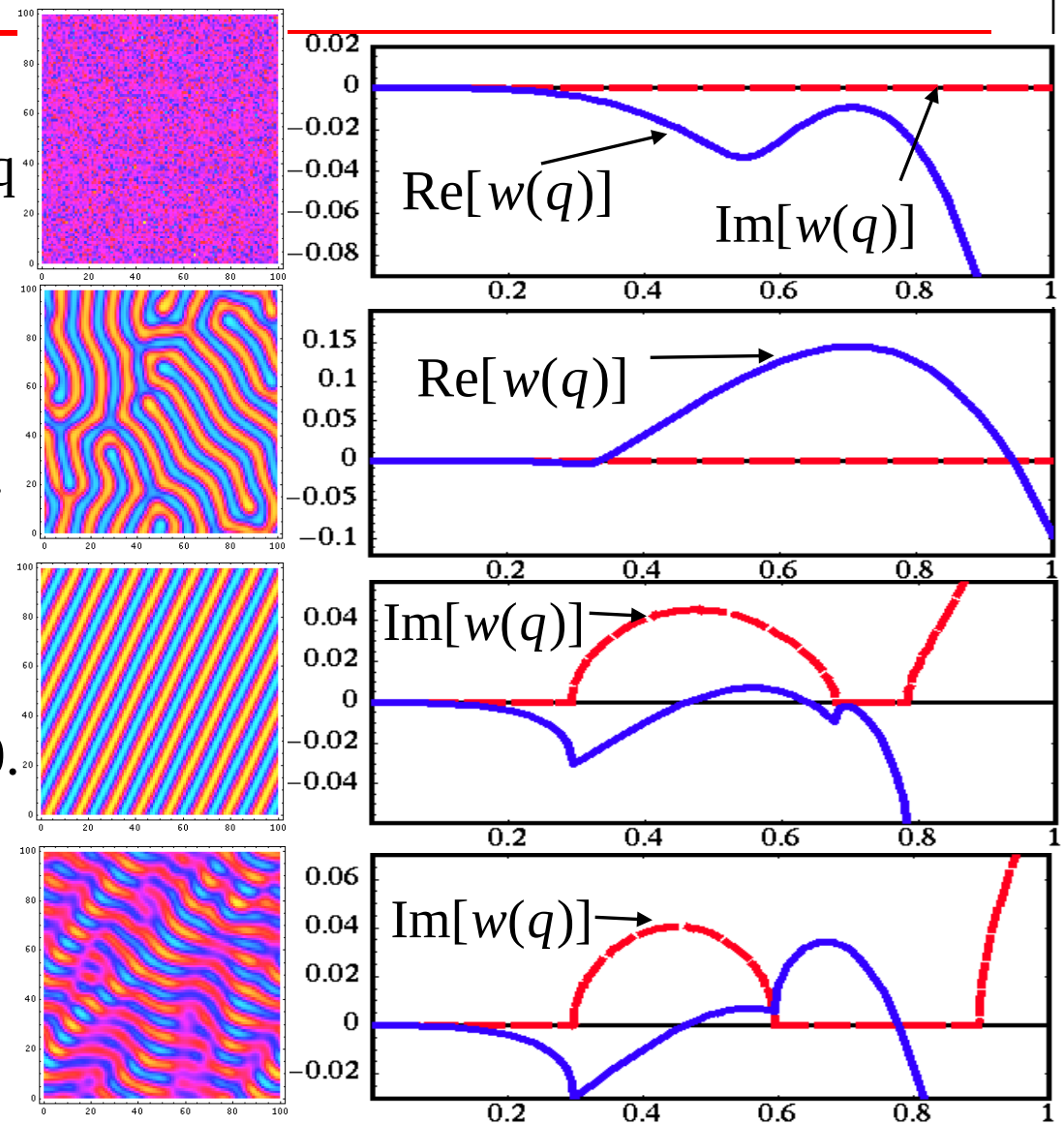
  - Characteristic equation: $\det \left| L_{ij} - w(q) \delta_{ij} \right| = 0;$

$$L = \begin{vmatrix} M_\varphi \left[ -\gamma_\varphi q^4 + q^2 (2a_{20} - \kappa H_0^2 \right] - \Gamma & -M_\varphi q^4 \kappa H_0 \\ -M_h \kappa H_0 q^2 + \Gamma \xi & -M_h \left[ \kappa q^4 + \sigma q^2 \right] \end{vmatrix}$$

- Growth rate of $q$ mode of fluctuation $w(q) = \frac{1}{2} \left[ Tr[L] \pm \sqrt{Tr[L]^2 - 4 \det[L]} \right]$

## Linear Stability Analysis in Binary Case: Possible Scenarios

- **Uniform state is stable**
  - ☞ $\mathrm{Re}[w(q)] < 0$ at any q
- **Turing-like pattern**
  - ☞ $\mathrm{Re}[w(q)] > 0$ & $\mathrm{Im}[w(q)] = 0$ at $q \neq 0$.
- **Traveling waves**
  - ☞ $\mathrm{Re}[w(q)] > 0$ & $\mathrm{Im}[w(q)] \neq 0$ at $q \neq 0$.
- **Turing-like patterns and waves**
  - ☞ Both regions are present at different q.



## Critical Condition on Systems Parameters

- **Uniform state is stable if**

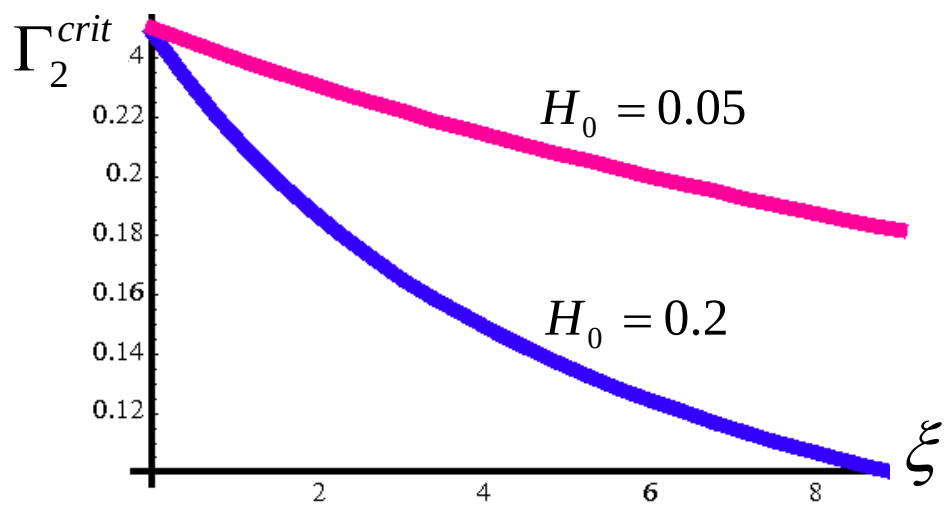
$$\Gamma \geq \Gamma_1^{crit} \equiv \frac{M_\varphi}{4} \frac{\left(-2a_{20} + H_0^2 \kappa + \frac{M_H}{M_\varphi}\sigma\right)^2}{\gamma_\varphi + \kappa \frac{M_H}{M_\varphi}}$$

  - Increase in spontaneous curvature, $H_0$ , increases $\Gamma_1^{crit}$.
  - Increase in film's interfacial tension, $\sigma$ , increases $\Gamma_1^{crit}$.
  - Increase in AB interfacial tension, $\gamma_\varphi$ , decreases $\Gamma_1^{crit}$.

- **Turing-like patterns if**

$$\Gamma_2^{crit} \leq \Gamma < \Gamma_1^{crit}.$$

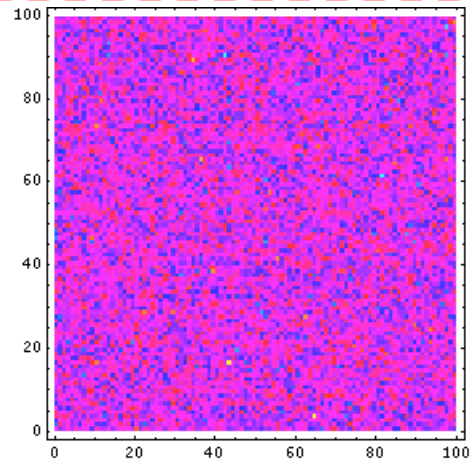
  - Increase in $H_0$ or $\xi$ decreases $\Gamma_2^{crit}$.



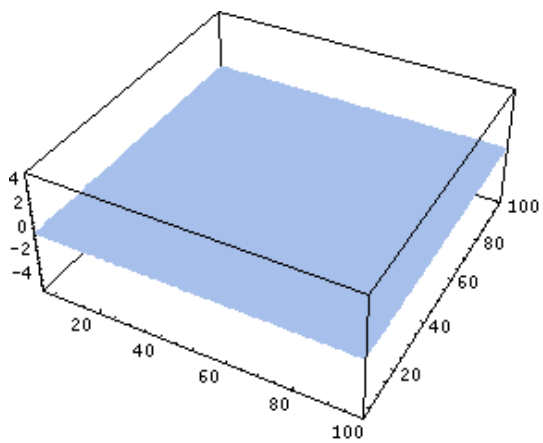
# Late Time Morphology in AB Blends: Possible Scenarios

❑ **Uniform mixed state**

$\varphi(x, y)$



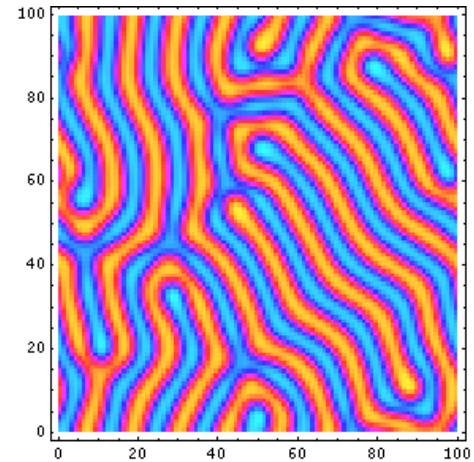

$h(x, y)$



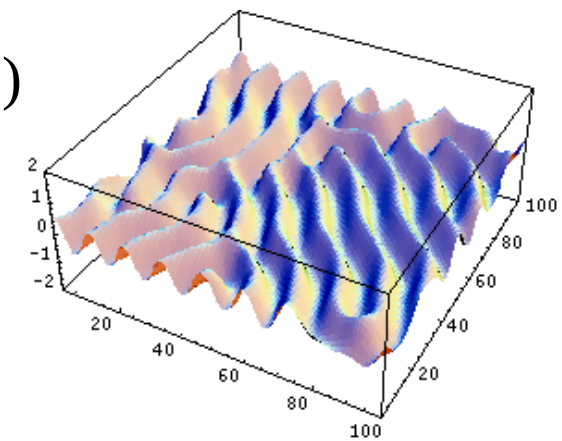

☞ Uniform state is stable at high $\Gamma$

❑ **Turing patterns**

$\varphi(x, y)$




$h(x, y)$



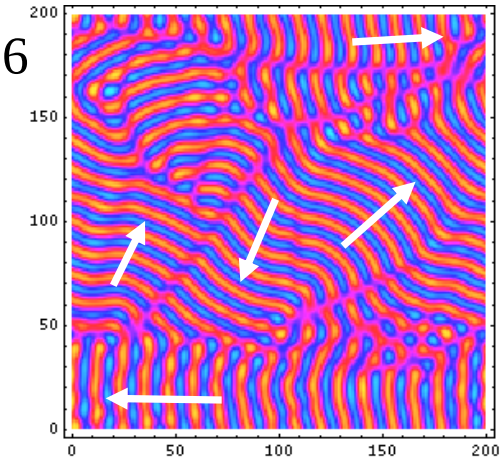

☞ Patterns are stationary with characteristic domain size & height

# Traveling Waves: Scenario 1

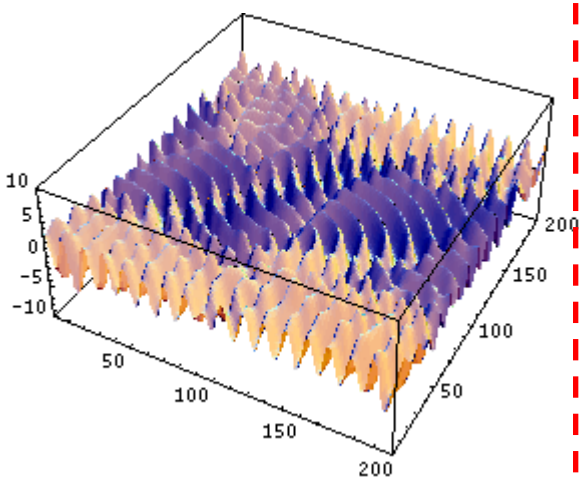
- **Early times:**

$\xi = 6; \Gamma = 0.126$

$\varphi(x, y)$

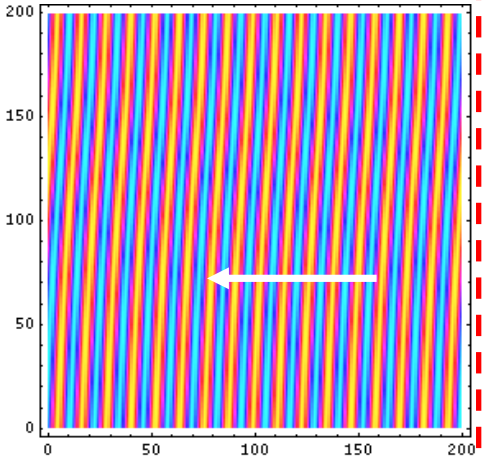



$h(x, y)$

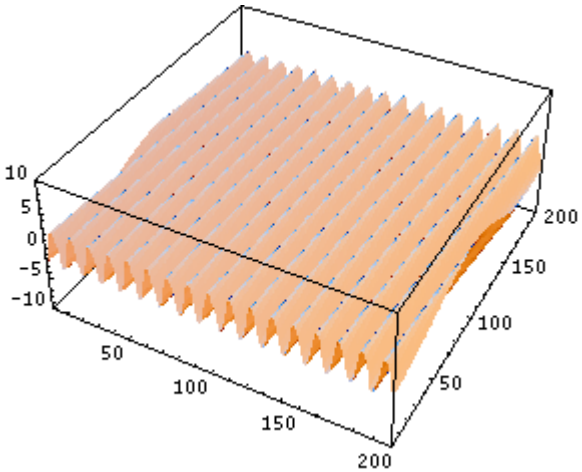



- **Late times:**

$\varphi(x, y)$



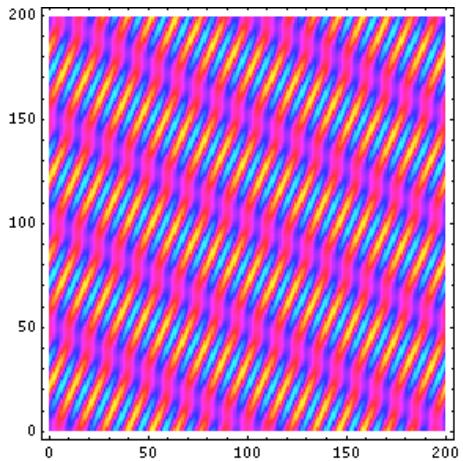

$h(x, y)$



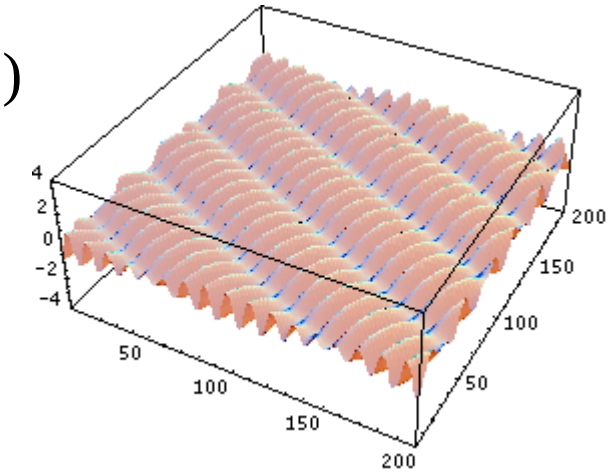
# Traveling Waves: Scenario 2

- **Observed close to bifurcation point;** $\varphi(x, y) << 1$ $(\xi = 8; \Gamma = 0.143)$

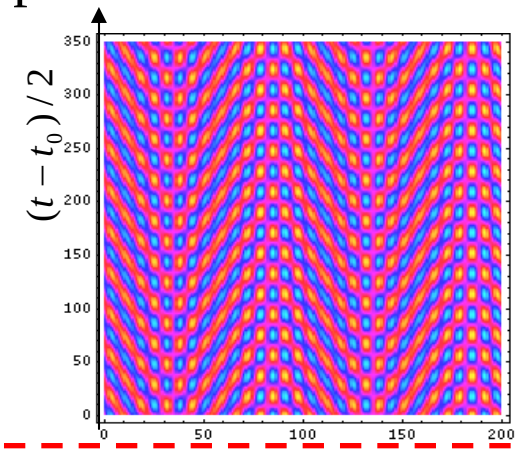
$\varphi(x, y)$

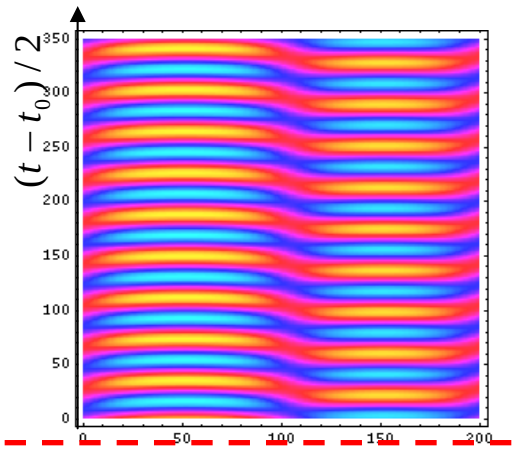


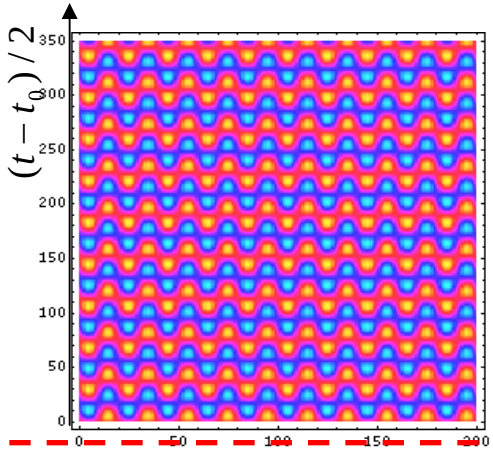

$h(x, y)$




☞ Depends on initial random seed:



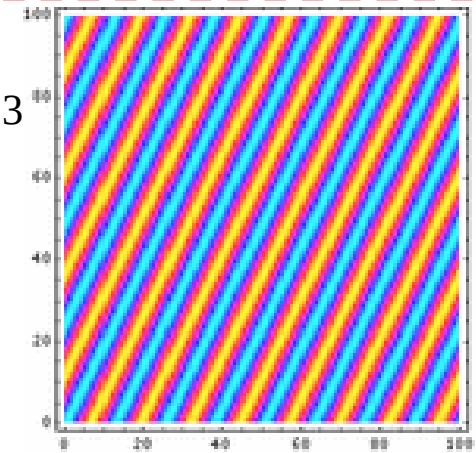



# Late Time Morphology in AB Blends: Traveling Waves

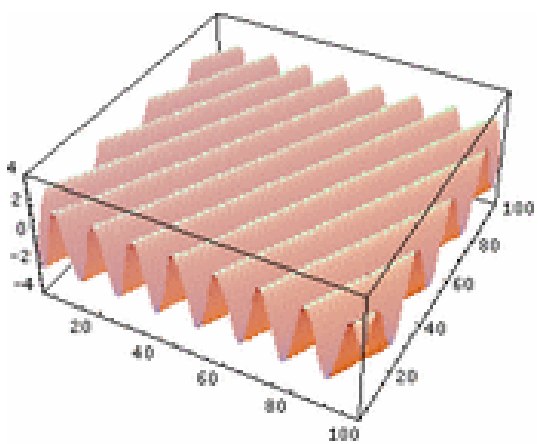
❑ **Case 1:**

$\xi = 5.5; \Gamma = 0.13$

$\varphi(x, y)$



$h(x, y)$

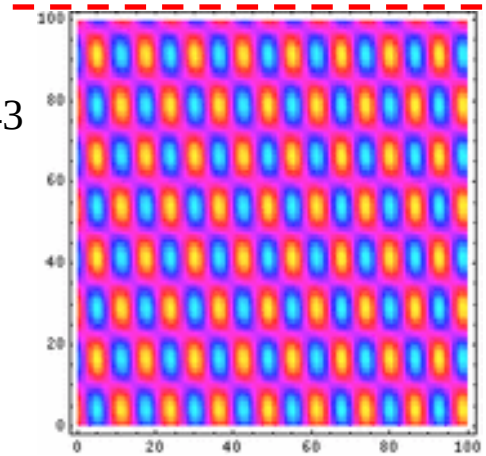


☞ Observed only if $\xi \neq 0$

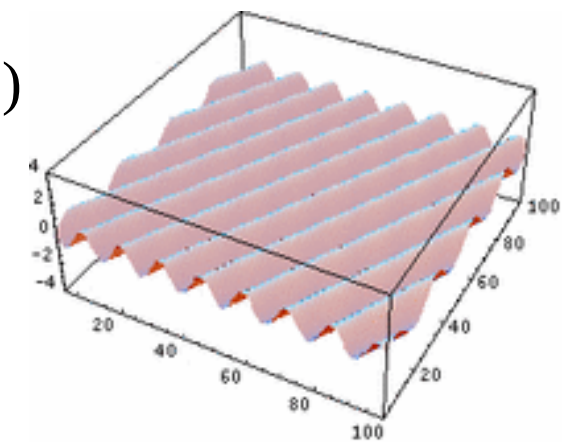
❑ **Case 2:**

$\xi = 8; \Gamma = 0.143$

$\varphi(x, y)$



$h(x, y)$



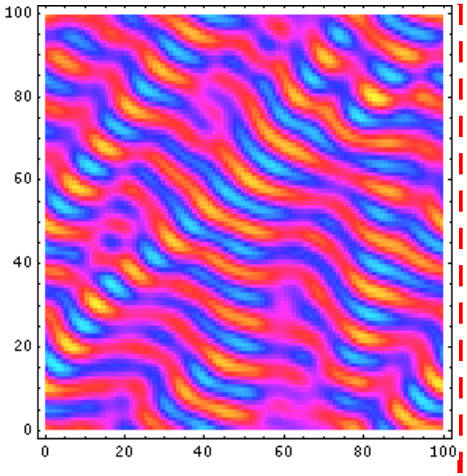
☞ Observed close to bifurcation point; requires $\varphi(x, y) << 1$

# Interacting Wave and Turing Patterns: A Memory of Initial Fluctuation

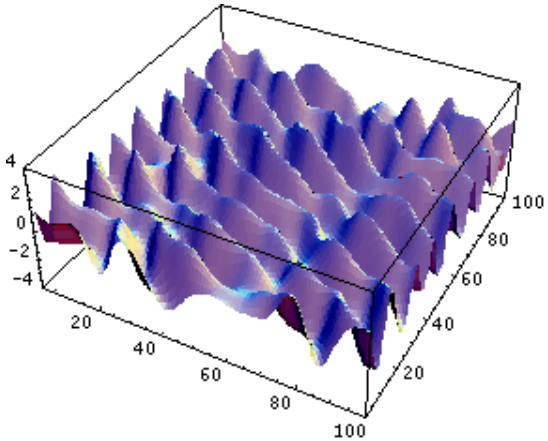
## ❑ Large initial fluctuation in $\varphi$

$\xi = 4.8; \Gamma = 0.13$

$\varphi(x, y)$




$h(x, y)$

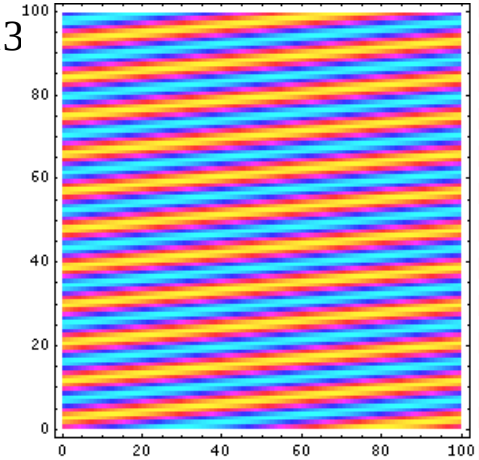



☞Dynamic structure

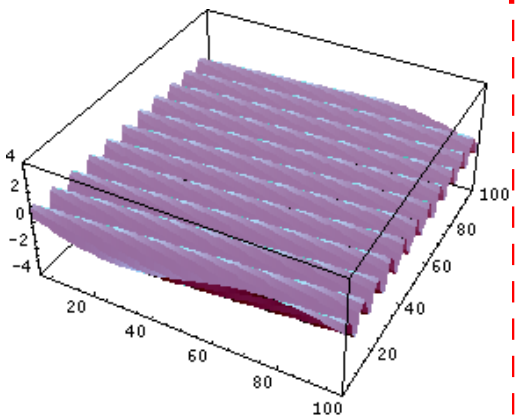
## ❑ Small initial fluctuation in $\varphi$

$\xi = 4.8; \Gamma = 0.13$

$\varphi(x, y)$

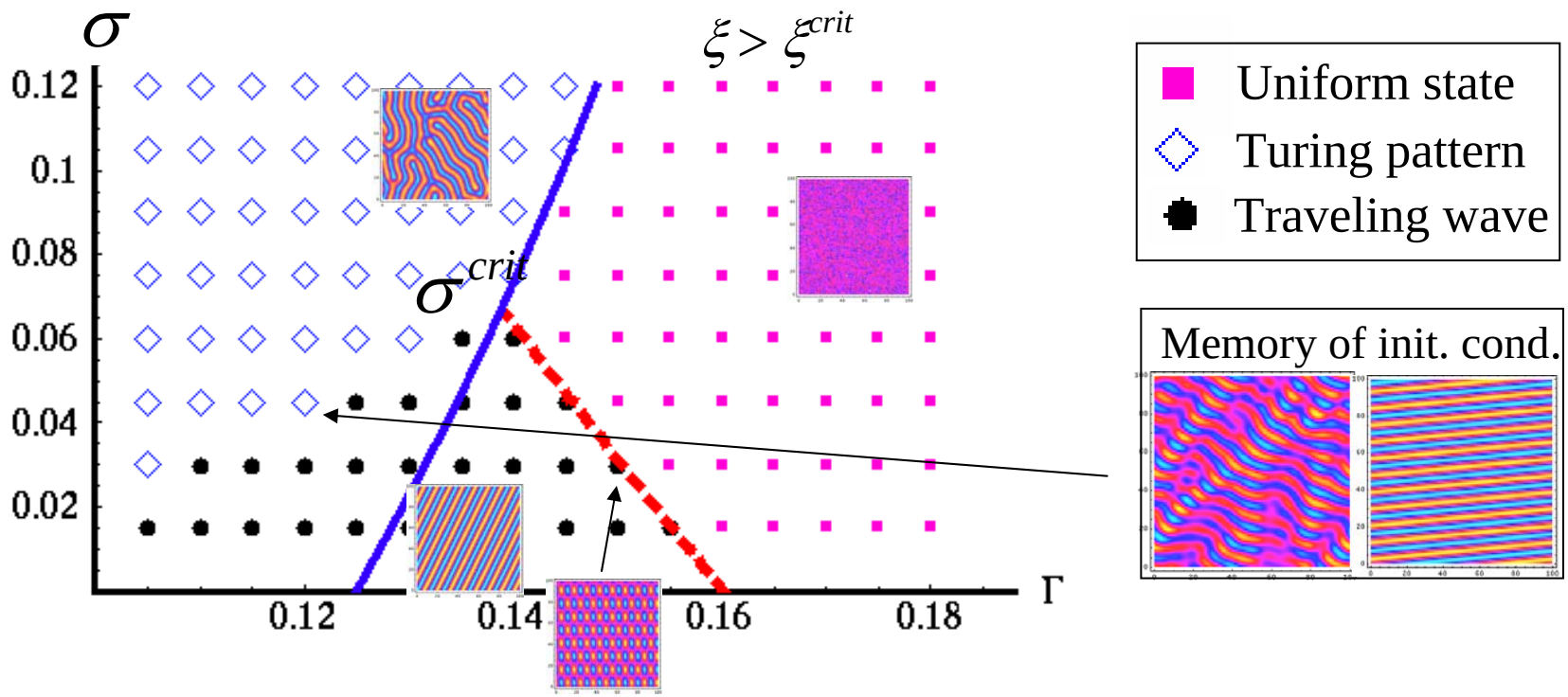



$h(x, y)$




☞ Stationary structure

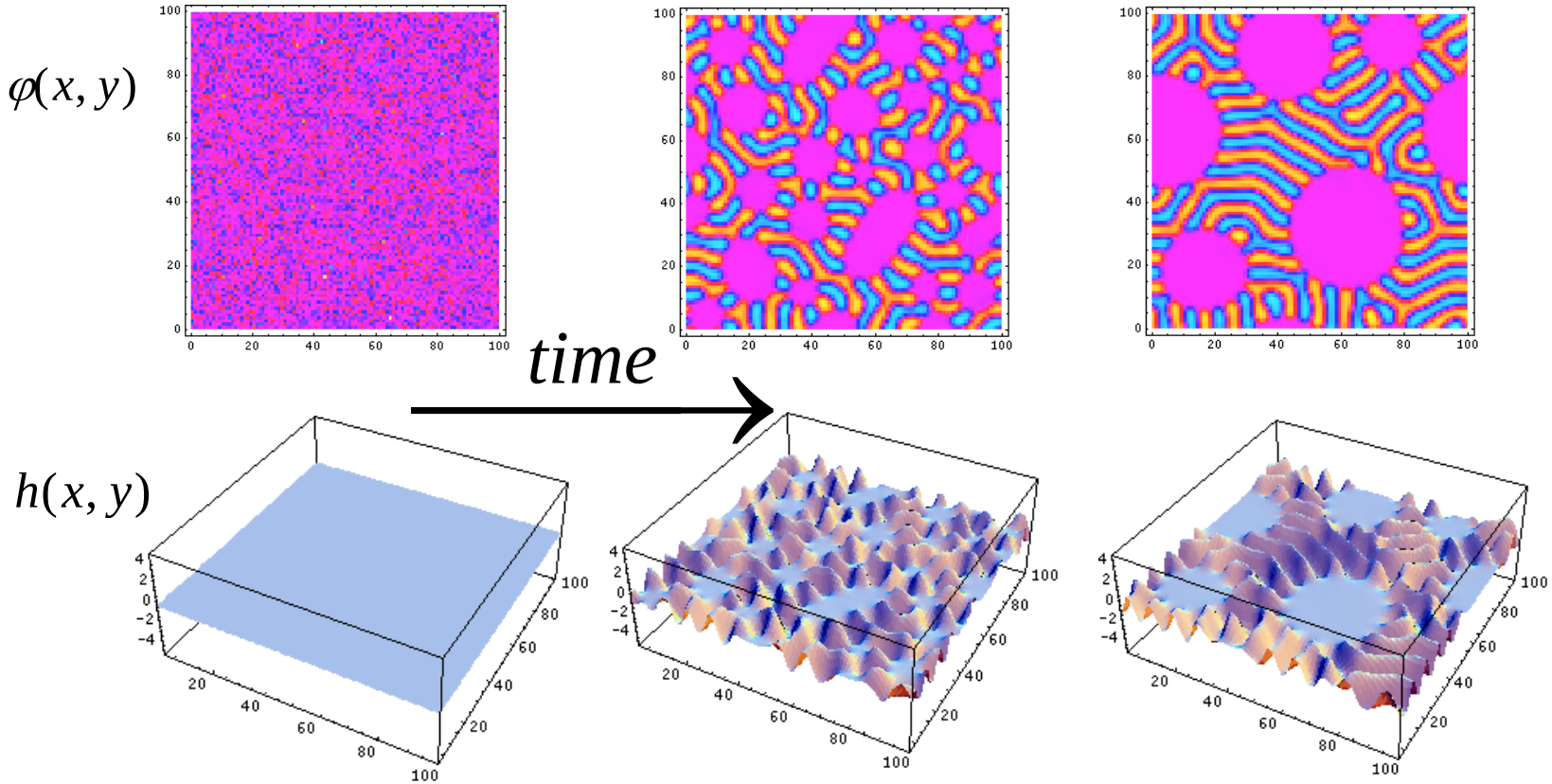
## Phase Diagram in $(\Gamma, \sigma)$




- Behavior strongly depends on surface tension
  - Increasing bending elasticity $\kappa$ decreases $\sigma^{crit}$

- **Traveling waves occur in flexible (low $\kappa$ ) reactive membrane, if:**
  - Lateral surface tension is low: $\sigma \leq \sigma^{crit}$
  - Strong coupling between reaction and change in height: $\xi \geq \xi^{crit}$

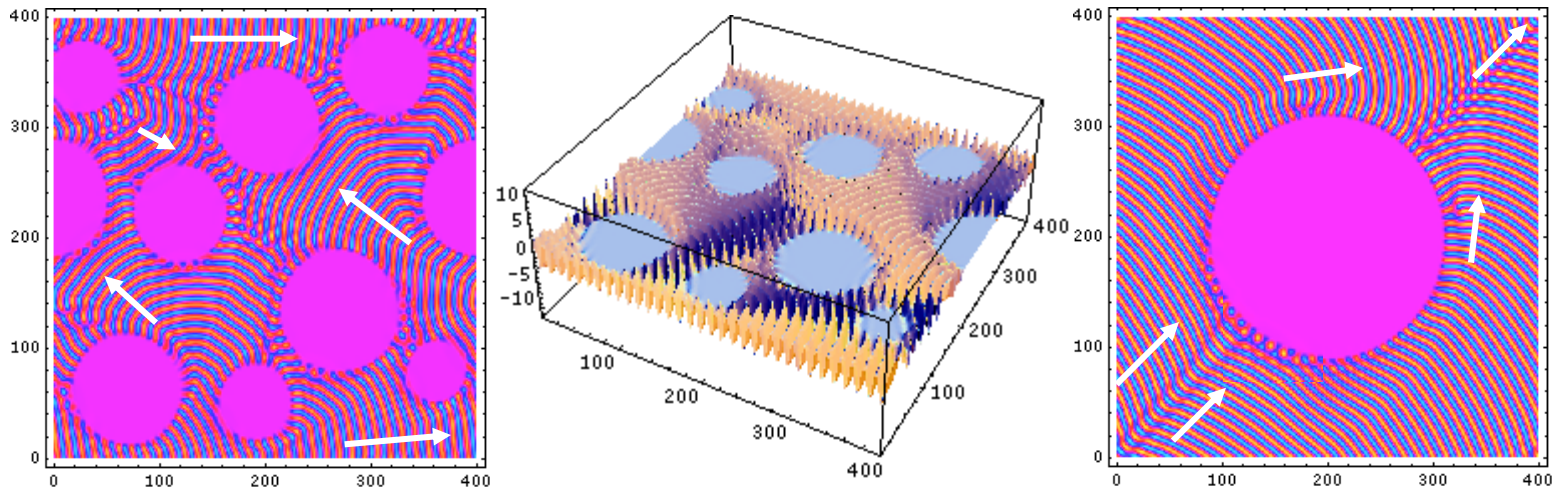
# Evolution in Ternary Membranes




- *A*, *B* and *C* phase separate & local height depends on composition
- Morphology and topology within *AB* domain as in binary case, but:
  - *AB* lamellae orient perpendicularly to C domains

# Evolution in Ternary Membranes: Waves

- ***A*, *B* and *C* phase separate; traveling waves within *AB* domains**
  - Intermediate times
  - Late times

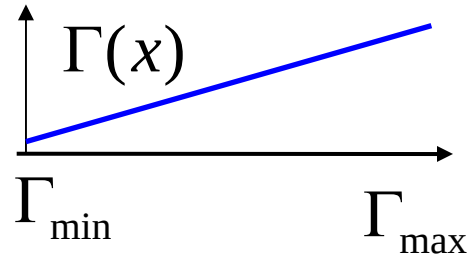



  - Waves confined between *C* domains
    - Prevents appearance of coherent traveling pattern (as in *AB* case)

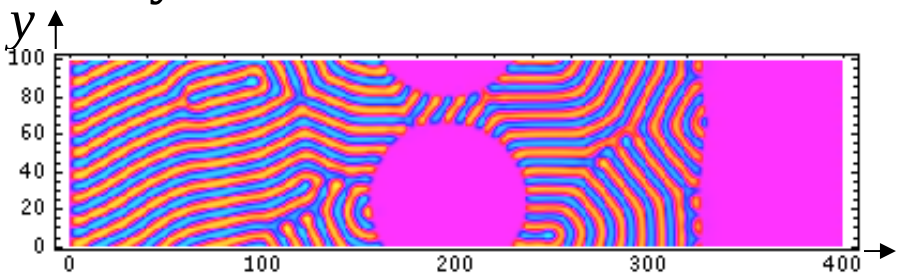
- **Non-reactive *C* component strongly affects membrane's behavior**
  - Rich dynamic behavior & opportunities for dynamic control

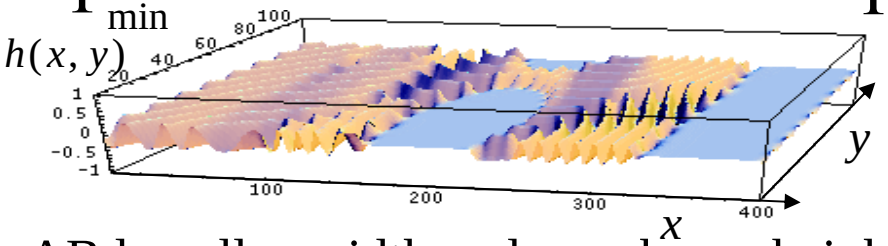
# Evolution of Ternary Membrane in Gradient Fields

- **Externally controlled reaction rate coefficient:**



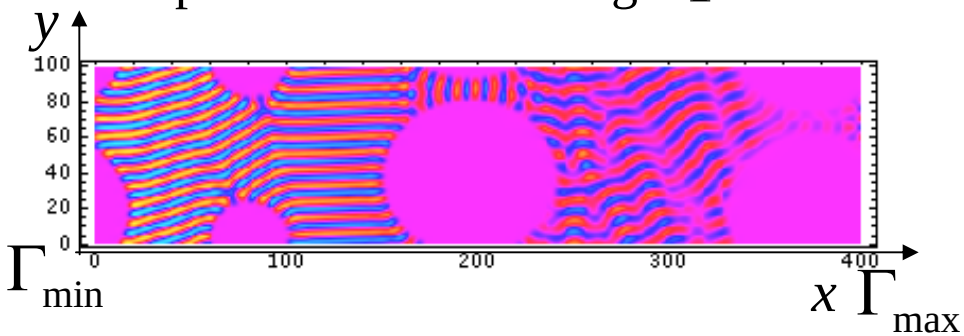

$\xi = 0$




- ☞ AB lamellae width and membrane height decrease with increase in $\Gamma$
- ☞ C component diffuses to high $\Gamma$ : controlled transport along membrane

$\xi = 5$




- **"Gradient sensing": Patterns critically depend on external gradient**

# Conclusions

- **Developed model for three-component reactive flexible membrane**
  - Externally controlled reaction (light, chemical flux)
    - Composition & topology can be altered dynamically
  - Non-reactive *C* component strongly affects membrane's dynamics
  - Rich dynamical behavior
    - Perform gradient sensing