Fronts

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Patterns from moving fronts

(1) Importance of moving fronts: Patterns are manufactured in them.

Examples: Crystal growth, DLA, reaction fronts.
Dynamics of interfaces separating phases of different stability.
Classification of fronts: pushed and pulled.

(2) Invasion of an unstable state.

Velocity selection.
    Example: Population dynamics.
    Stationary point analysis of the Fisher-Kolmogorov equation.
Wavelength selection.
    Example: Cahn-Hilliard equation and coarsening waves.

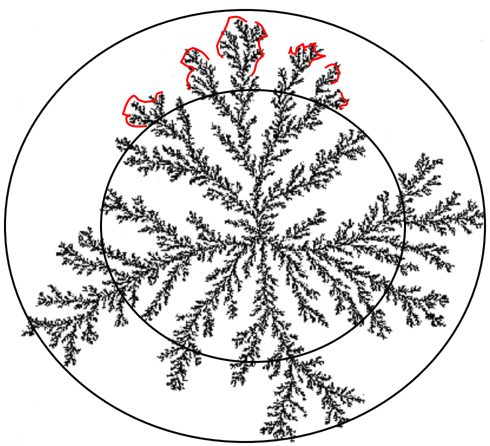
(3) Diffusive fronts.

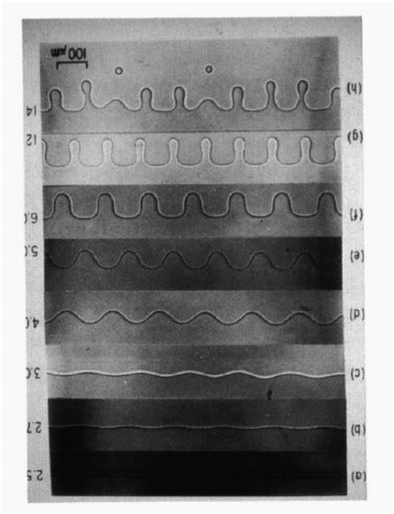
Liesegang phenomena (precipitation patterns in the wake of diffusive reaction fronts - a problem of distinguishing the general and particular).

Literature

W. van Saarloos, **Front propagation into unstable state,** Physics Reports, 386 29-222 (2003)
M. C. Cross and P. C. Hohenberg, **Pattern Formation Outside of Equilibrium**, Rev. Mod. Phys. 65, 851 (1993).

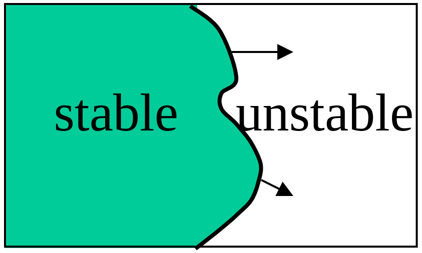
Fronts separating stable and unstable phases





crystallization fronts
chemical reaction fronts

The problems:



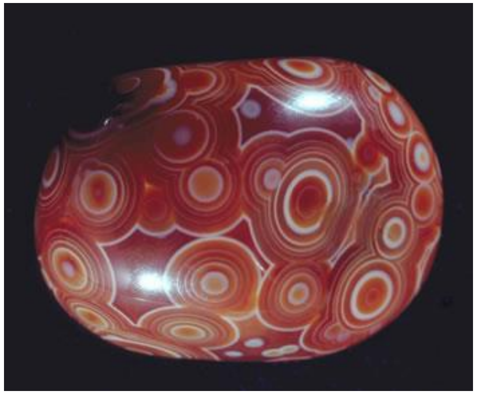
(1) What is the speed of the front?

(2) Is there any nontrivial structure
in the wake of the front?

Liesegang phenomena

Naturwiss. Wochenschrift
11, 353 (1896)

Nontrivial patterns
in d=1-3 dimensions

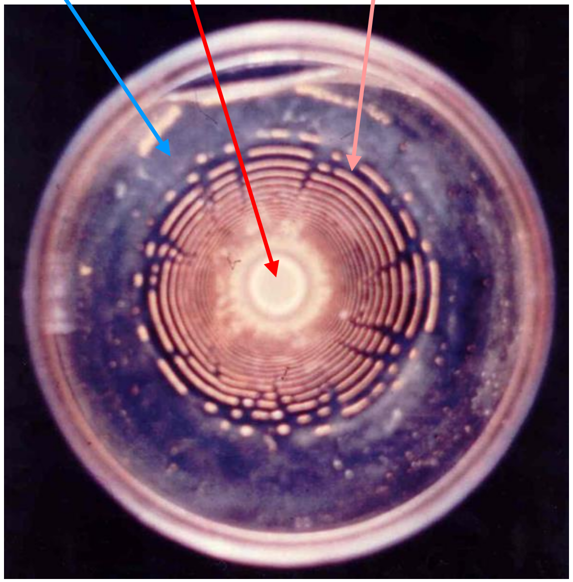


agates

A random experiment

$$\boxed{MgCl_2} + 2\cdot\boxed{NH_4OH} \rightarrow \underline{Mg(OH)_2} + 2\cdot NH_4Cl$$

precipitate



d=2

Zrínyi, 95

A

C

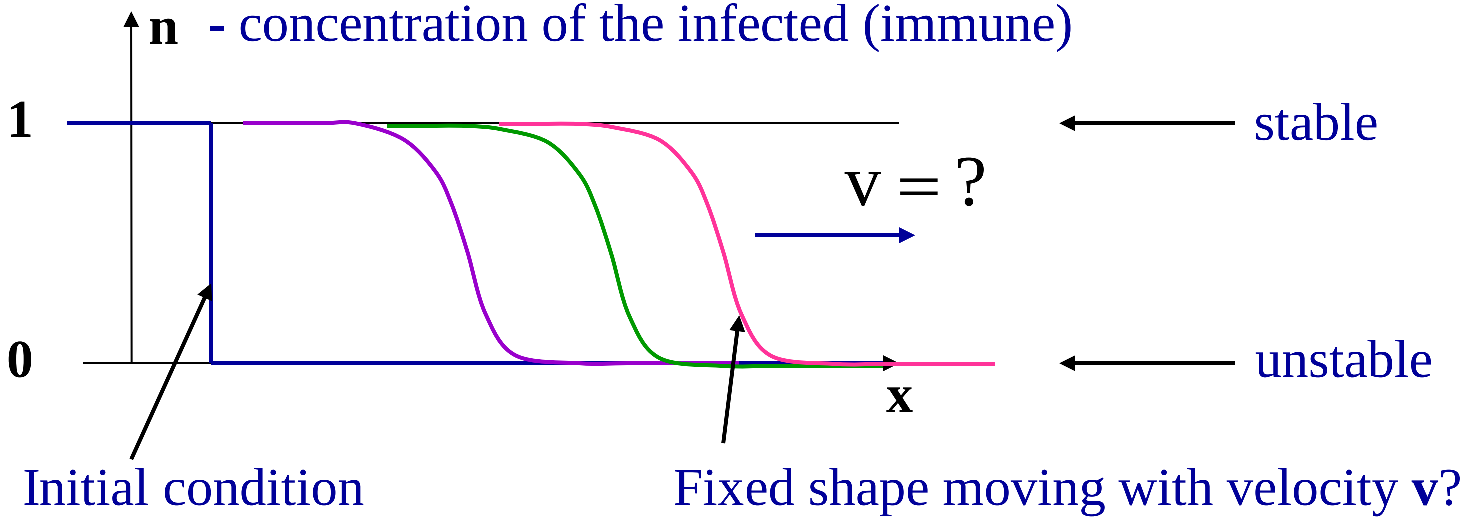
B

d=1

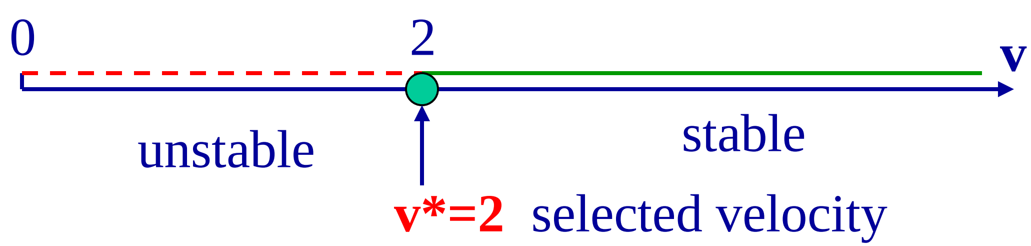
d=3

Infection front: Fisher-Kolmogorov-Piskunov equation

$$\frac{\partial n}{\partial t} = \frac{\partial^2 n}{\partial x^2} + n - n^2$$

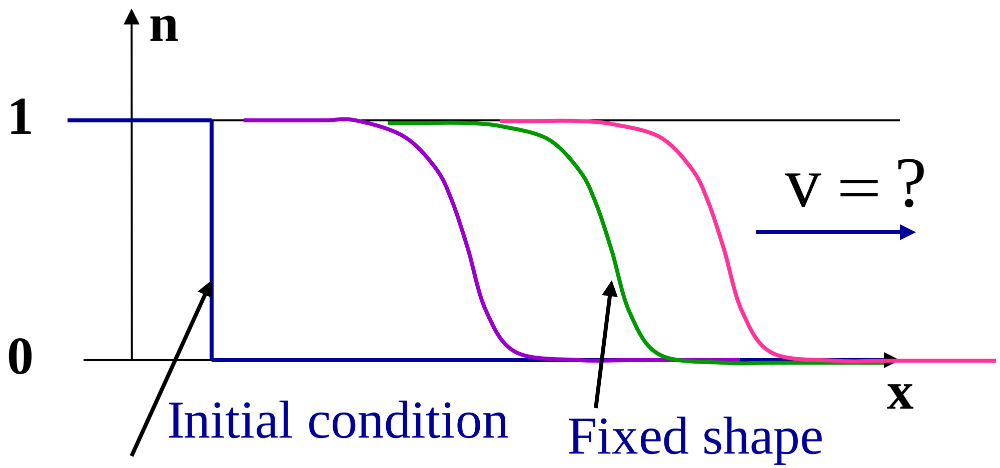


Solution exists for arbitrary **v** $\longrightarrow$ $n(x,t) = \Phi(x - \mathrm{v}t)$



FKP equation: Instability at small velocities

$$\frac{\partial n}{\partial t} = \frac{\partial^2 n}{\partial x^2} + n - n^2$$



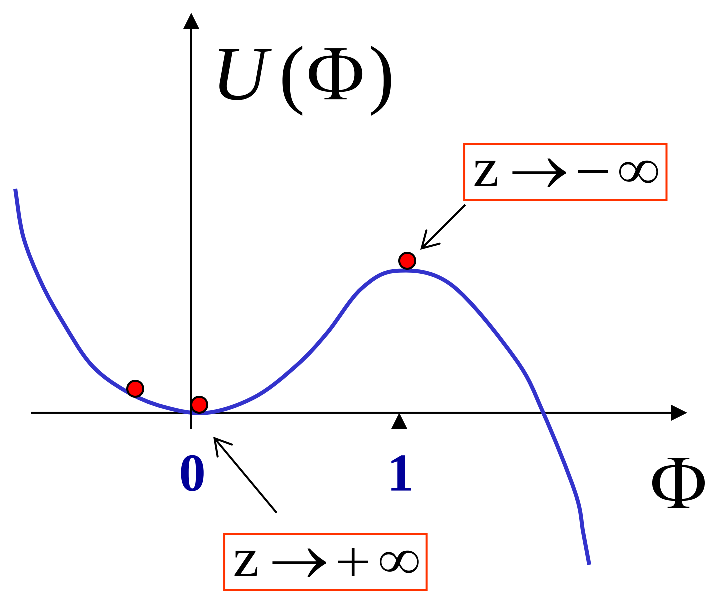
Solution exists for arbitrary **v**

$$n(x,t) = \Phi(\underbrace{x - vt}_{\boxed{z}})$$

$$\ddot{\Phi} = -\mathrm{v}\dot{\Phi} - \frac{d}{d\Phi}\left(\frac{1}{2}\Phi^2 - \frac{1}{3}\Phi^3\right)$$

v - friction

$$U(\Phi)$$

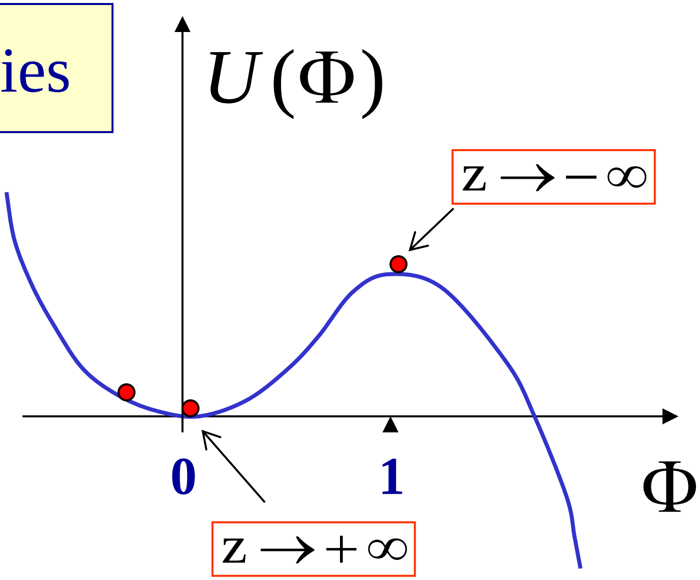


v (friction) small ⇒ oscillations around 0

unphysical (n<0)

FKP equation: Instability at small velocities

$$\ddot{\Phi} = -\mathrm{v}\dot{\Phi} - \frac{d}{d\Phi}\left(\frac{1}{2}\Phi^2 - \frac{1}{3}\Phi^3\right)$$



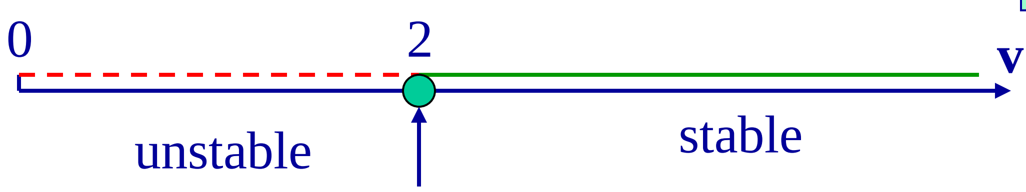
Unphysical (n<0) oscillations for small v

Small Φ limit: $$\ddot{\Phi} = -\mathrm{v}\dot{\Phi} - \Phi$$

Solution $$\Phi = ae^{\omega t}$$

$$\omega^2 + \mathrm{v}\omega + 1 = 0$$

$$\omega_{1,2} = \tfrac{1}{2}\left(-\mathrm{v} \pm \sqrt{\mathrm{v}^2 - 4}\right)$$



v*=2 selected velocity

(marginal stability theories)

FKP equation: Leading edge analysis

$$\partial_t n = \partial_x^2 n + n - n^2$$

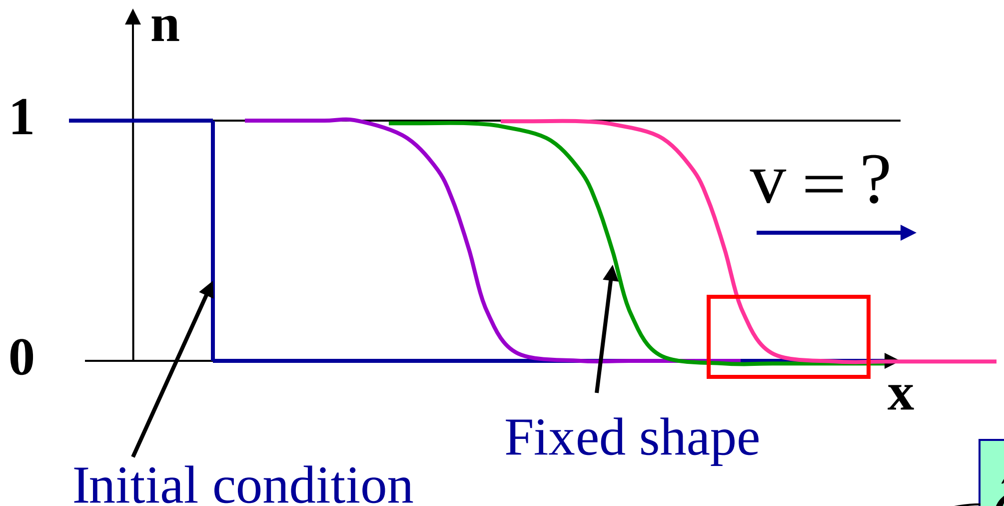
linearization

$$\partial_t n \approx \partial_x^2 n + n$$

Fourier transform

$$\partial_t n_k \approx (-k^2 + 1) n_k = \omega_k n_k$$

Assumption: Leading edge determines the velocity
(the front is pulled by the leading edge)



$$n(x,t) \approx \int_{-\infty}^{\infty} dk\, \tilde{n}_k\, e^{ikx+\omega_k t}$$

$$x = \mathrm{v}t, \quad t \to \infty$$

$$n(\mathrm{v}t,t) \approx \int_{-\infty}^{\infty} dk\, \tilde{n}_k\, e^{(ik\mathrm{v}+\omega_k)t}$$

looking for stationary point in the moving frame

FKP equation: Leading edge analysis II

$$\partial_t n = \partial_x^2 n + n - n^2$$

$$\omega_k = 1 - k^2$$

Looking for stationary point in the moving frame

$$n(\mathrm{v}t, t) \approx \int_{-\infty}^{\infty} dk\, \tilde{n}_k\, e^{(ik\mathrm{v} + \omega_k)t}$$

~const

Stationary phase

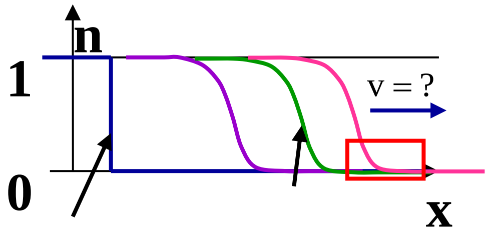
$$i\mathrm{v} + \frac{d\omega_k}{dk} = 0$$

$$k^* = k^*(\mathrm{v})$$

$$n(\mathrm{v}t, t) \approx e^{(ik^*\mathrm{v} + \omega_{k^*})t} A$$

Stationarity in the moving frame:

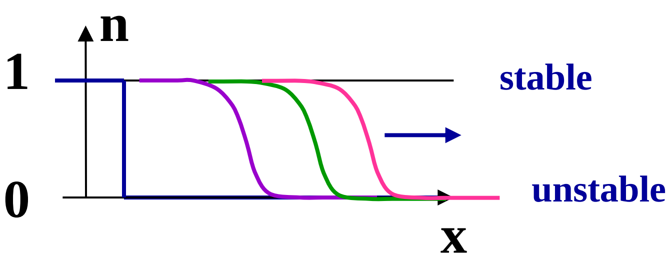
$$ik^*\mathrm{v} + \omega_{k^*} = 0$$

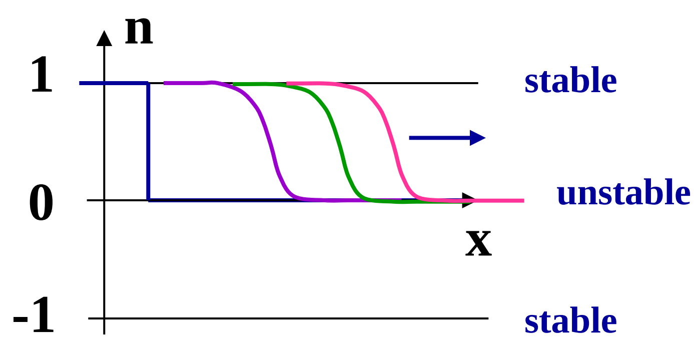


Selected velocity:

$$\mathrm{v}^* = 2$$

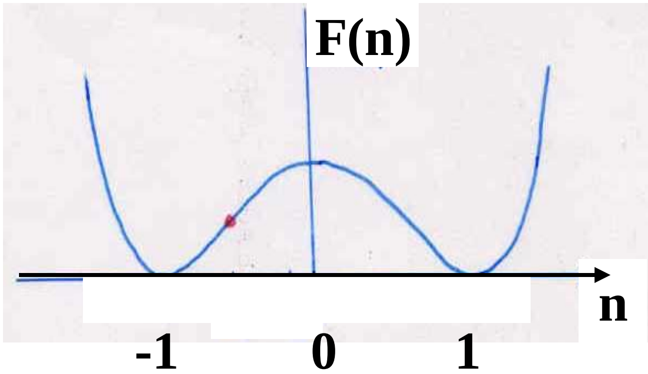
Conservation laws and moving fronts: Cahn-Hilliard equation

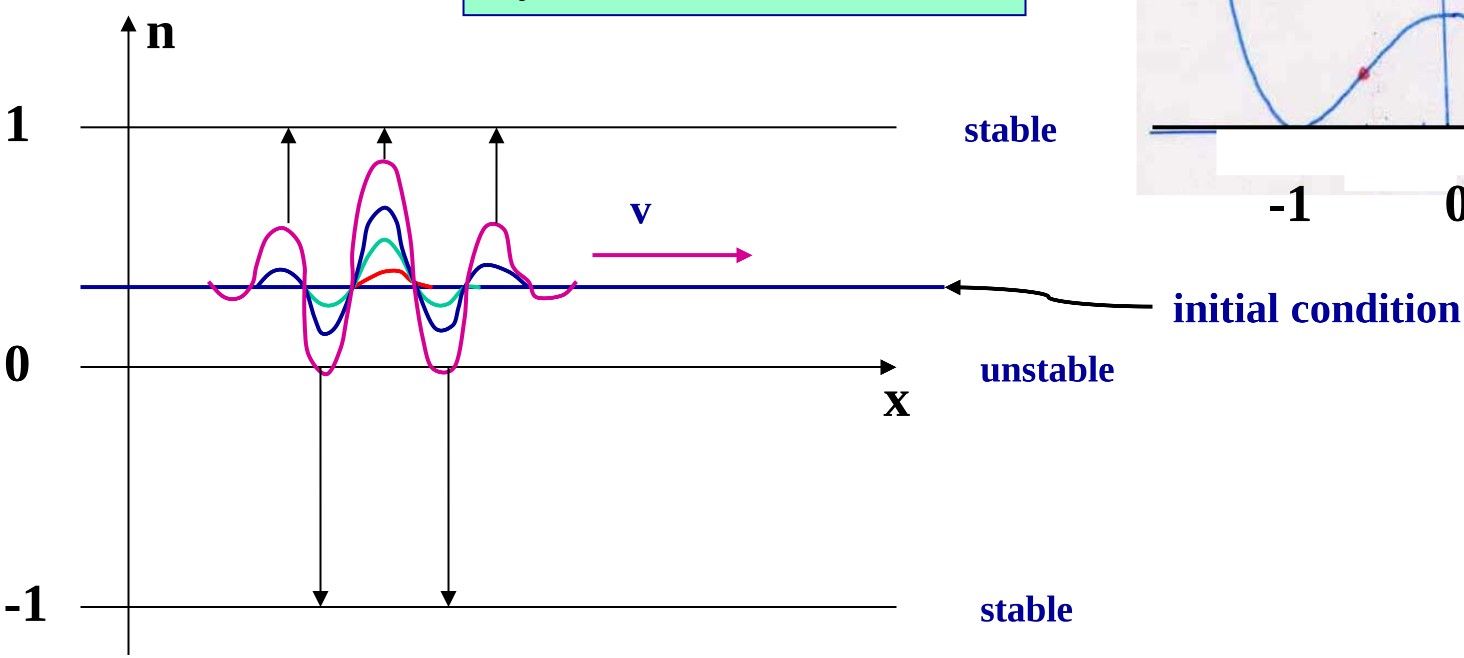




n is conserved:

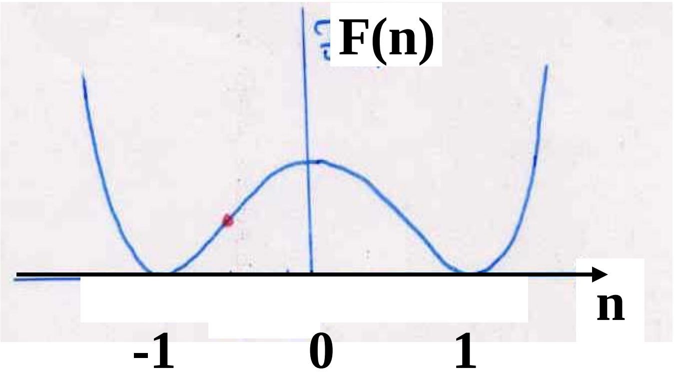
$$\int_{-\infty}^{\infty} n(x,t)\,dx = const.$$





Derivation of the Cahn-Hilliard equation

n is conserved: $\int n(x,t)dx = const$



● $\partial_t n = -\nabla \vec{j}_n$ continuity equation

● $$F \sim \int \left\{ -\frac{\varepsilon}{2} n^2 + \frac{\gamma}{4} n^4 + \frac{\sigma}{2} (\nabla n)^2 \right\} dx$$

The flux of particles should reduce the chemical potential:

$$\mu = -\frac{\delta F}{\delta n} \longrightarrow \vec{j}_n = -\lambda \vec{\nabla} \mu = \lambda \vec{\nabla} \frac{\delta F}{\delta n}$$ ●

λ → kinetic coefficient

From ● ● ● :

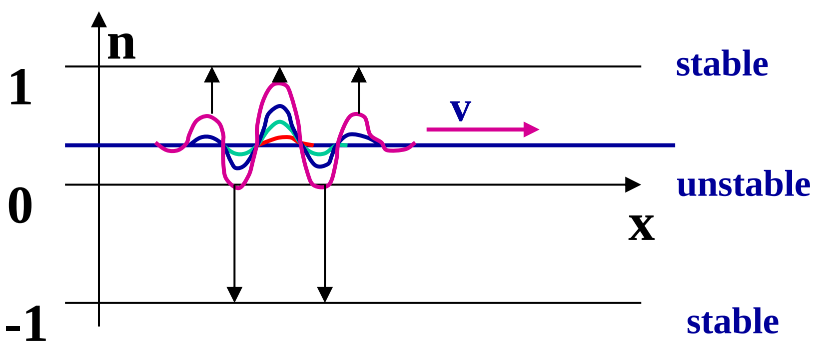
$$\partial_t n = -\lambda \Delta [\varepsilon n - \gamma n^3 + \sigma \Delta n]$$

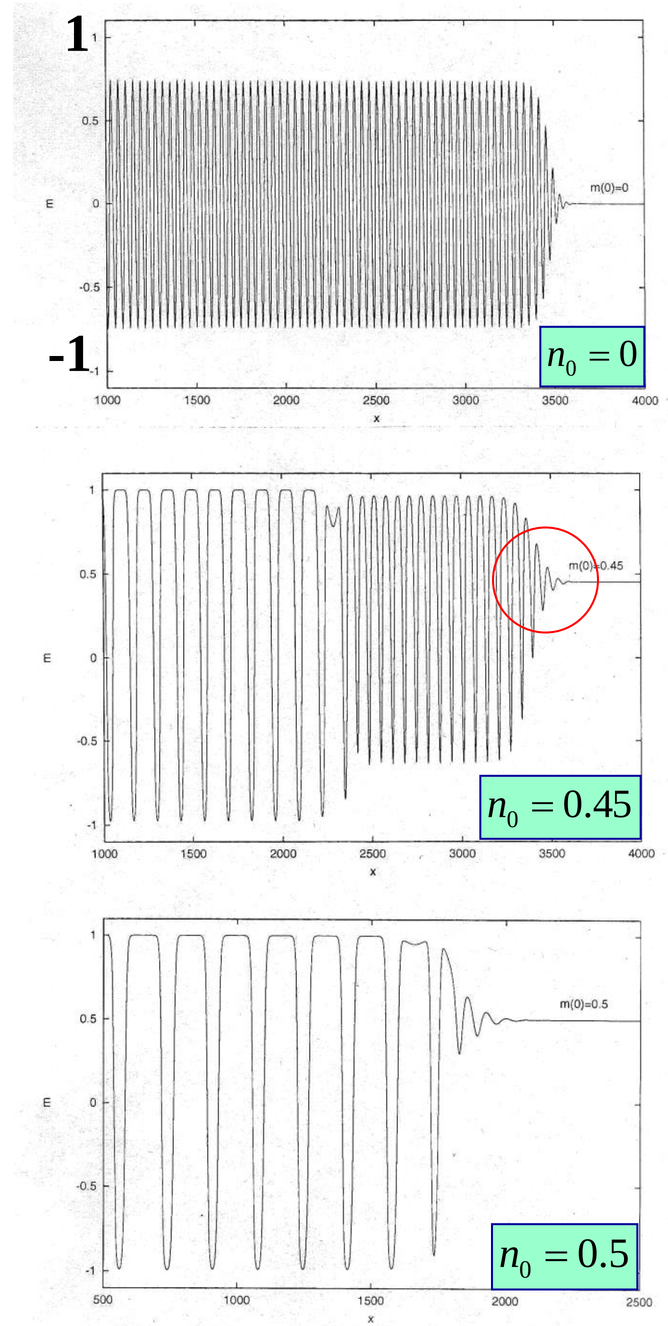
$\lambda, \varepsilon, \gamma, \sigma$
can be scaled out

Conservation laws and moving fronts: Cahn-Hilliard equation

Standard form:

$$\partial_t n = -\partial_x^2 [n - n^3 + \partial_x^2 n]$$



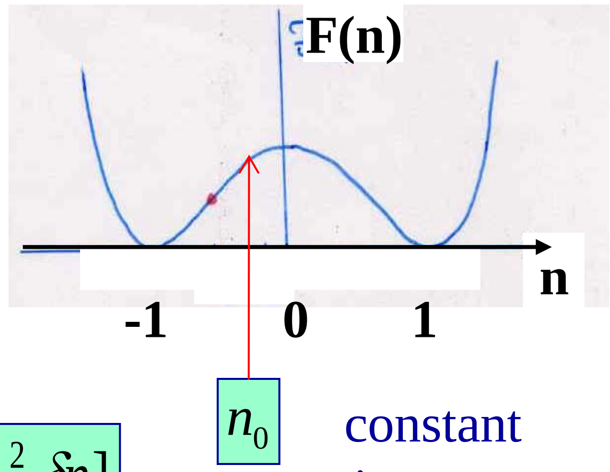


Questions:

(1) What is the velocity of the front?

(2) What is the wavelength of the pattern left in the wake of the front?

Linear stability analysis of the CH equation



constant in space

$$\partial_t n = -\partial_x^2 [n - n^3 + \partial_x^2 n]$$

Linearization:

$$n = n_0 + \delta n$$

$$\partial_t \delta n = -\partial_x^2 [(1-3n_0^2)\,\delta n + \partial_x^2 \delta n]$$

Fourier modes

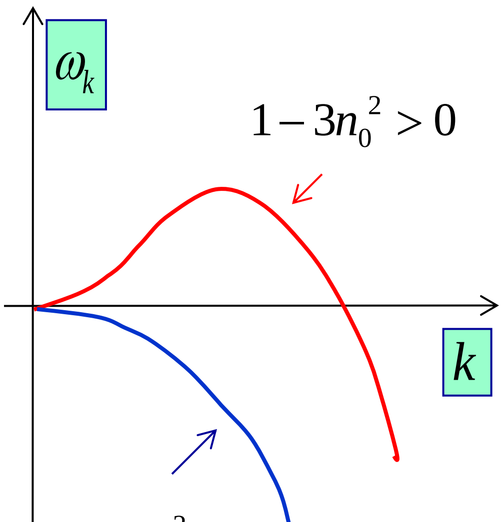
$$\delta n = n_k(t) e^{ikx}$$

$$\partial_t n_k = [(1-3n_0^2)k^2 - k^4] n_k$$

Dispersion

$$n_k(t) = n_k^0 e^{\omega_k t}$$

$$\omega_k = (1-3n_0^2)k^2 - k^4$$

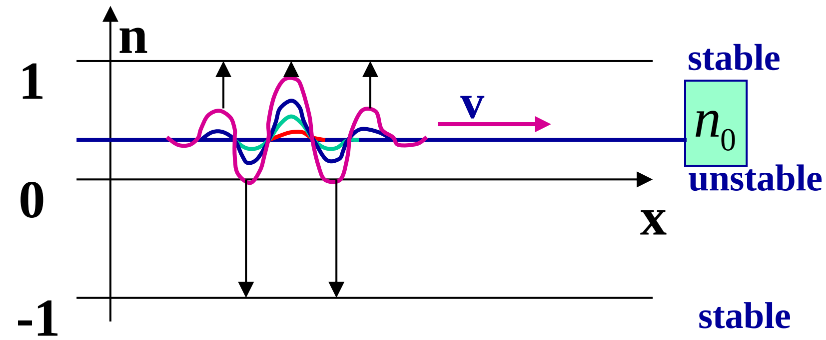


$$-\frac{1}{\sqrt{3}} < n_0 < \frac{1}{\sqrt{3}}$$

Inflection points in F(n)

Linear instability:
It leads to spinodal decomposition

Pulled front in the CH equation



$$\partial_t n = -\partial_x^2 [n - n^3 + \partial_x^2 n]$$

Linearization + Fourier modes

$$\partial_t n_k = [(1-3n_0^2)k^2 - k^4] n_k$$

$$\omega_k = (1-3n_0^2)k^2 - k^4 \equiv a\, k^2 - k^4$$

goes to zero at spinodal

Looking for stationary point in the moving frame

$$n(\mathrm{v}t, t) \approx \int dk\, \tilde{n}_k e^{(ik\mathrm{v}+\omega_k)t}$$

~const

Stationary phase

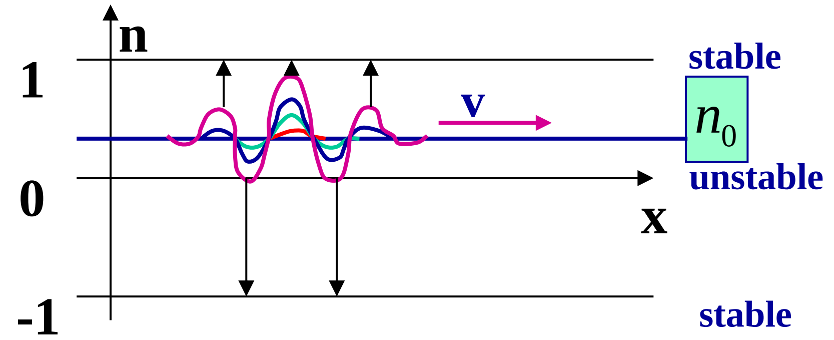
$$i\mathrm{v} + \frac{d\omega_k}{dk} = 0$$

$$n(\mathrm{v}t, t) \approx e^{(ik^*\mathrm{v}+\omega_{k^*})t} A$$

Stationarity in the moving frame:

$$\mathrm{Re}(ik^*\mathrm{v} + \omega_{k^*}) = 0$$

Pulled front in the CH equation



$$\omega_k = \underbrace{(1-3n_0^2)}_{a}k^2 - k^4$$

Stationary phase

$$iv + \frac{d\omega_k}{dk} = 0 \longrightarrow i\,v + 2\,a\,k^* - 4\,k^{*3} = 0$$

$$k^* = \mathrm{Re}\;k^* + i\,\mathrm{Im}\;k^*$$

Stationarity in the moving frame:

$$\mathrm{Re}(ik^* v + \omega_{k^*}) = 0 \longrightarrow -v\;\mathrm{Im}\;k^* + \mathrm{Re}\;(a\,k^{*2} - k^{*4}) = 0$$

Results:

$$v = \tfrac{2}{3}\sqrt{\tfrac{7\sqrt{7}+17}{6}}\,a^{3/2}$$

$$\mathrm{Re}\,k^* = \sqrt{\tfrac{\sqrt{7}+3}{8}}\,a^{1/2}$$

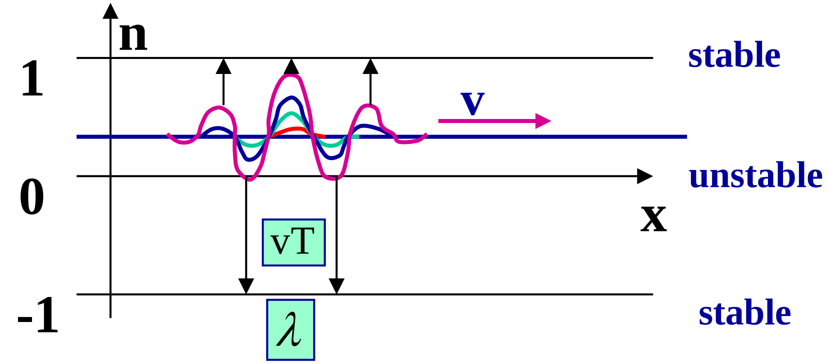
$$\mathrm{Im}\,k^* = \sqrt{\tfrac{\sqrt{7}-1}{24}}\,a^{1/2}$$

$$v = \frac{2(\sqrt{7}+2)}{3\sqrt{\sqrt{7}+1}}\,a^{3/2} \approx 1.622\,a^{3/2}$$

$$\mathrm{Re}\,\omega_{k^*} = \frac{\sqrt{7}+5}{18}\,a^2$$

$$\mathrm{Im}\,\omega_{k^*} = -\tfrac{1}{12}\sqrt{\tfrac{2\sqrt{7}+1}{3}}\,a^2$$

Wavelength observed in the lab



In the moving frame:

$$n(\mathrm{v}t,t) \approx e^{(ik^*\mathrm{v}+\omega_{k^*})t} A \longrightarrow \sim e^{i\tilde{\omega}t} \sim e^{i(\mathrm{Re}\,k^*\mathrm{v}+\mathrm{Im}\,\omega_{k^*})t}$$

$$\mathrm{Re}(ik^*\mathrm{v}+\omega_{k^*})=0$$

Oscillation in the comoving frame with period

$$T=\frac{2\pi}{\tilde{\omega}}$$

In the laboratory frame:

Wavelength: distance between the maximal densities

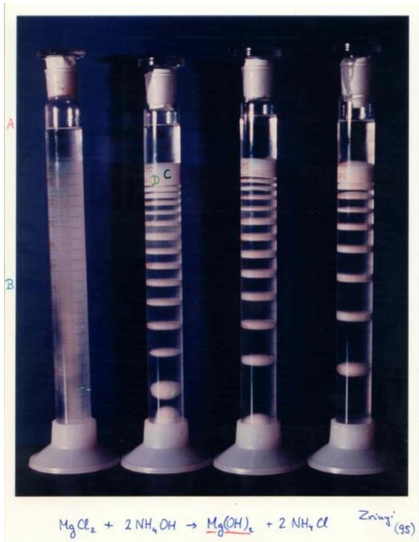
$$\lambda = \mathrm{v}T = \frac{2\pi\,\mathrm{v}}{\mathrm{Re}\,k^*\mathrm{v}+\mathrm{Im}\,\omega_{k^*}} \longrightarrow \approx 8.21\,a^{-1/2}$$

Wavenumber:

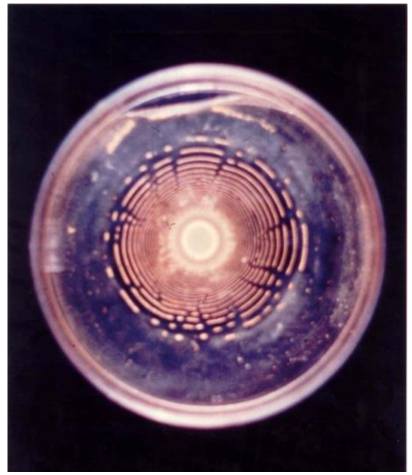
$$q=\frac{2\pi}{\lambda}=\mathrm{Re}\,k^*+\frac{\mathrm{Im}\,\omega_{k^*}}{\mathrm{v}}=\frac{1}{8}\sqrt{19+7\sqrt{7}}\,a^{1/2}\approx 0.765\,a^{1/2}$$

Liesegang mintázatok

Nemtriviális mintázatok
d=1-3 dimenzióban



d=1



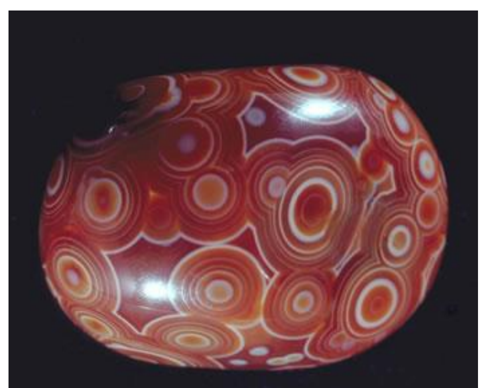
d=2

d=3

Zrínyi, 95

d=3

Achátok



Történeti megjegyzés:
Gyógyítja a: kígyómarást,
skorpiószúrást, lázat.
Megvéd: fertőzéstől, villámlástól.
Hosszú életet biztosít.

Perzsa mágusok, bizánci császárok
és reneszánsz uralkodók kedvencei.

Characterization of patterns

Time law

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

- Spacing law

$$x_{n+1} = (1+p) \cdot x_n$$

- Width law

$$w_n \sim x_n$$

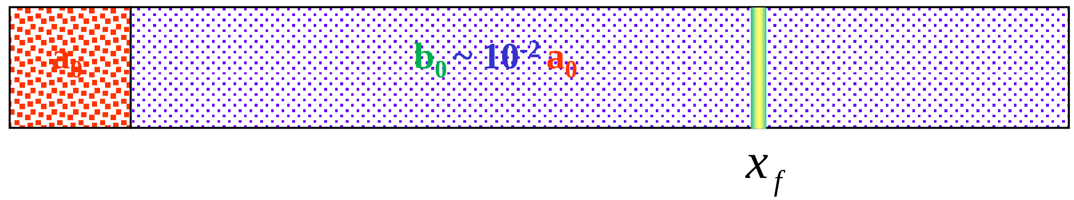
- Matalon-Packter law

$$p = F(b_0) + G(b_0)\frac{b_0}{a_0}$$

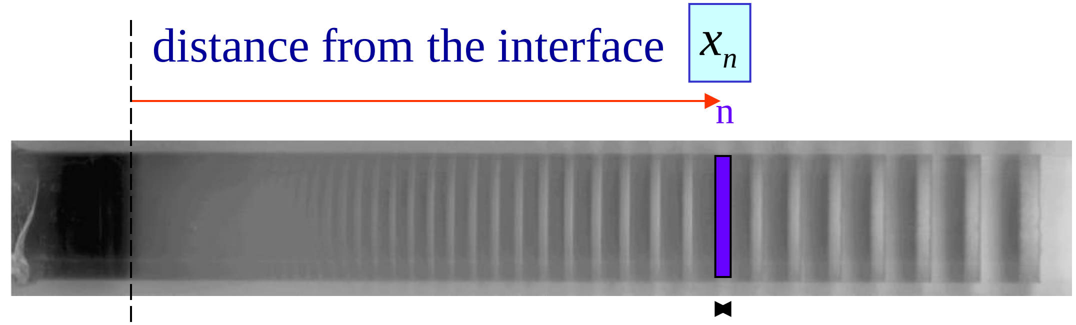
Experiment

$$MgCl_2 + 2NH_4OH \to \underline{Mg(OH)_2} + 2NH_4Cl$$

A + **B** $\longrightarrow$ **C**



distance from the interface x_n



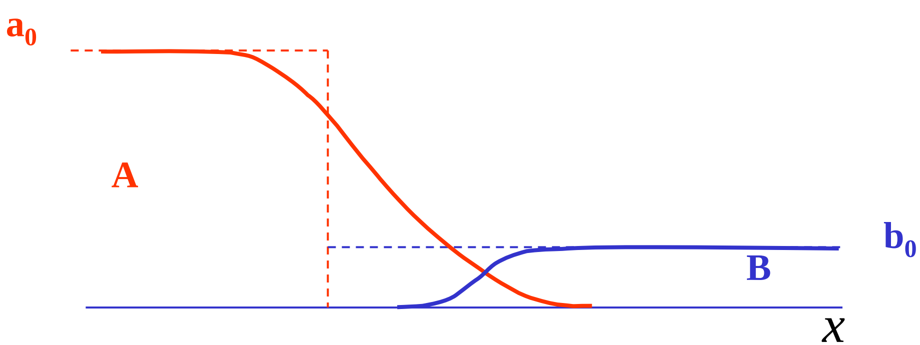
width w_n

time of appearence t_n

Other (not general) observations: inverse patterns, fine structure between bands, …

Elméletek

W. Ostwald (1897), N.R. Dhar et al. (1925), C. Wagner (1950), S. Prager (1956), Ya.B. Zeldovitch et al. (1960), S. Shinohara (1970), M. Flicker et al. (1974), S. Kai et al. (1982), G.T. Dee (1986), B. Chopard et al. (1994), …



$A + B \rightarrow I_1 \rightarrow I_2 \rightarrow ? \rightarrow C$

$$\partial_t a = D_a \partial_x^2 a - k \cdot a \cdot b$$
$$\partial_t b = D_b \partial_x^2 b - k \cdot a \cdot b$$

forrása

$$S(x,t)$$

1

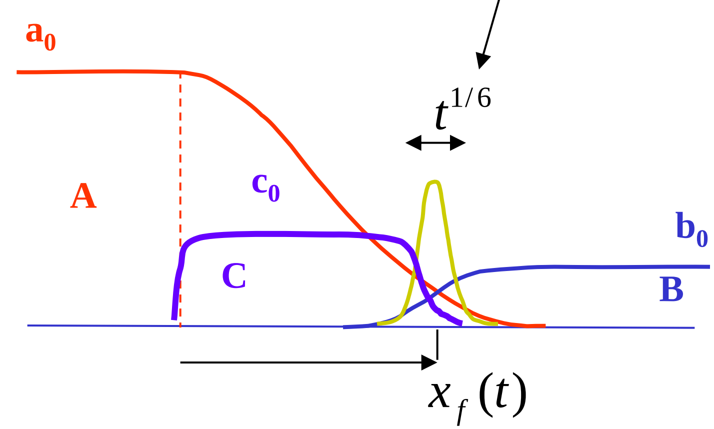
$$\partial_t c = k_1 \theta(a \cdot b - q) + k_2 a \cdot b \cdot c$$

ion-szorzat túltelítés

2

$$\partial_t c = ka \cdot b + D_c \partial_x^2 c - \partial_t d$$
$$\partial_t d = k_1 \theta(c - c^*) + k_2 c \cdot d$$

nukleáció és növekedés



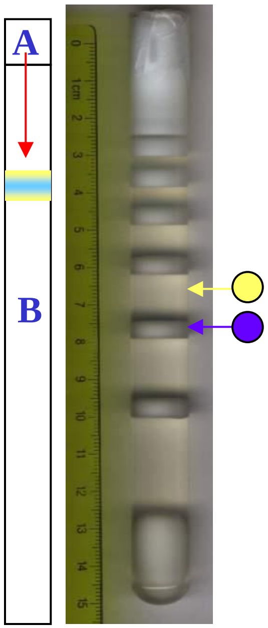
$$x_f \approx \sqrt{D_f t}$$

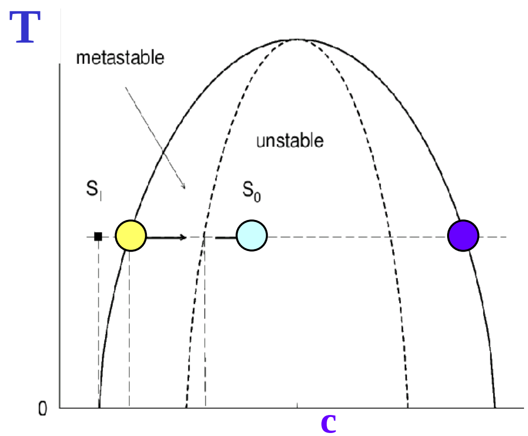
$$c_0 = const$$

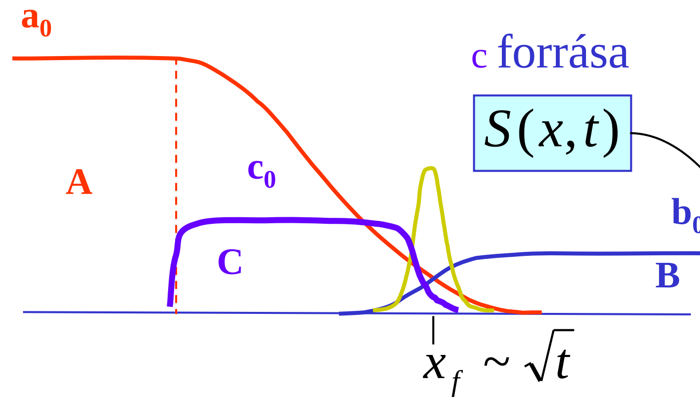
L. Gálfi and Z.R., PRA 38, 3151 (1988)

Liesegang sávok fázisszeparáció modellje

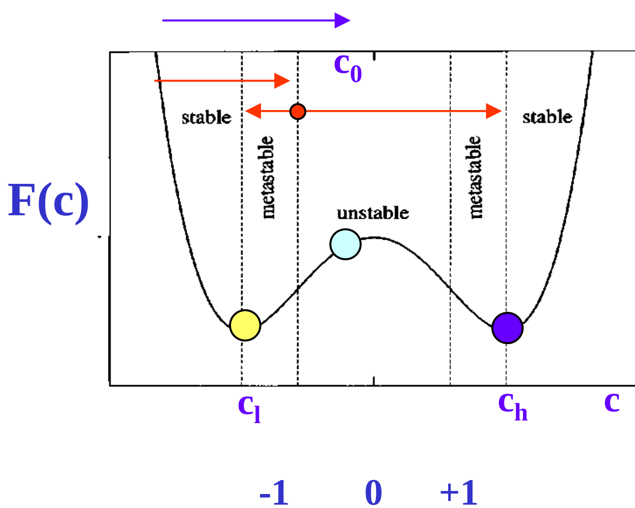
PRL 83, 2880 (1999)







$$\partial_t c = -\lambda\, \Delta(\, c - \; c^3 + \sigma\, \Delta c\,) + S(x,t)$$



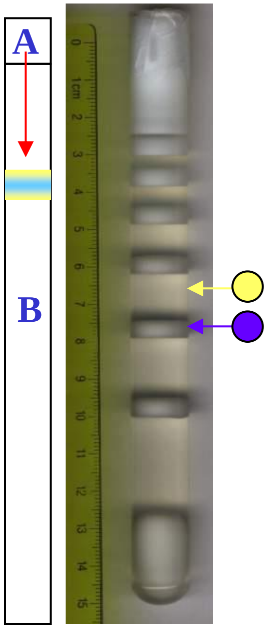
Megmaradási törvény:

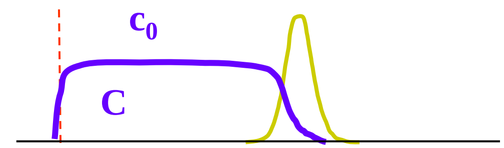
$$\partial_t c = -\nabla \vec{j}_c = \lambda \Delta \frac{\delta F}{\delta c}$$

Szabadenergia:

$$F(c) = -\frac{1}{2} c^2 + \frac{1}{4} c^4$$

Liesegang sávok fázisszeparáció modellje II

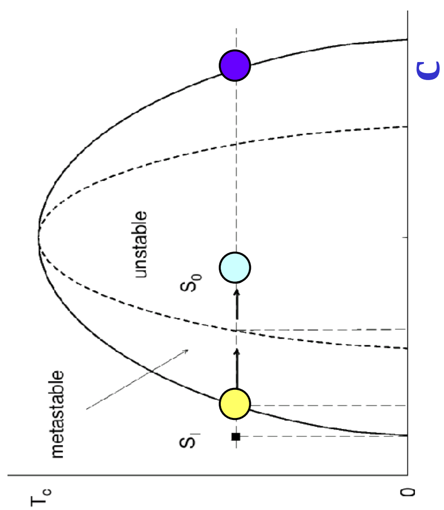


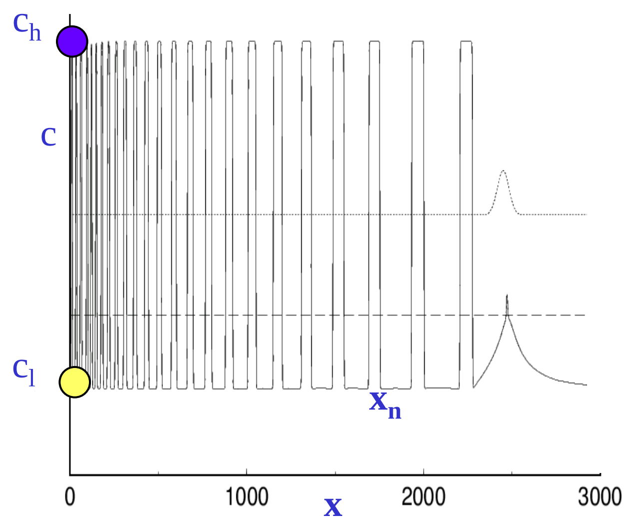


$S(x,t)$

Cahn-Hilliard egyenlet forrással

$$\partial_t c = -\lambda\,\Delta(\,c - c^3 + \sigma\,\Delta c\,) + S(x,t)$$





$x_n \sim Q\,(1+p\,)^n$

$$p = F(b_0) + G(b_0)\,\frac{b_0}{a_0}$$

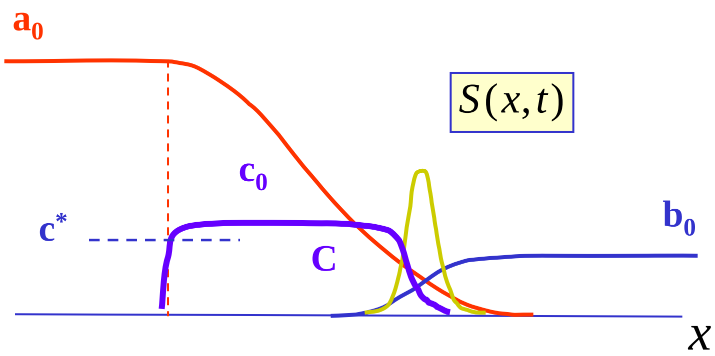
movie

Termodinamika rögzíti c_h és c_l-t,
és c megmaradásából következik

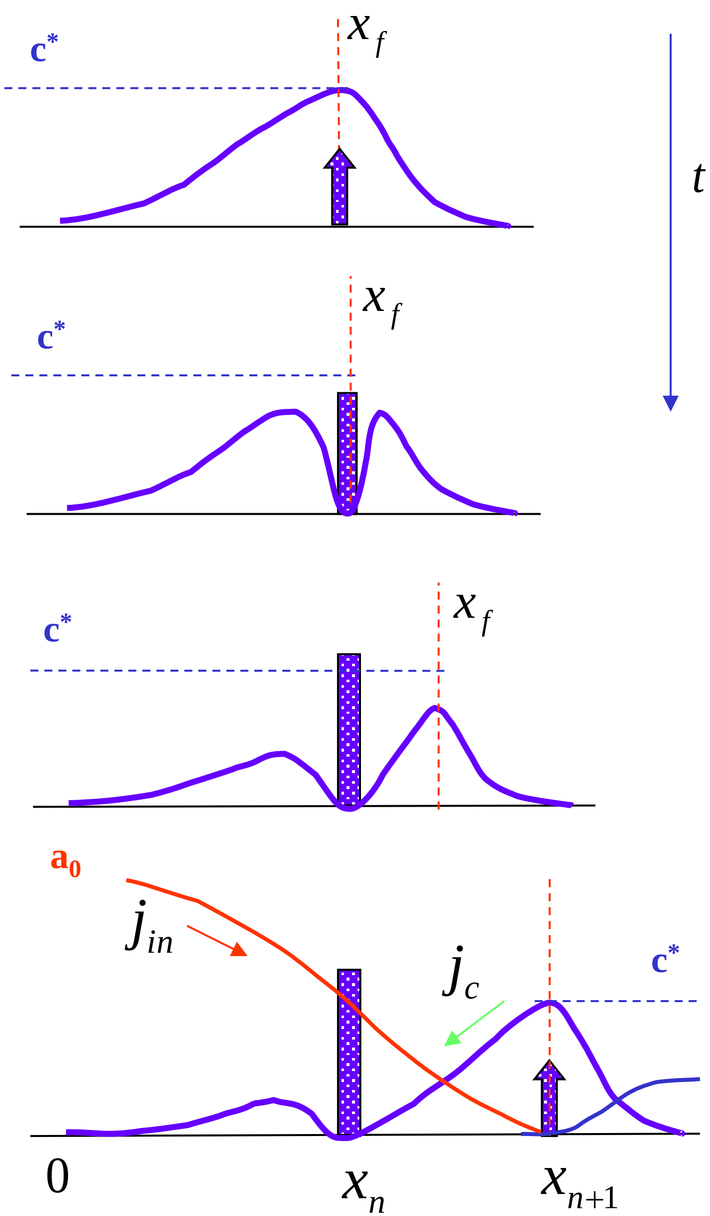
$w_n \sim x_n$

Távolság-törvény

T. Antal et al., J.Chem.Phys. 109, 9479 (1998)



CsapadékképzŐdés feltétele **$c>c^*$**



Megmaradási törvény:

$$\frac{D_a a_0}{x_{n+1}} \longrightarrow \boxed{j_{in} \approx j_c} \longleftarrow \frac{D_c c^*}{x_{n+1} - x_n}$$

Matalon-Packter

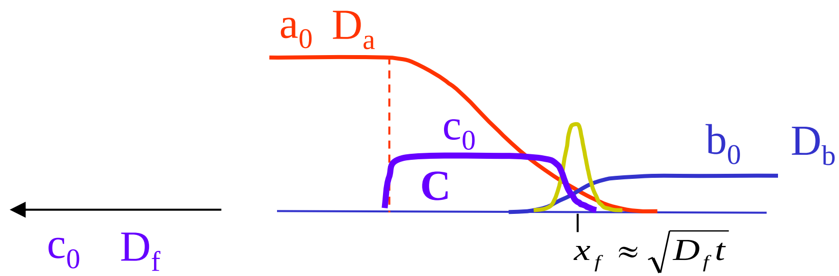
$$\boxed{\frac{x_{n+1}}{x_n} \approx 1 + \frac{D_c c^*}{D_a a_0}}$$

Prognosztika: egy sáv megjelenési ideje

Physica A274, 50 (1999)

Paraméterek meghatározása kísérletből

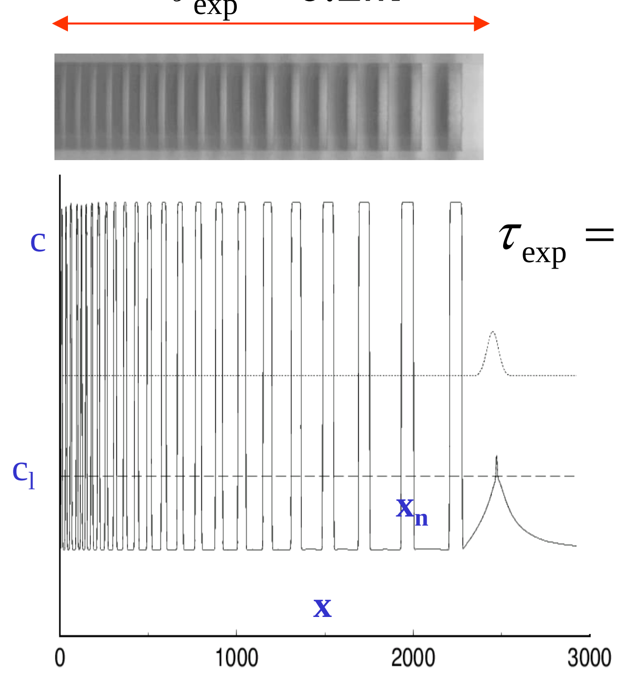
$$\partial_t c = -\lambda\,\Delta(\,c - c^3 + \sigma\,\Delta c\,) + S(x,t)$$



hossz-skála: $\ell_{th} = \sqrt{\sigma} = 2\cdot 10^{-4}\,m$

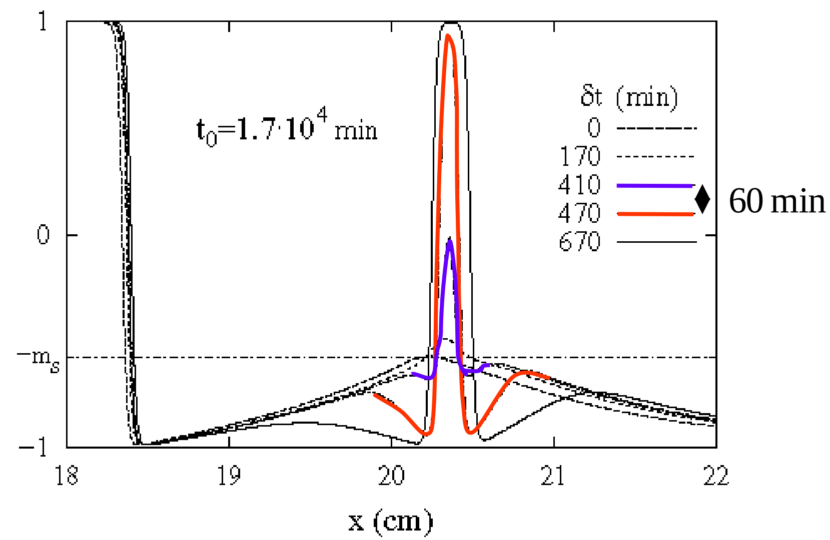
időskála: $\tau_{th} = \sigma / \lambda = 40\,s$

$\ell_{exp} = 0.2m$



$\tau_{exp} = 10^6\,s$

A dinamika részletei:



Solidification (Stefan problem in d=1)

T_0 – melting temperature

D_S – heat diff.coeff. in solid

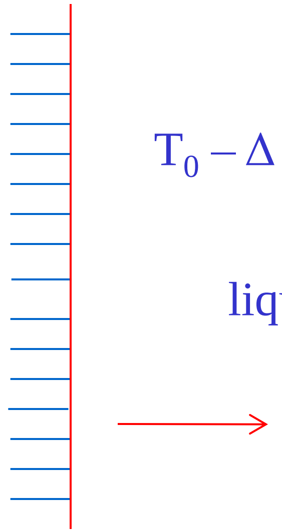
D_l – heat diff.coeff. in liquid

$\boxed{\kappa_S\,,\kappa_\ell}$ – heat cond. coeff.

L – latent heat

$T_S \leq T_0$ $\qquad$ $T_0 - \Delta$ $\qquad$ supercooled

solid $\qquad$ liquid



$\boxed{\mathrm{v} = ?}$

Equations:

$$\boxed{\partial_t T = D_s \Delta T} \qquad \text{(solid)}$$

$$\boxed{\partial_t T = D_\ell \Delta T} \qquad \text{(liquid)}$$

Boundary conditions:

$$\boxed{T(x \to \infty, t) = T_0 - \Delta}$$

$$\boxed{T(x \to -\infty, t) = T_S}$$

At the solid-liquid (plane) interface:

$$\boxed{T(x_f, t) = T_0}$$

Equilibrium at melting temperature (assumption).

$$\boxed{L\mathrm{v} = \kappa_s \nabla T \,|_{x_f - 0} - \kappa_\ell \nabla T \,|_{x_f + 0}}$$

Latent heat must be conducted away.