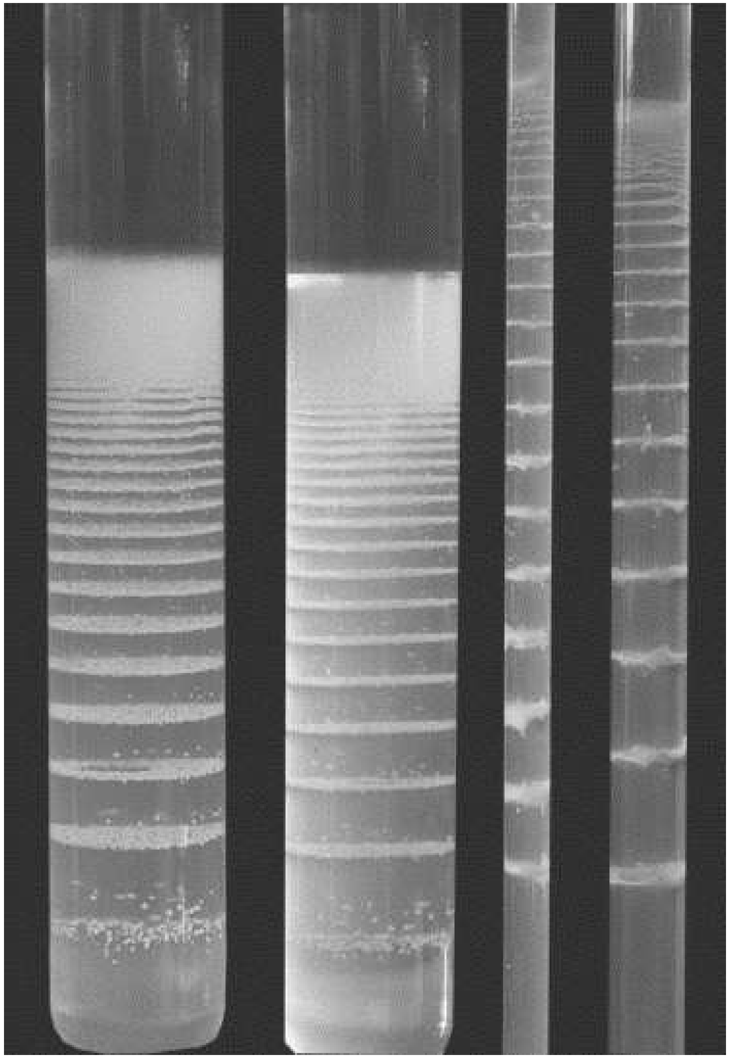
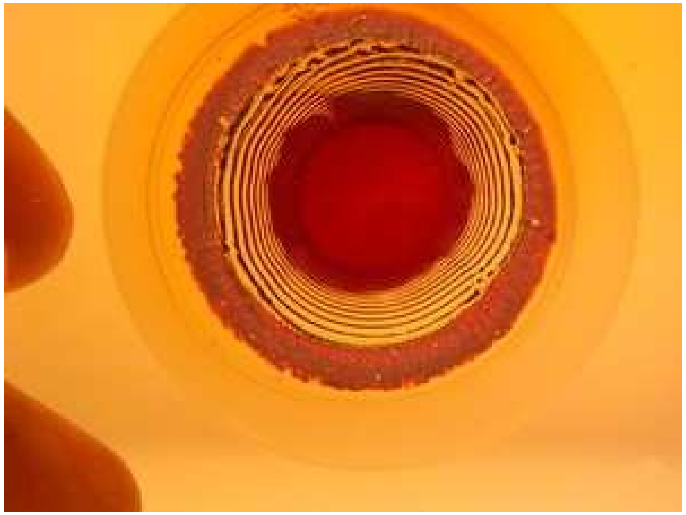
Liesegang Patterns
Phenomena and Models

Samantha Mesuro

Liesegang Patterns



[George & Varghese, J.Coll.Int.Sci]



Characteristic Laws

Space Law:

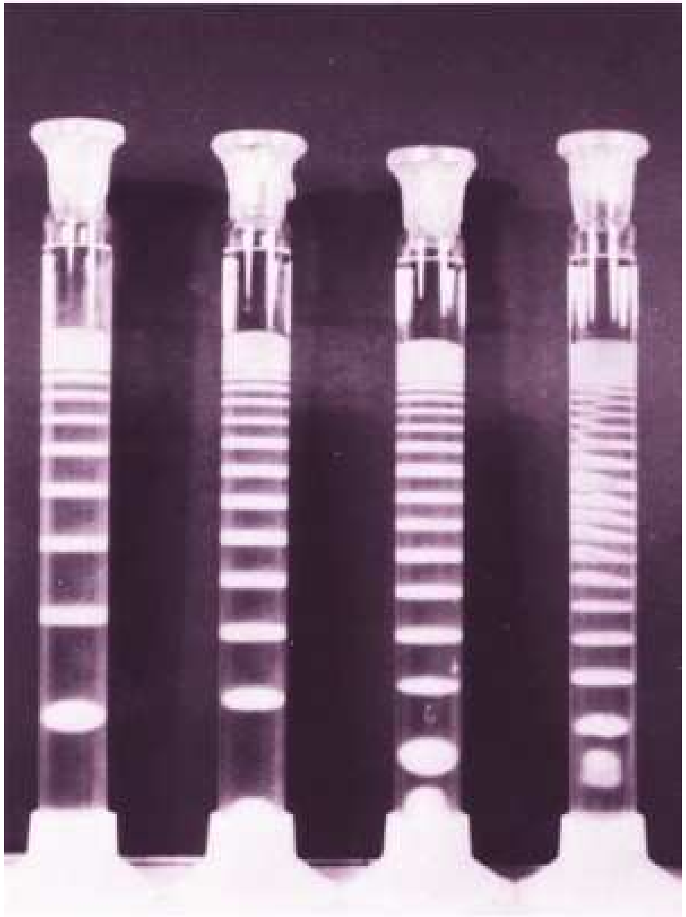
$$\frac{x_n}{x_{n-1}} \rightarrow 1 + p$$

Time Law:

$$x_n \sim \sqrt{t_n}$$

Width Law:

$$w_n \sim x_n^{\alpha}$$



Keller-Rubinow Model

$$\nu_a A + \nu_b B \Leftrightarrow \nu_c C$$
$$C \Rightarrow E$$

$$a_t = d_a a_{xx} - \nu_a r$$
$$b_t = d_b b_{xx} - \nu_b r$$
$$c_t = d_c c_{xx} + \nu_c r - p$$
$$e_t = p$$

$$Boundary\ Conditions:$$
$$a(0,t) = a_0 \quad b_x(0,t) = 0$$
$$c_x(0,t) = 0 \quad e_x(0,t) = 0$$

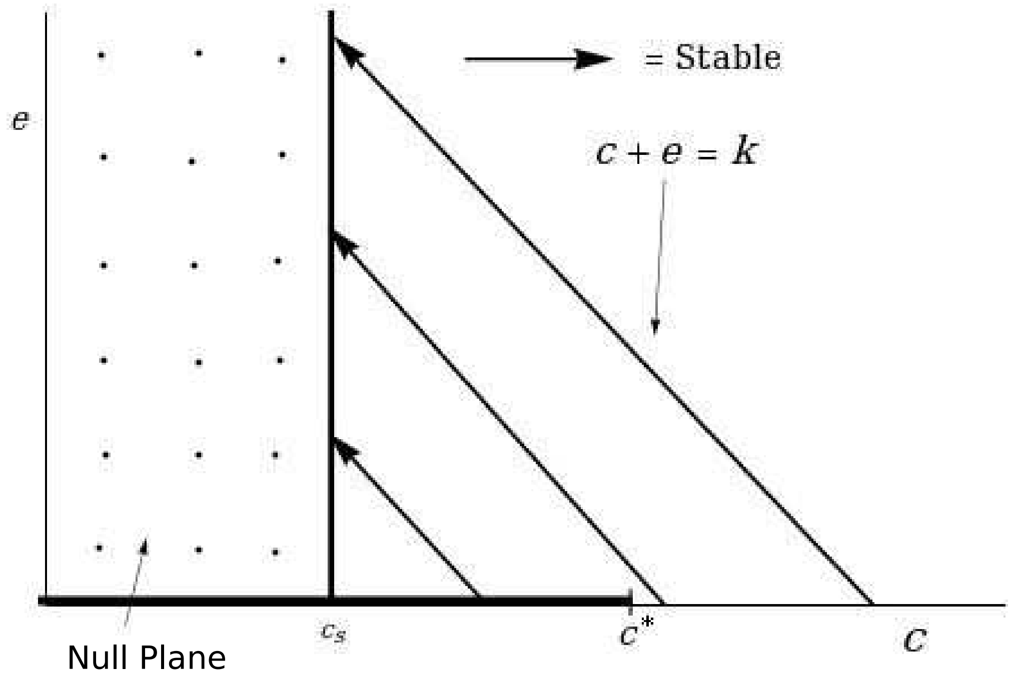
where r is the mass action term:

$$r = k_1 a^{\nu_a} b^{\nu_b} - k_2 c^{\nu_c}$$

and p is the precipitation kinetics:

$$p(c,e) = 0 \qquad if\ c < c* \quad \& \quad e = 0$$
$$p(c,e) = q(c - c^s)_{pos} \quad if\ c \geqslant c* \quad \vee \quad e > 0$$

Keller-Rubinow Model



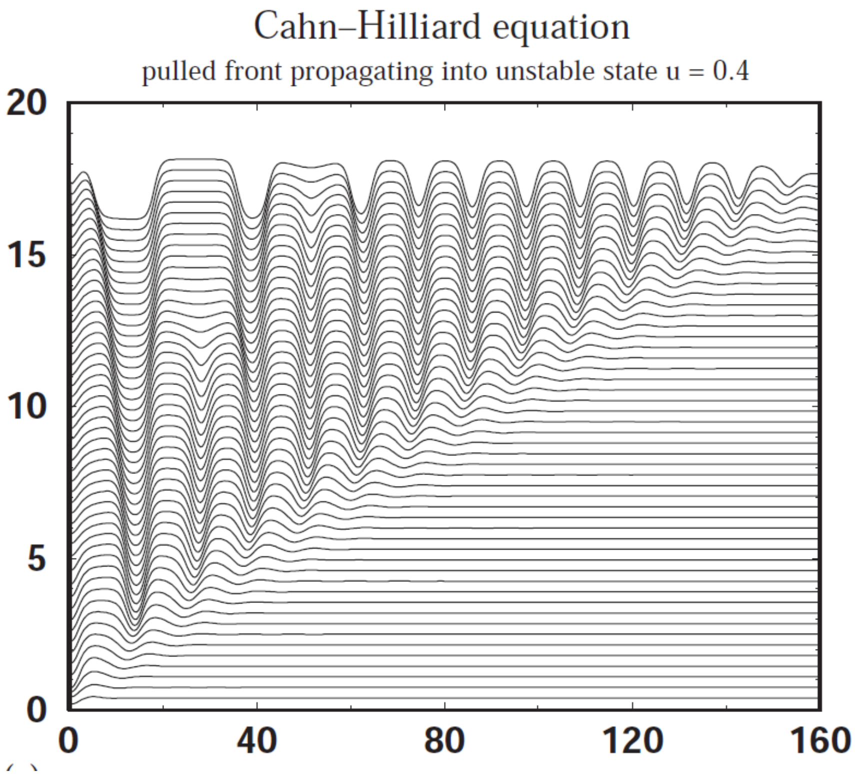
Advantages:
- Threshold kinetics
- Simple
- Nearly explicitly solvable

Disadvantages:
- Over-simplified?
- Discontinuous, no smooth analysis
- No width law

Cahn-Hilliard Model

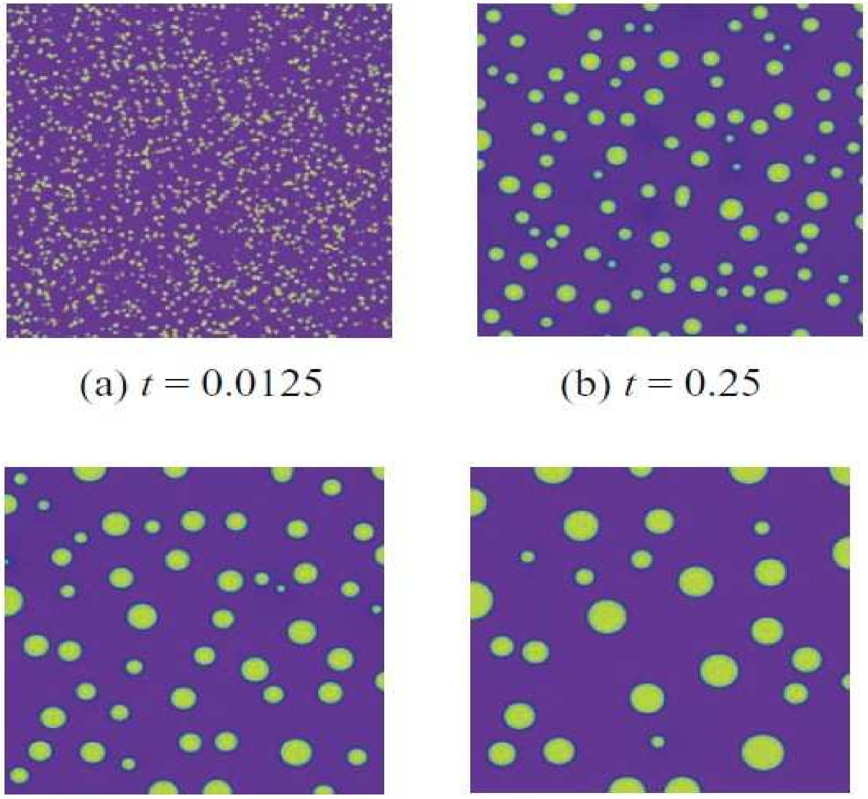
$$a_t = d_a a_{xx} - ab$$
$$b_t = d_b b_{xx} - ab$$
$$u_t = -d\,\partial_{xx}(\partial_{xx} u + u - u^3)$$

Spinodal Decomposition



[Van Saarloos, Phys.Rep.]

Ostwald Ripening



(a) $t = 0.0125$ (b) $t = 0.25$ (c) $t = 2.25$ (d) $t = 6.7$

[Garcke, et al, Acta Materialia]

Our Modeling Approach

$$a_t = d_a a_{xx} - ab$$
$$b_t = d_b b_{xx} - ab$$
$$c_t = d_c c_{xx} + ab - f(c,e)$$
$$e_t = d_e e_{xx} + f(c,e)$$

Boundary Conditions:

$$a(0,t) = a_0 \quad a_x(L,t) = 0 \quad b_x(0,t) = b_x(L,t) = 0$$
$$c_x(0,t) = c_x(L,t) = 0 \quad e_x(0,t) = e_x(L,t) = 0$$

We want:

- f(c,e) smooth conversion rate
- Threshold kinetics
- c+e=k conserved when ab=0
- f(c,e)=0 spatially homogenous equilibrium

PDE Stability/Instability

Considering isolated C-E reaction:

$$c_t = d_c c_{xx} - f(c, e)$$
$$e_t = d_e e_{xx} + f(c, e)$$

Linearization:

$$\begin{pmatrix} \dot{c}_k \\ \dot{e}_k \end{pmatrix} = \begin{pmatrix} -f_c - k^2 & -f_e \\ f_c & f_e - d_e k^2 \end{pmatrix} \begin{pmatrix} c_k \\ e_k \end{pmatrix}$$

Eigenvalues:

k=0

$$\lambda_1 = 0 \qquad \lambda_2 = f_e - f_c$$

k>0

$$\lambda_1 = -Dk^2 + O(k^4) \qquad \lambda_2 = f_e - f_c + O(k^2) \qquad D = \frac{f_e - d_e f_c}{f_e - f_c}$$

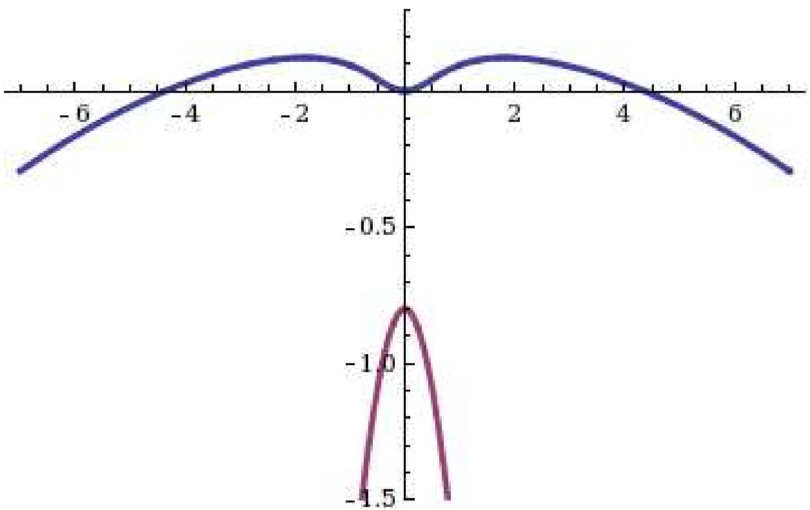
Two Types of Instability

Stability:

$$f_e - f_c < 0 \quad AND \quad D > 0 \quad \rightarrow \quad f_e - d_e f_c < 0$$

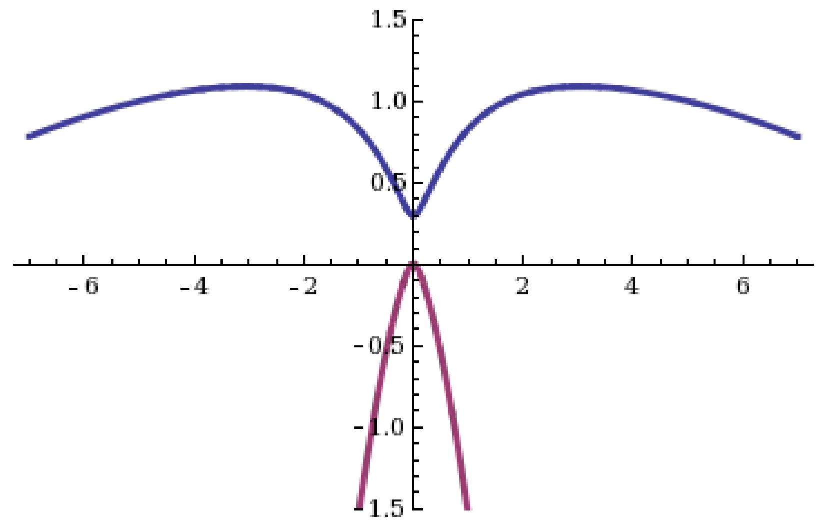
Spinodal Instability:

$$f_e - f_c < 0 \quad AND \quad D < 0 \quad \rightarrow \quad f_e - d_e f_c > 0$$



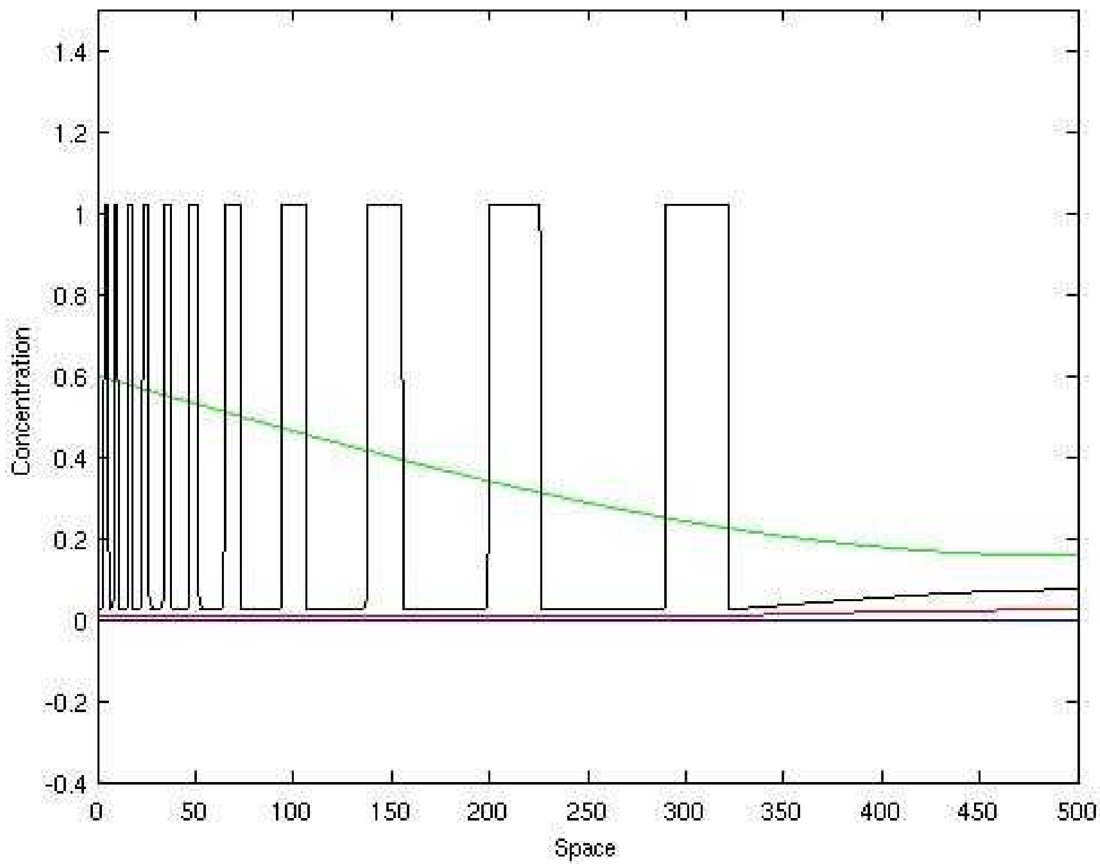
Homogenous Instability:

$$f_e - f_c > 0 \quad AND \quad D > 0 \quad \rightarrow \quad f_e - d_e f_c > 0$$



Our First Successful Model

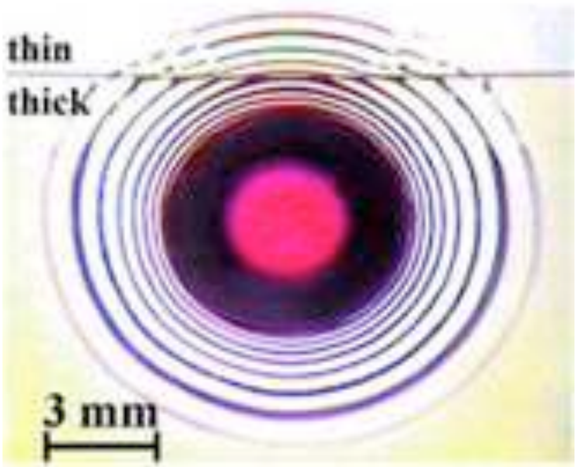
$$f(c,e)=c+\delta e(1-e)(e-\alpha)$$



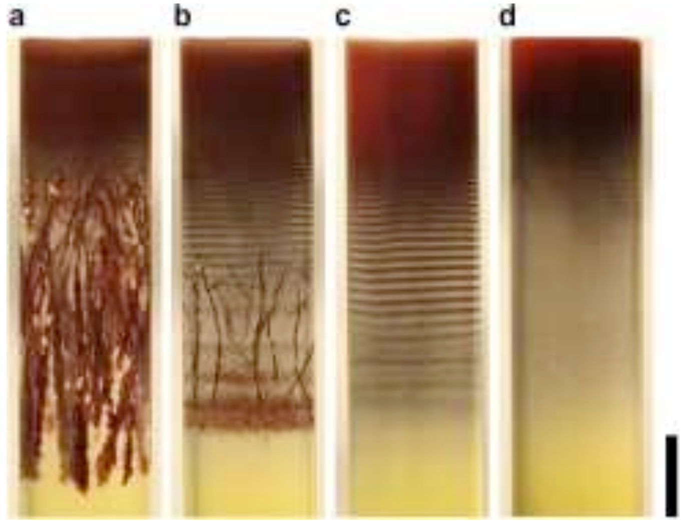
Liesegang Patterns:

Phase-Field Dynamics

Ryan Goh



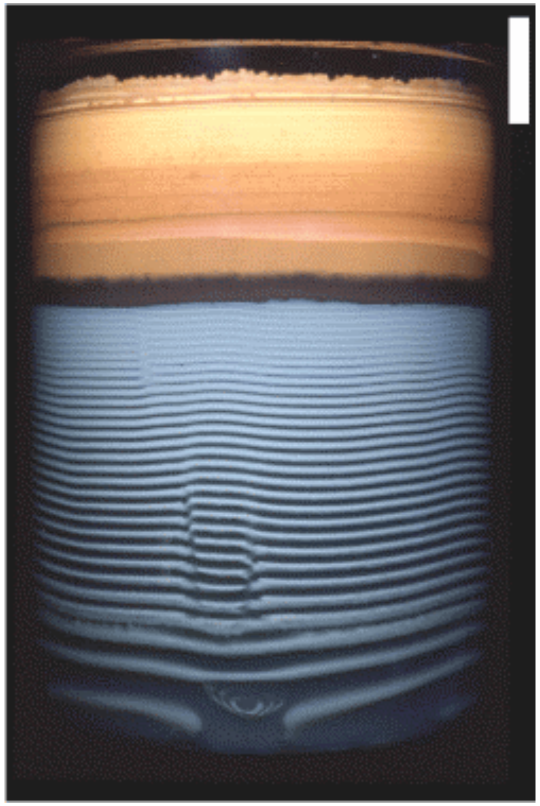
(FialKowski,Bitner,Grzybowski 2005)



(Lagzi,Ueyama 2008)

Our General Model

$$A + B \rightarrow C \leftrightarrow E$$



(Stone,Goldstein 2004)

$$a_t = d_a a_{xx} - ab$$

$$b_t = d_b b_{xx} - ab$$

$$c_t = d_c c_{xx} + ab - f(c,e)$$

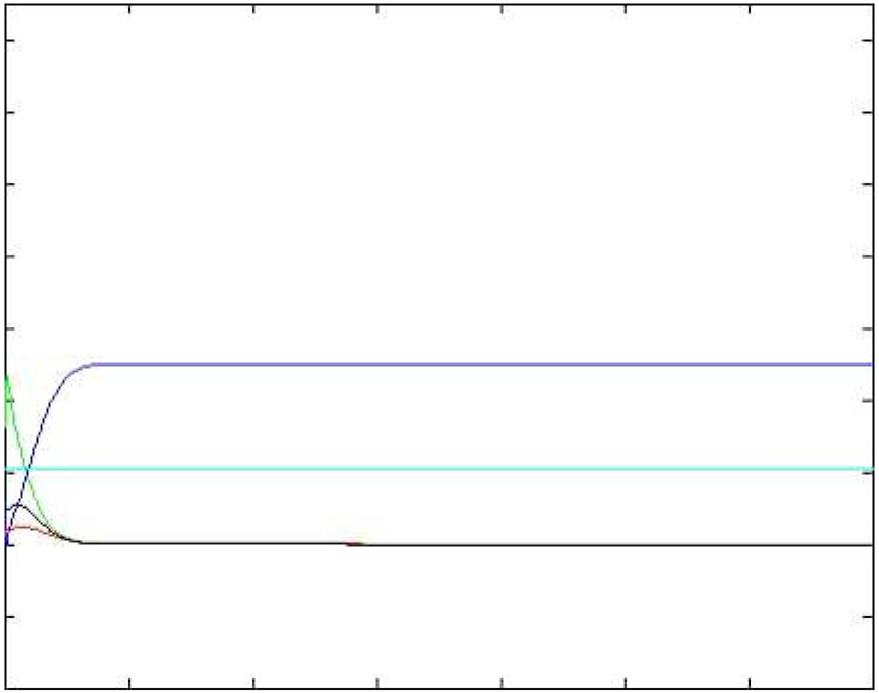
$$e_t = d_e e_{xx} + f(c,e)$$

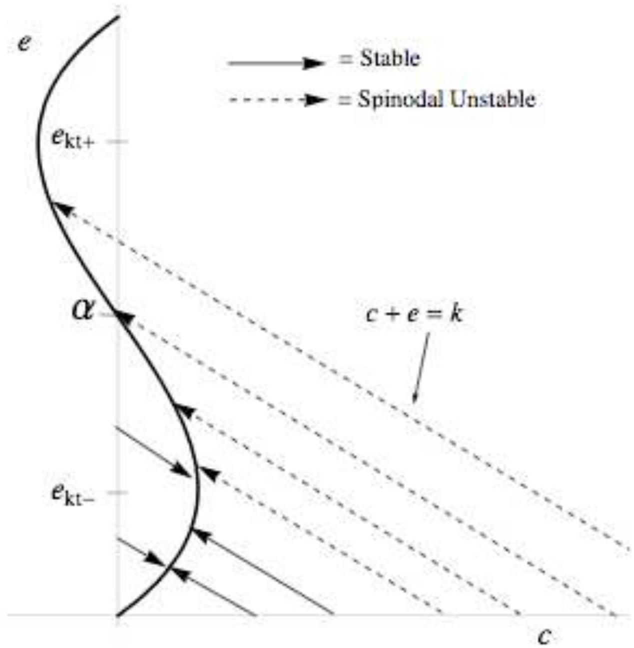
Simple Cubic: Spinodal Regime

$$f(c,e) = \gamma c + \delta g(e) = \gamma c + \delta e(1-e)(e-\alpha)$$

- Conditions: $\gamma = 1,\ \alpha = 0.5 \Rightarrow \delta < 4$

- Phase Portrait of ODE dynamics:





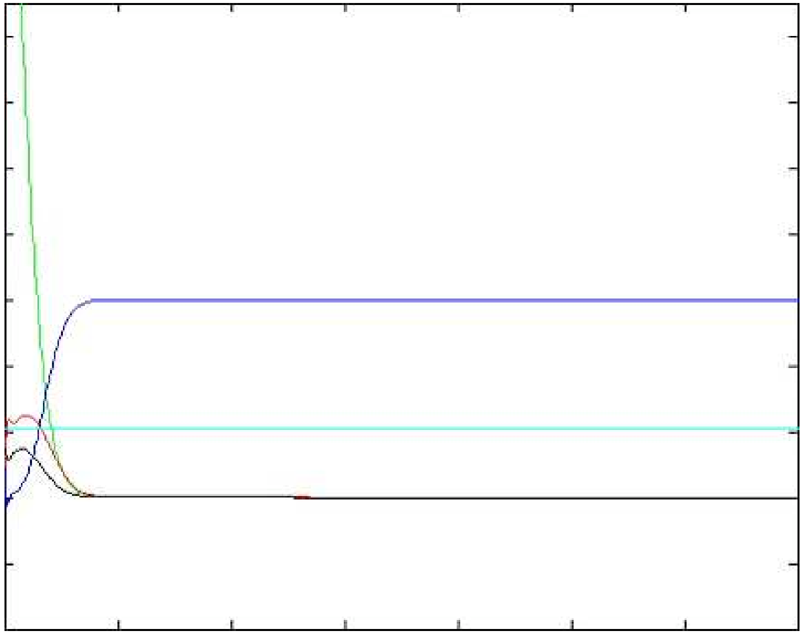
$$g'(e_{kt-}) = g'(e_{kt+}) = 0$$

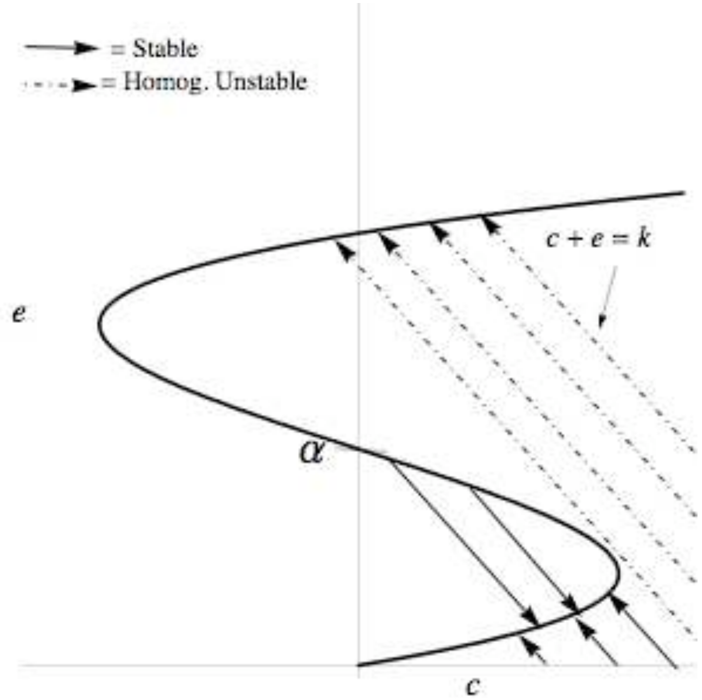
For: $e_{kt-} < e < e_{kt+} \Rightarrow g'(e) < 0$

Simple Cubic: Homogeneous (Bistable)

$$f(c,e) = \gamma c + \delta g(e) = \gamma c + \delta e(1-e)(e-\alpha)$$

- Conditions: $\gamma = 1,\ \alpha = 0.5 \Rightarrow \delta > 4$
- Phase Portrait of ODE dynamics:





Phase-Field Analogy

C,E-Dynamics:

$$c_t = d_c c_{xx} - f(c,e)$$

$$e_t = d_e e_{xx} + f(c,e)$$

Scalings:

$\theta = c + e$

$\hat{e} = e/\rho$

$\hat{\theta} = \dfrac{\theta}{\tau}$

$\tau = \dfrac{\delta}{\gamma}$

$\sigma = (\rho\delta)^{-1}$

$\hat{d} = \sigma d$

$l = \dfrac{(1-d)}{\rho\tau}$

$$\Downarrow$$

$$\theta_t + (1-d)e_t = \theta_{xx}$$

$$e_t = de_{xx} + \delta g + \gamma(\theta - de)$$

$$\Downarrow$$

$$\hat{\theta}_t + \frac{(1-d)}{\rho\tau} e_t = \hat{\theta}_{xx}$$

$$e_t = de_{xx} + \rho\delta g + \rho\gamma(\tau\hat{\theta} - de)$$

$$\Downarrow$$

Phase Field:

$$\hat{\theta}_t + le_t = \hat{\theta}_{xx}$$

$$\sigma e_t = \hat{d}e_{xx} + \rho\delta g + \rho\gamma(\tau\hat{\theta} - de)$$

Existing Models as Limits:

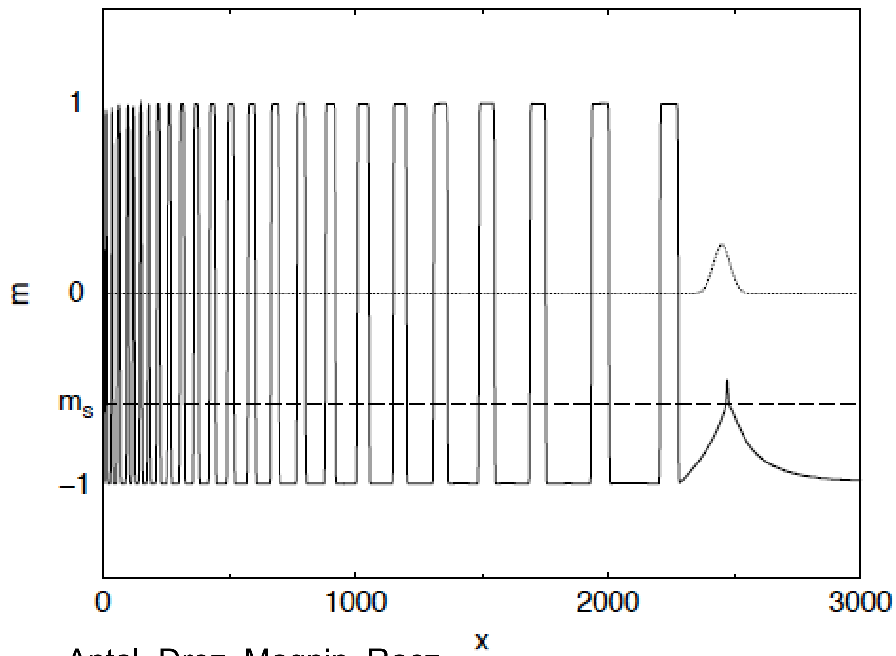
Cahn Hilliard (spinodal decomp.):

$$l \to \infty \quad (\delta \to 0) \qquad e_t = \hat{\theta}_{xx}$$

$$\hat{\theta} = (\hat{d}e_{xx} + \rho\delta g + -de)(\rho\gamma\tau)^{-1}$$

$$\Downarrow$$

$$e_t = (\rho\gamma\tau)^{-1}(\hat{d}e_{xx} + \rho\delta g - de)_{xx}$$

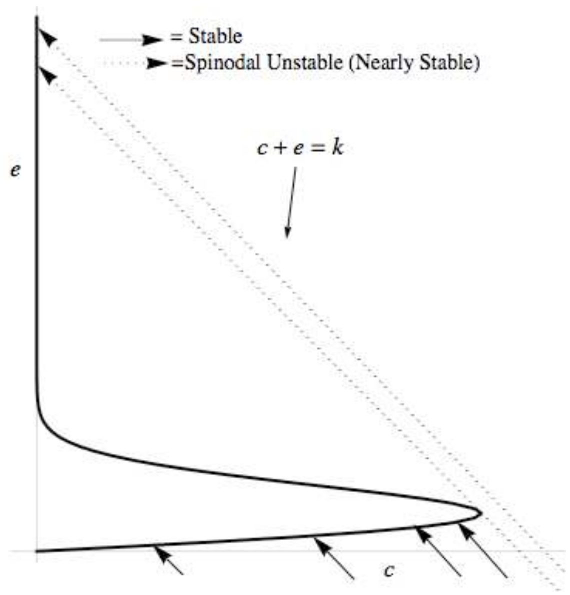


Antal, Droz, Magnin, Racz

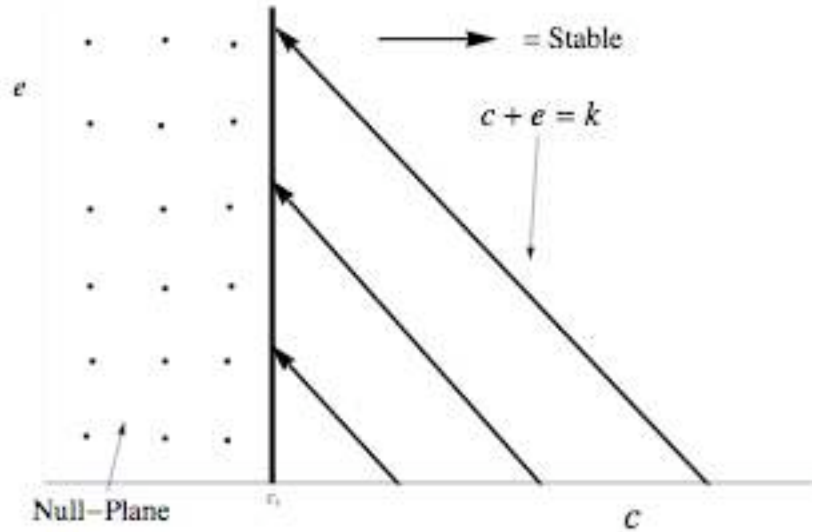
Existing Models as Limits

$$f(c,e) = \gamma c + g(e) = c - \frac{e}{\sqrt{\alpha}} Exp(-e^2 / \alpha)$$

$d \to 0, \quad \alpha \to 0 \Rightarrow$ Keller Model (bistable): $f(c,e) = c\,H(c - c_s)$



$\Rightarrow$

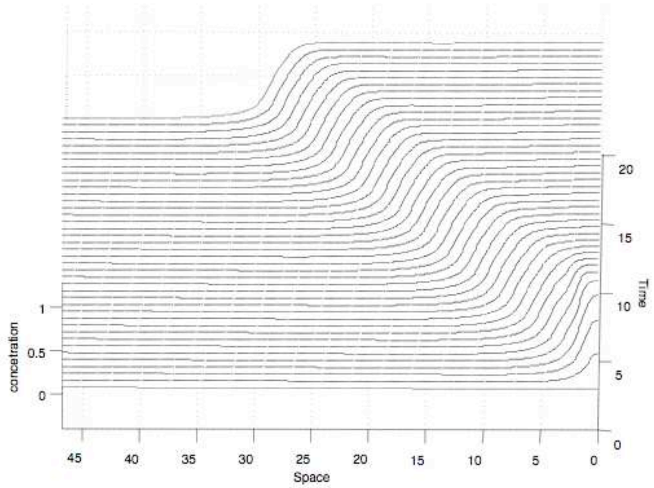


Difference Between Bistable and Spinodal

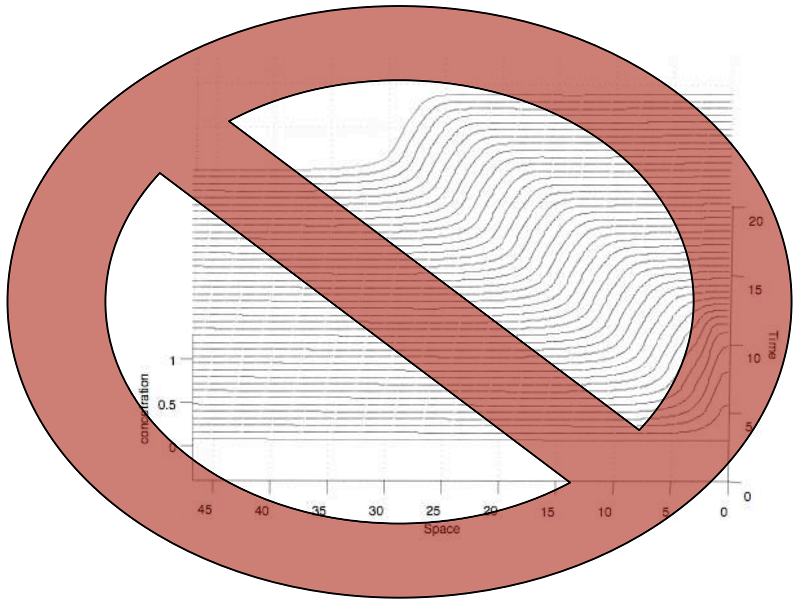
Triggered Fronts: $c_t = c_{xx} - f + A\,\delta(x - s\,t)$

$e_t = de_{xx} + f$

Spinodal



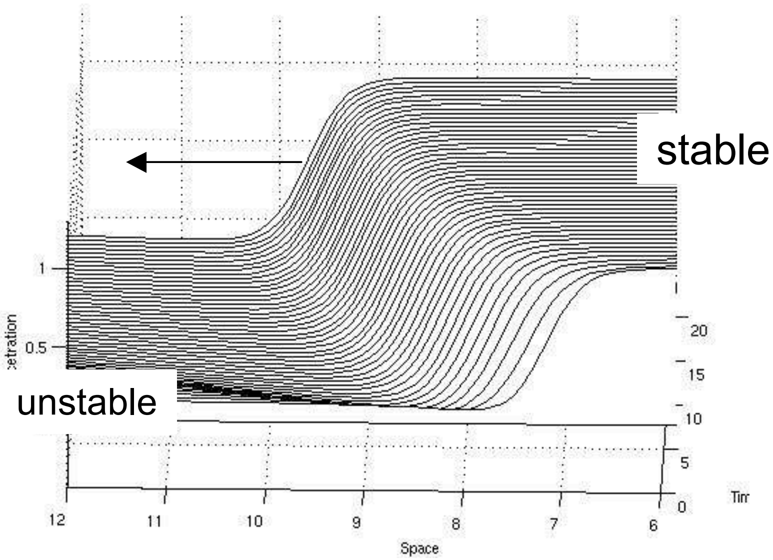
Bistable (Homogeneoous)



Difference Between Bistable and Spinodal:

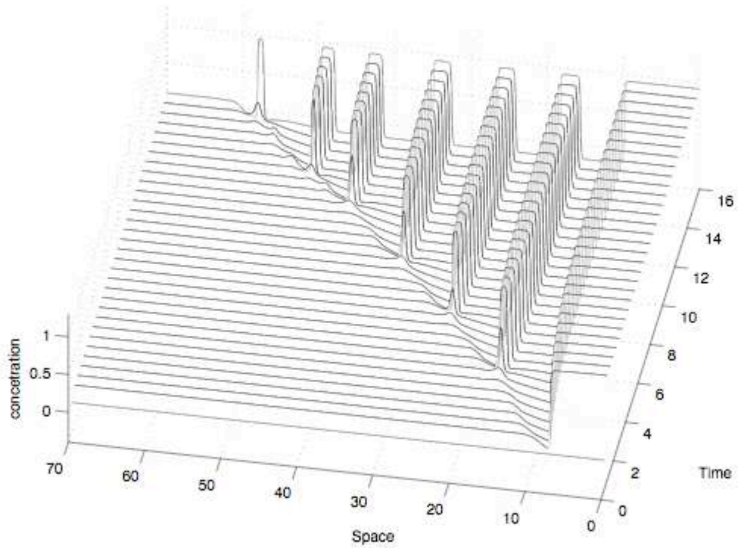
Pushed and Pulled Fronts

- <u>Pushed</u>



Bistable

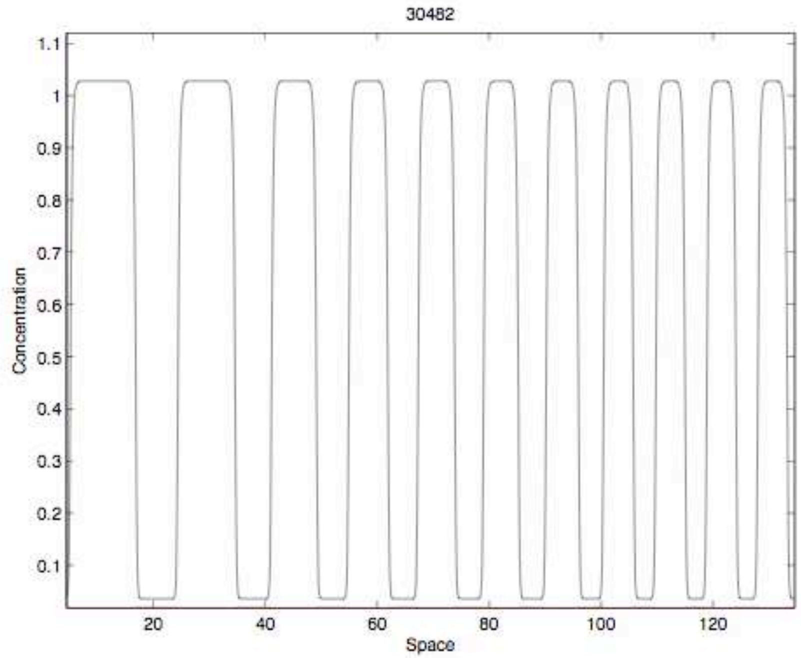
- <u>Pulled</u>

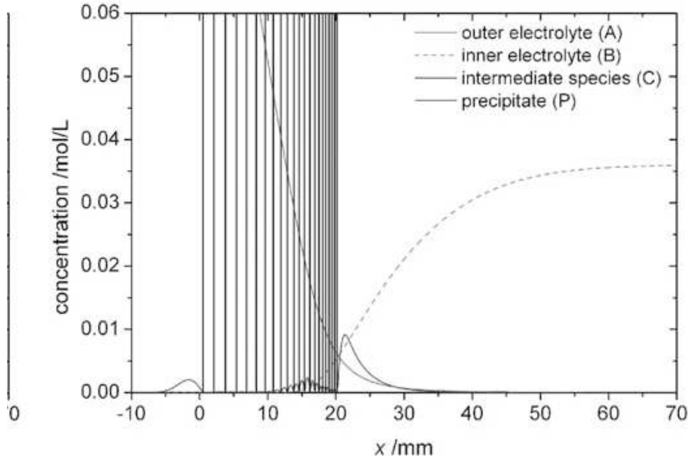


Bistable & Spinodal

Revert Patterns

- Wavelength determined by f_e
- f_e determined by e
- e determined by initial concentrations
- Only occurs in spinodal regime





Molná, Izsák, Lagz, (2008)i