Multi-Component Reactive Membranes: A Computer Simulation Study

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Introduction

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

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

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

- **Three components (A,B,C)**
  - Local composition \( \varphi(x, y) = \rho_A - \rho_B, \quad \psi(x, y) = \rho_C; \sum \rho_i = 1. \)

- **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

\[
\begin{aligned}
 f_{\text{local}}(\varphi, \psi) + \frac{\gamma_\varphi}{2} (\nabla \varphi)^2 + \frac{\gamma_\psi}{2} (\nabla \psi)^2 \\
\frac{\sigma}{2} (\nabla h)^2 + \frac{\kappa}{2} \left( \nabla^2 h - H_{eq}(\varphi) \right)^2
\end{aligned}
\]

- \( \kappa \) 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

\[
\frac{\partial \phi}{\partial t} = M_\phi \nabla^2 \frac{\delta F}{\delta \phi} - \Gamma \phi
\]

- Evolution of AB composition

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

- Evolution of C

\[
\frac{\partial h}{\partial t} = -M_h \frac{\delta F}{\delta h} + \Gamma \phi \xi
\]

- Evolution of height

- \( M_i \) is mobility of i-th order parameter; \( \Gamma_+ \equiv \Gamma_- \equiv \frac{1}{2} \Gamma \)

- Reactive term \( \Gamma \phi \xi \) 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:**
  \[
  \frac{\partial \varphi}{\partial t} = M_\varphi \nabla^2 \left[ \frac{\partial f_{\text{local}}(\varphi, \psi)}{\partial \varphi} - \gamma_\varphi \nabla^2 \varphi + \kappa H_0^2 \varphi - \kappa H_0 \nabla^2 h \right] - \Gamma \varphi
  \]
  \[
  \frac{\partial h}{\partial t} = M_h \nabla^2 \left[ \sigma h + \kappa \varphi H_0 - \kappa \nabla^2 h \right] + \Gamma \varphi \xi
  \]

- **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** \( w(q) = \frac{1}{2} \left[ \text{Tr}[L] \pm \sqrt{\text{Tr}[L]^2 - 4 \text{det}[L]} \right] \)
Linear Stability Analysis in Binary Case: Possible Scenarios

- Uniform state is stable
  - \( \text{Re}[w(q)] < 0 \) at any \( q \)

- Turing-like pattern
  - \( \text{Re}[w(q)] > 0 \) & \( \text{Im}[w(q)] = 0 \) at \( q \neq 0 \)

- Traveling waves
  - \( \text{Re}[w(q)] > 0 \) & \( \text{Im}[w(q)] \neq 0 \) 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**
  \[
  \Gamma \geq \Gamma_1^{\text{crit}} \equiv \frac{M_\phi}{4} \left( -2a_{20} + H_0^2 \kappa + \frac{M_H}{M_\phi} \sigma \right)^2
  \]
  - Increase in spontaneous curvature, \( H_0 \), increases \( \Gamma_1^{\text{crit}} \).
  - Increase in film’s interfacial tension, \( \sigma \), increases \( \Gamma_1^{\text{crit}} \).
  - Increase in AB interfacial tension, \( \gamma_\phi \), decreases \( \Gamma_1^{\text{crit}} \).

- **Turing-like patterns if**
  \( \Gamma_2^{\text{crit}} \leq \Gamma < \Gamma_1^{\text{crit}} \).
  - Increase in \( H_0 \) or \( \xi \) decreases \( \Gamma_2^{\text{crit}} \).
Late Time Morphology in AB Blends: Possible Scenarios

- **Uniform mixed state**
  \[ \varphi(x, y) \]

- **Turing patterns**
  \[ \varphi(x, y) \]

- Uniform state is stable at high \( \Gamma \)

- 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; \( \phi(x, y) \ll 1 \ (\xi = 8; \Gamma = 0.143) \)

\( \phi(x, y) \quad \text{\&} \quad h(x, y) \)

- 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 \( \varphi(x, y) \ll 1 \)
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
Behavior strongly depends on surface tension
- Increasing bending elasticity $\kappa$ decreases $\sigma^{\text{crit}}$

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

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

- “Gradient sensing”: Patterns critically depend on external gradient

\[ \xi = 0 \]

\[ \xi = 5 \]
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