Controlled precipitation patterns

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Problem: Creation of patterns at micro- and nanoscales:

Lithography vs. bottom-up-building,

True 3d structures.

Question: Can reaction-diffusion processes be used?

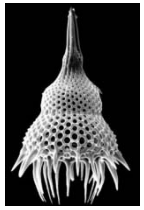
Relevant timescales, spatial control.

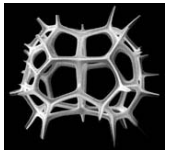
Model: Liesegang type phenomena:

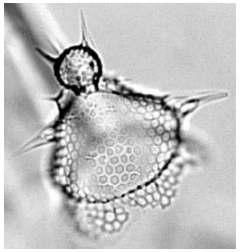
Spatial structures in the wake of reaction fronts.

Hope: Nature can do it.

Radiolarias:







Liesegang phenomena

Naturwiss. Wochenschrift
11, 353 (1896)

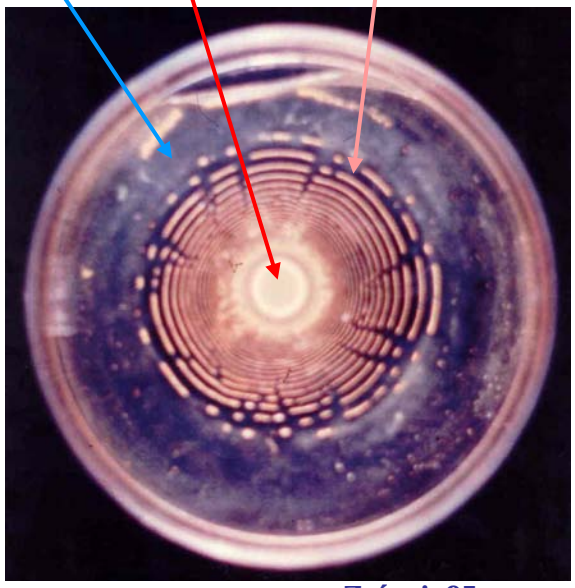
Nontrivial patterns
in d=1-3 dimensions

agates

A random experiment

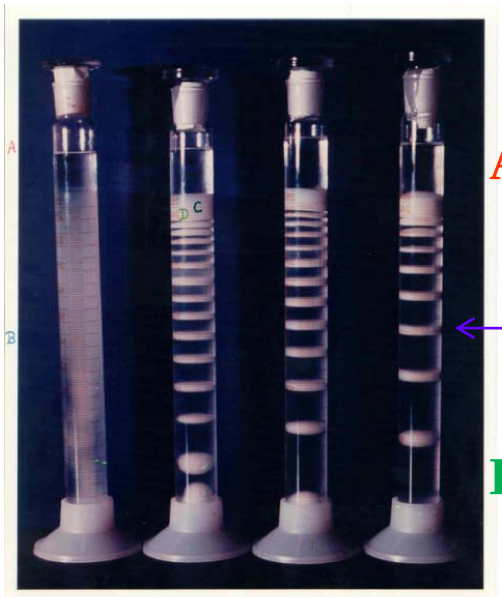
$$MgCl_2 + 2 \cdot NH_4OH \rightarrow Mg(OH)_2 + 2 \cdot NH_4Cl$$

precipitate



Zrínyi, 95

d=2



d=1

d=3

Characterization of patterns

Time law

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

- Spacing law

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

- Width law

$$w_n \sim x_n$$

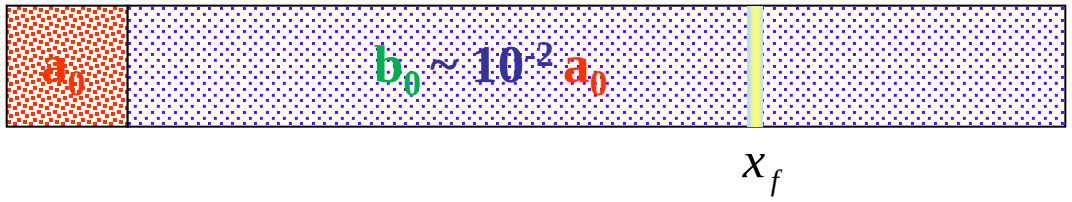
- Matalon-Packter law

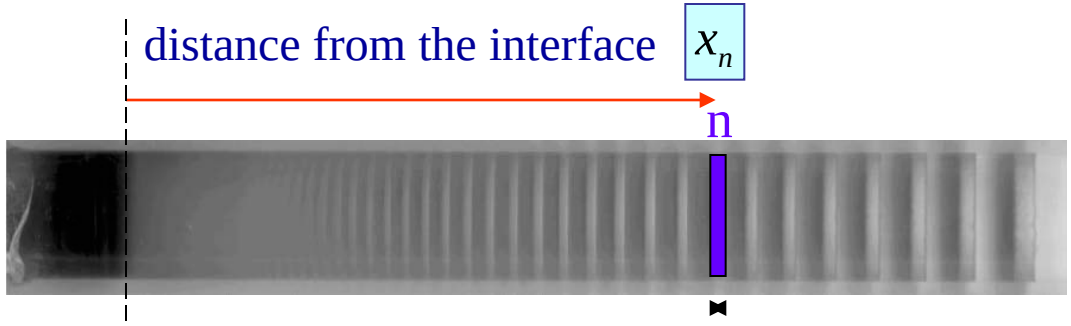
$$p = F(b_0) + G(b_0)\frac{b_0}{a_0}$$

Experiment

$$MgCl_2 + 2NH_4OH \rightarrow Mg(OH)_2 + 2NH_4Cl$$

A + B → C



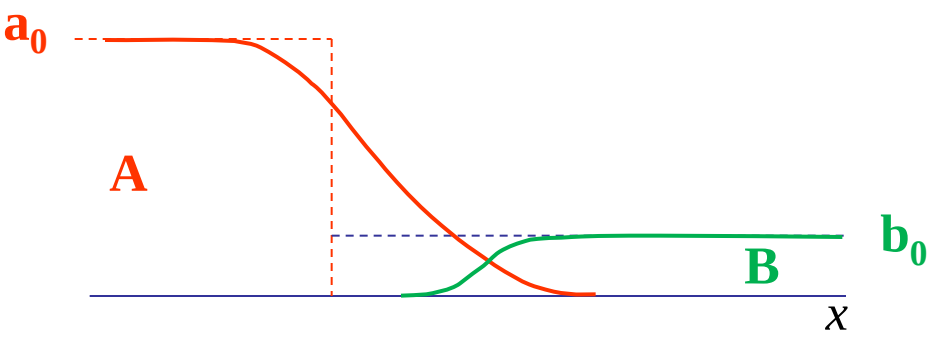


time of appearence t_n

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

Theories

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), …

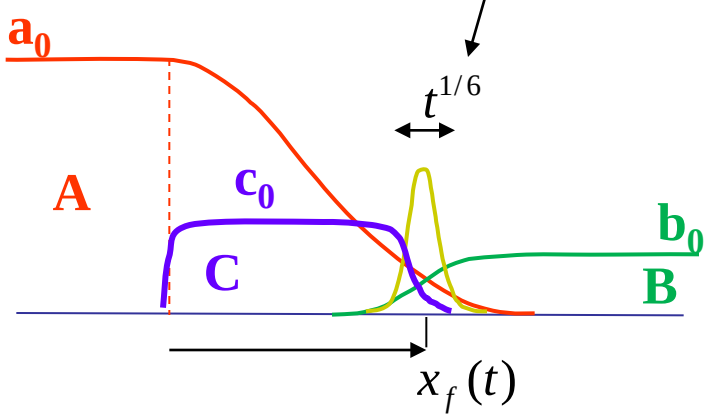


$$\partial_t a = D_a \partial_x^2 a - k \cdot a \cdot b$$
$$\partial_t b = D_b \partial_x^2 b - k \cdot a \cdot b$$

Source of $S(x,t)$

A + B → I_1 → I_2 → ? → C

Threshold processes:
- ion-product supersaturation
- ⋮
- phase-separation

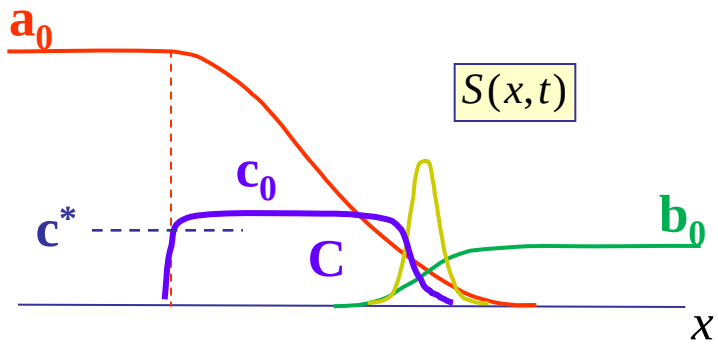


$x_f \approx \sqrt{D_f t}$ $\quad c_0 = const$

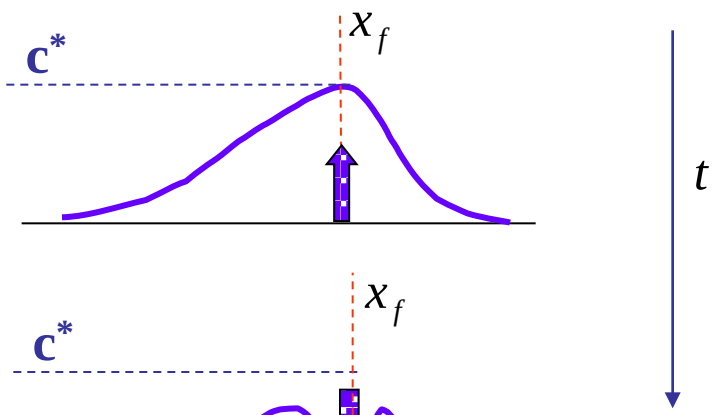
L. Gálfi and Z.R., PRA 38, 3151 (1988)

Spacing law

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

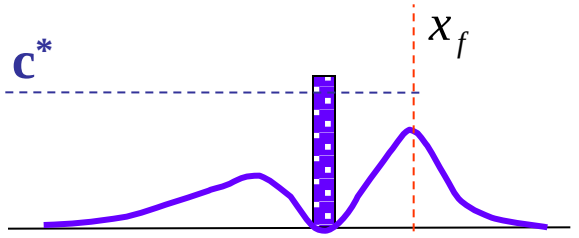


Condition for precipitation $c > c^*$



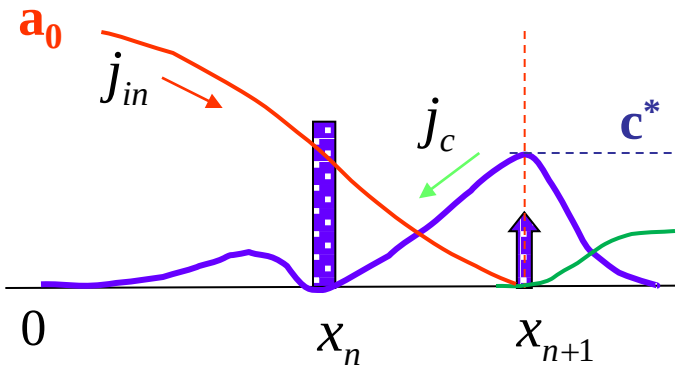
Conservation law:

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



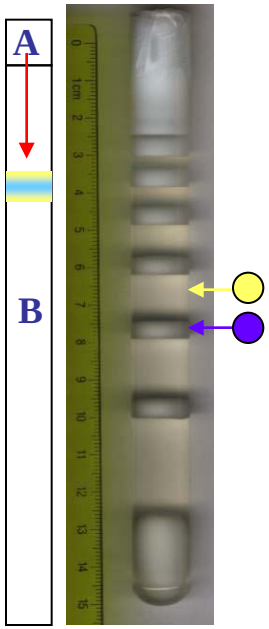
Matalon-Packter

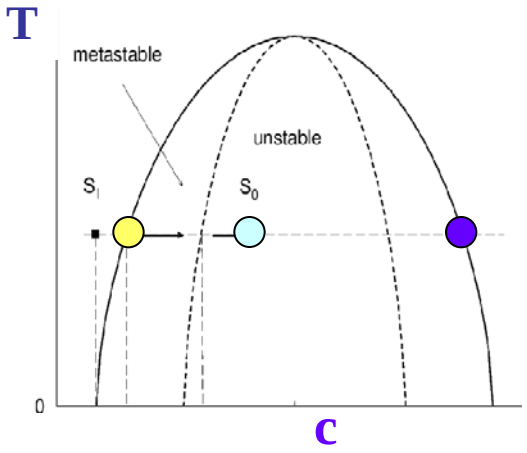
$$\frac{x_{n+1}}{x_n} \approx 1 + \frac{D_c c^*}{D_a a_0}$$

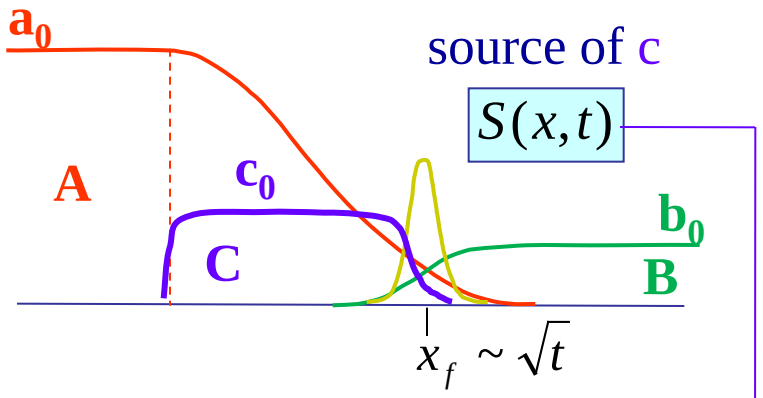


Phase separation model of Liesegang bands

T. Antal, M. Droz, J. Magnin and Z.R., PRL 83, 2880 (1999)

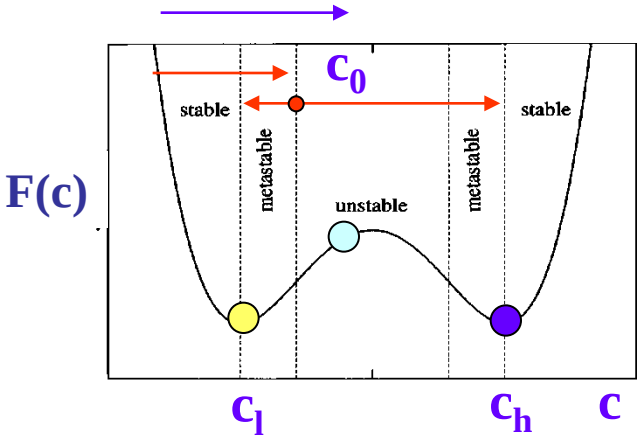


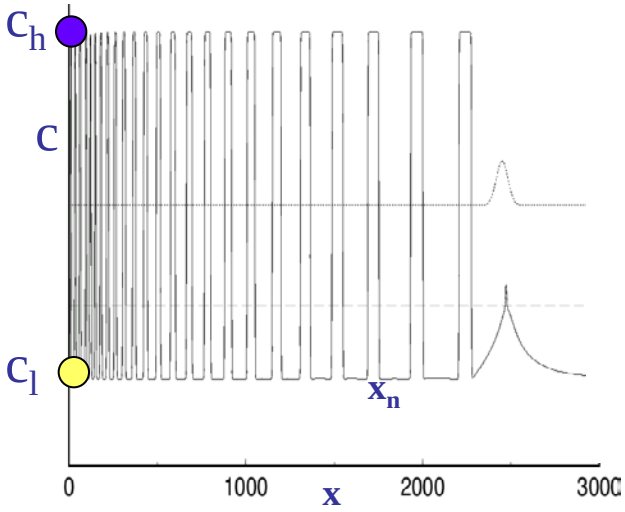




$$\partial_t c = -\lambda\Delta(c - c^3 + \sigma\Delta c) + S(x,t)$$

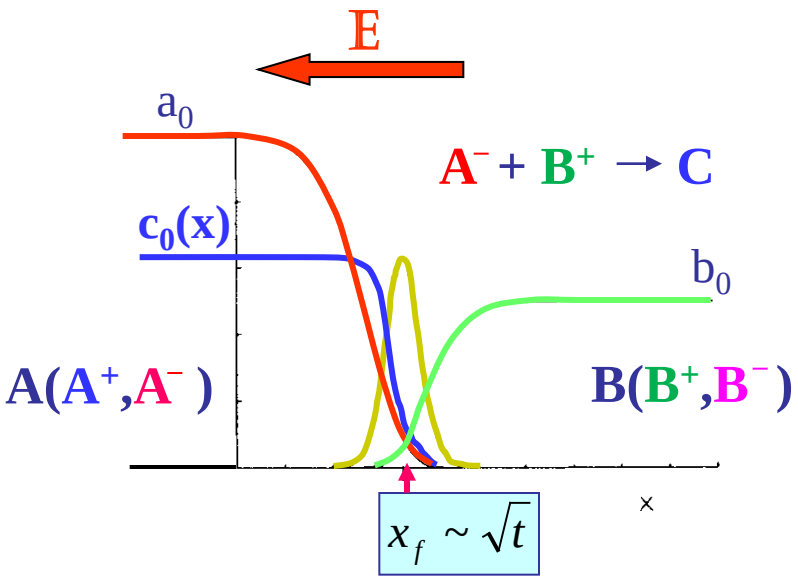
$$\frac{\delta F}{\delta c}$$

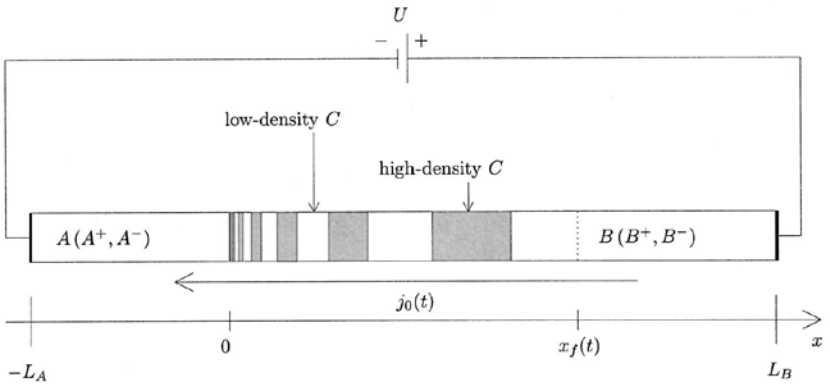


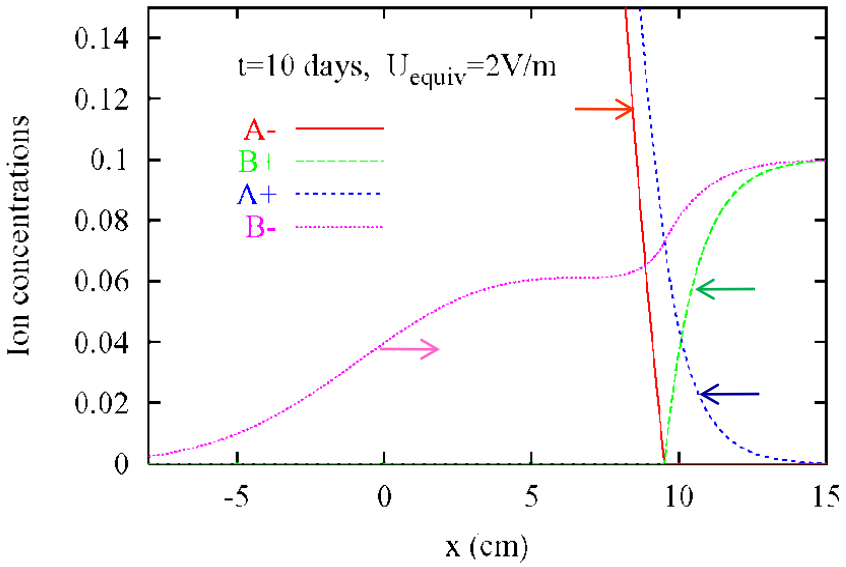


Reaction zones in electric field

T.Unger and Z.R., PRE61, 3583 (2000)
I. Bena et al., J.Chem.Phys. 122, 024512 (2005)





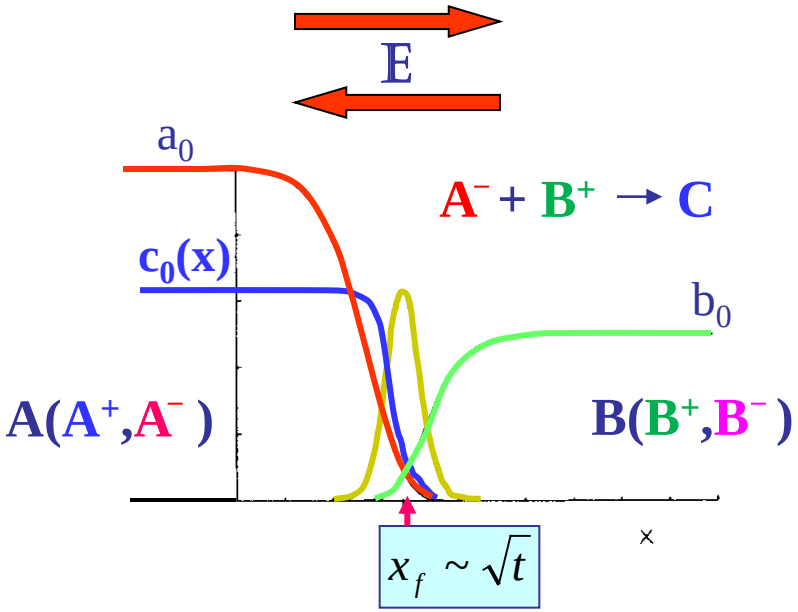


Front motion?

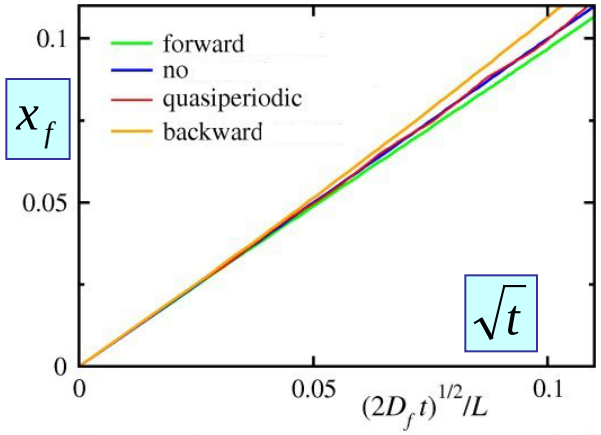
Spatial distribution
of reaction product?

Reaction zone in an electric field

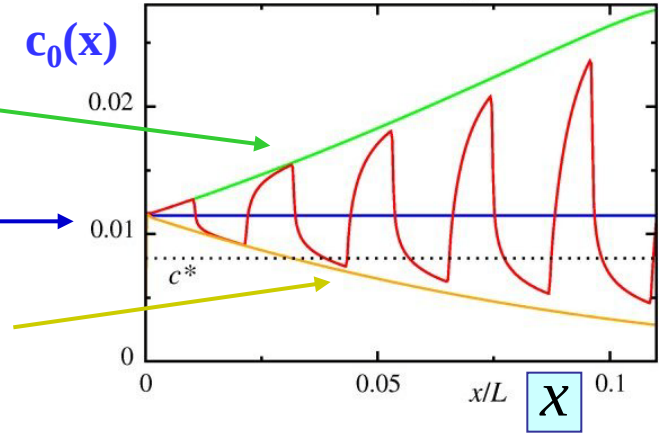
I. Bena et al.
J.Chem.Phys. 122, 024512 (2005)



- The front remains diffusive

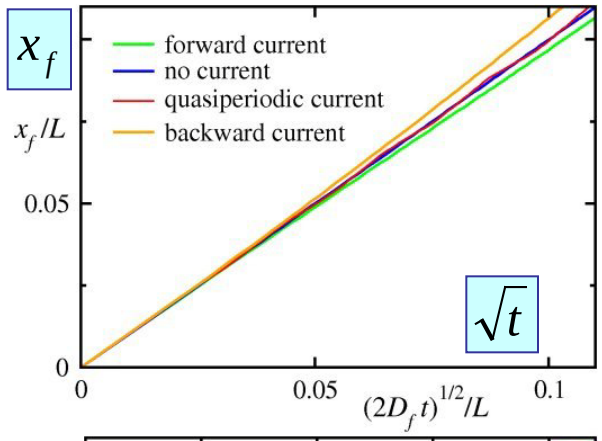


- Reaction product in the wake of the front
  - forward field:
  - no field:
  - backward field:

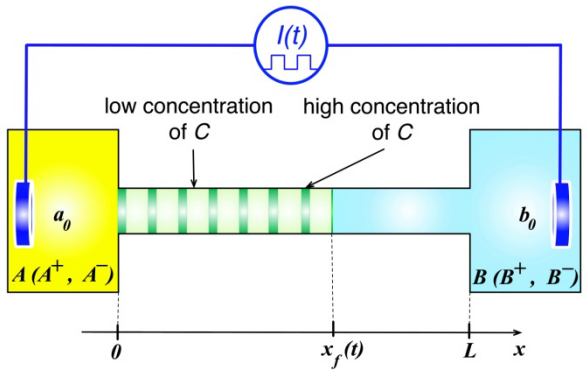


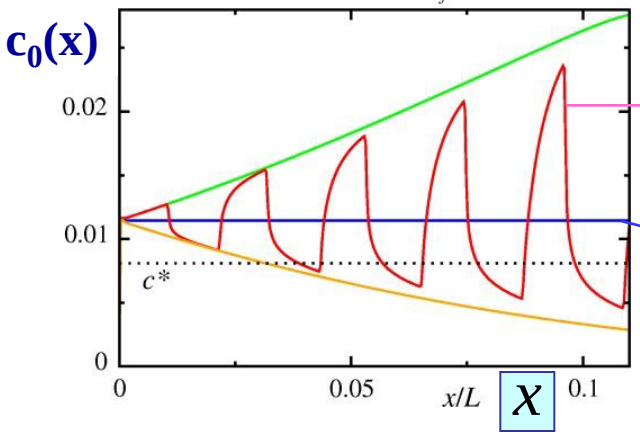
Control with electric current

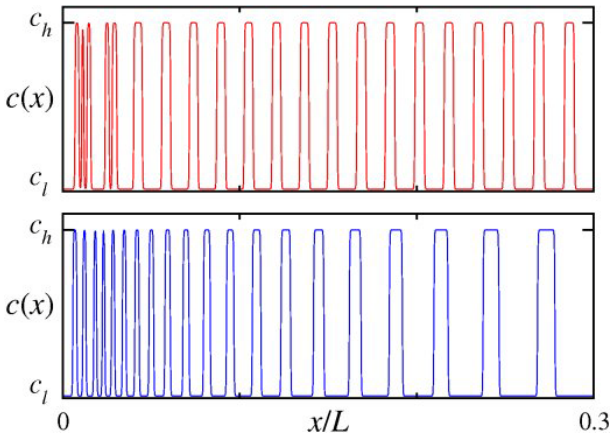
I. Bena et al., PRL 101, 075701 (2008)



Controlled current generator







Aim: periodic pattern

$x_n = an$

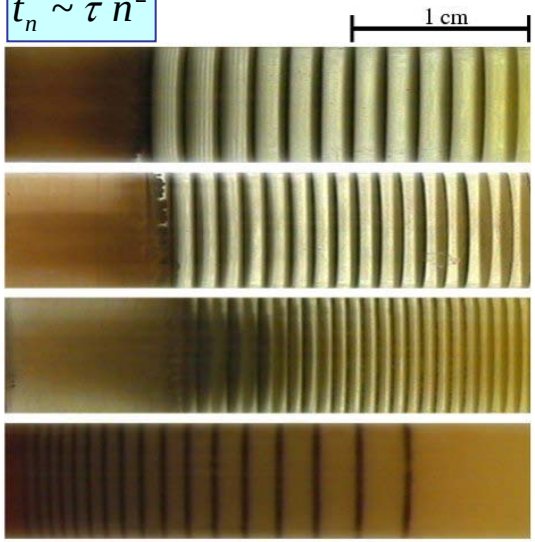
Front position: $x_n = \sqrt{2D_f t_n}$

Switching times: $t_n = \tau\, n^2 / 2$

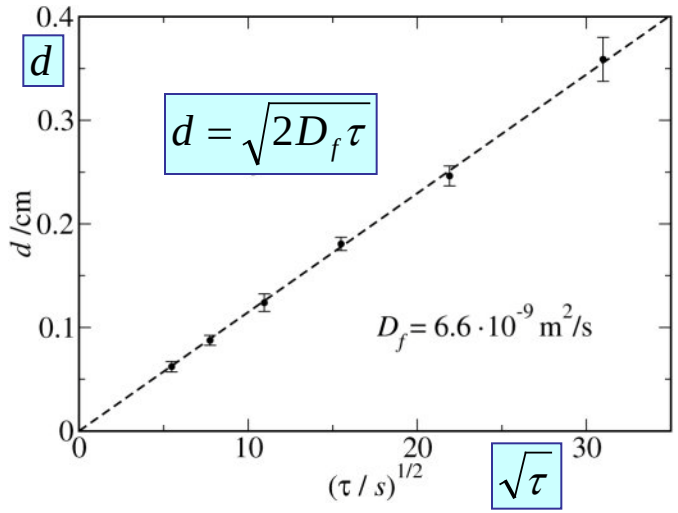
Period: $a = \sqrt{2D_f \tau}$

Periodic patterns
(I. Lagzi, A. Volford)

$t_n \sim \tau\, n^2$



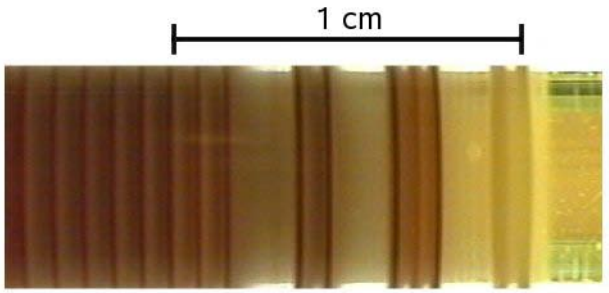
normal



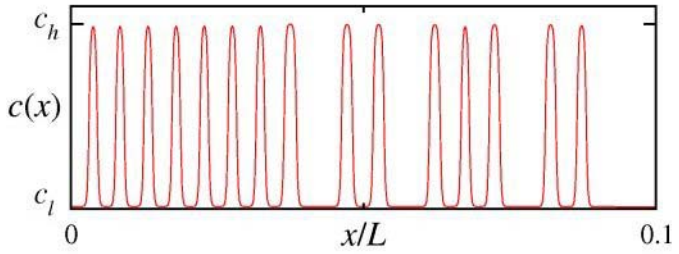
Periodic and designed patterns

$$2 \cdot AgNO_3 + K_2Cr_2O_7 \rightarrow Ag_2Cr_2O_7 + 2 \cdot KNO_3$$

2-3-2 pattern:



theory:



$d_{min} = ?$

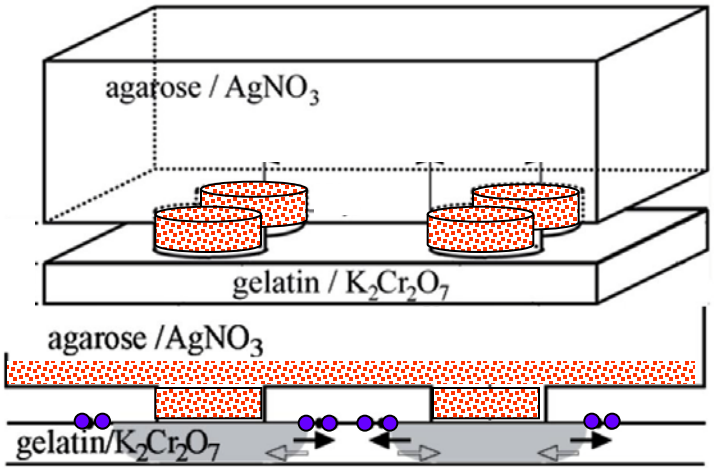
Possible problems:

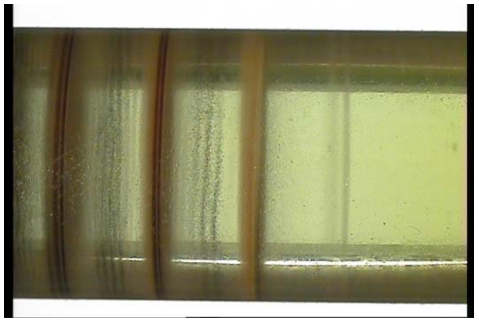
Width of the reaction zone,
noise (thermal, gel, impurities)

Relevant timescale:

L~10^{-6}m D~10^{-9}m^2/s → $\tau_{rel} \sim L^2/D \sim 10^{-3}$s

Secondary Liesegang patterns

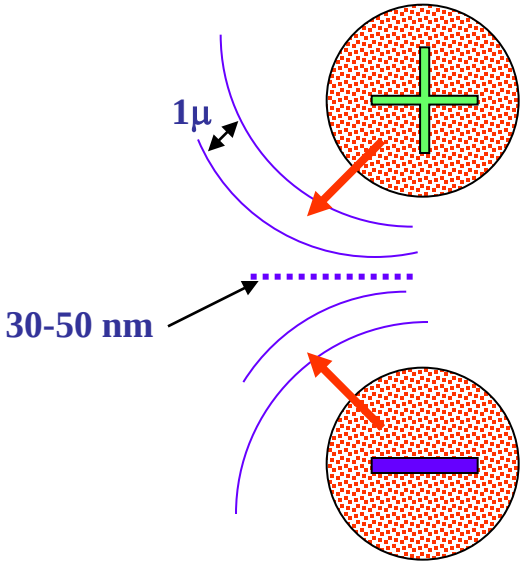


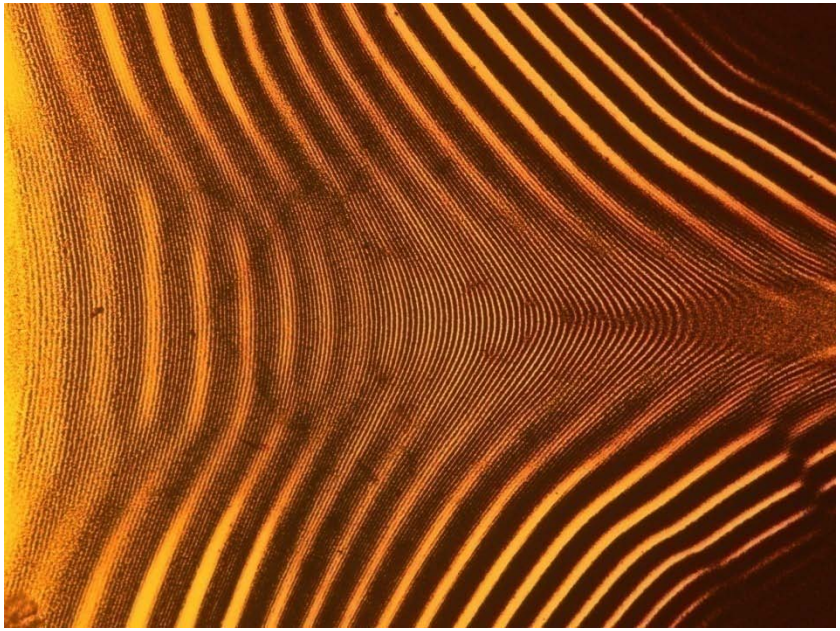


movie

AFM picture -- gelsurface

B.A. Grzybowski,
(Liesegang Workshop, Sils-Maria, 2006)

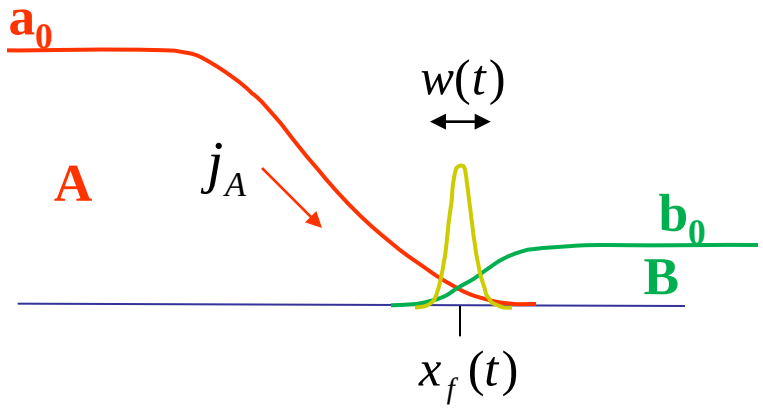




Problems with the fronts

(1) Width of the front:

$$w \sim \left(\frac{D^2}{k\ j_A} \right)^{1/3} \rightarrow w_0 \left(1 + a \frac{j_{el}/e}{j_A} \right)$$



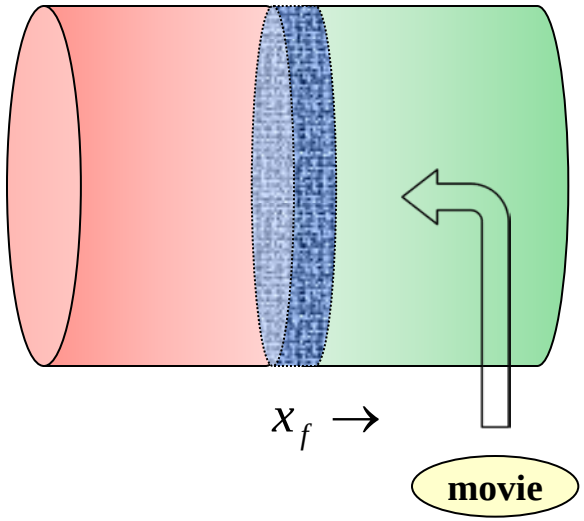
(2) Transvers instabilities in the front:

A + B → C

A + C → 0

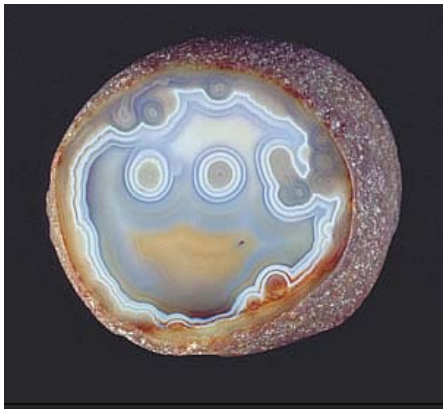
Transverse scale of patterns:

$$\ell(t) \sim \sqrt{t}$$



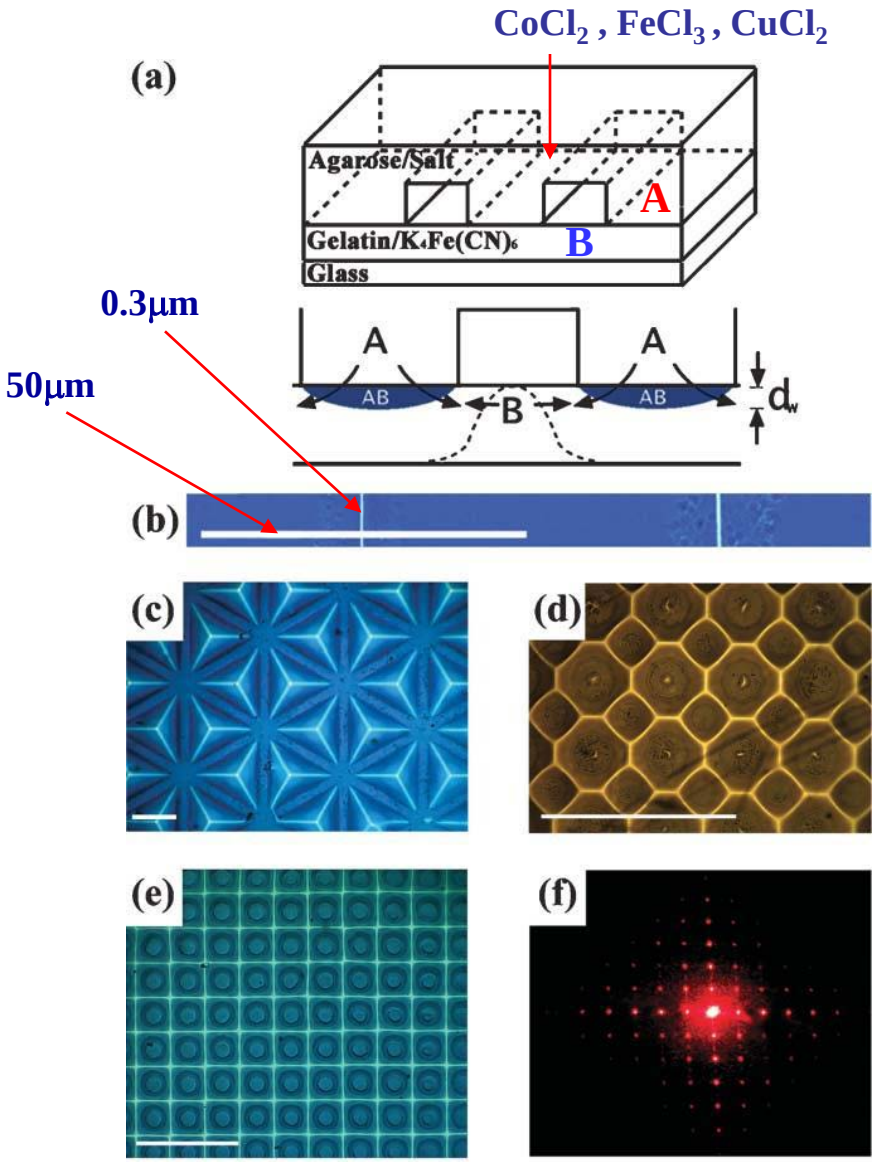
Thanks to:

L. Gálfi (Eötvös U., Budapest)
I. Lagzi --
K. Sas --
T. Antal (Harvard U.)
M. Droz (Geneva U.)
I. Bena --
K. Martens --
B. Chopard --
J. Magnin --
P. Hantz (EMBL Heidelberg)
M. Zrínyi (Technical U., Budapest)
A. Volford --
T. Unger --

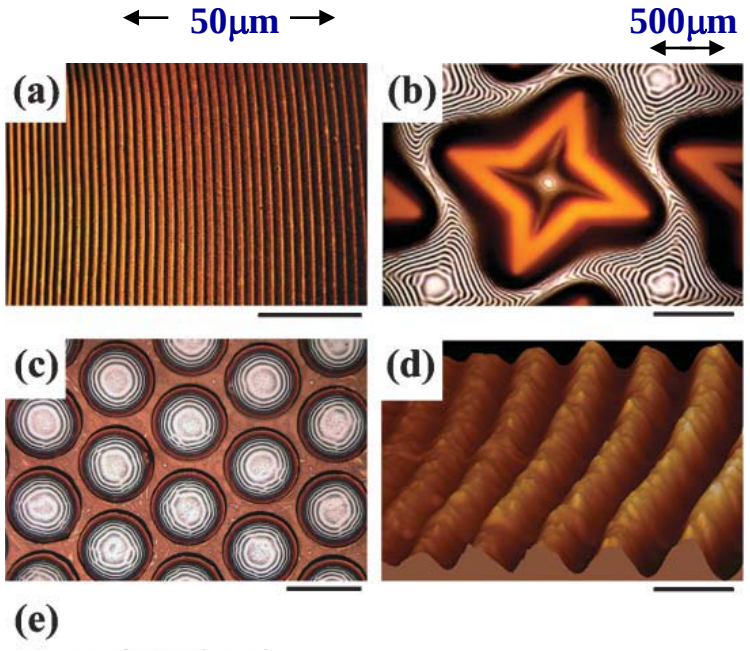


Wet stamping: Precipitation patterns at microscales

B.A. Grzybowski et al.
Northwestern University
Langmuir 21, 2637 (2005)
Nature Mater. 4, 93 (2005)



$AgNO_3$ + ($K_2Cr_2O_7$, KOH)



One can go down 1-2 orders of magnitude below lithographic scale.