

The Ostwald ripening phenomenon in reactive batch crystallizers and other chemical reaction processes

J.I. Díaz



Introduction.

Main subject: Non linear PDEs models arising in the dynamics of some chemical reactions giving rise to free boundaries

Part 1. Some periodic processes:

- a) The *Belousov-Zhabotinski* reaction.
- b) Periodic “dead cores” (Badii-Díaz (2010), Díaz-Ramos (2012))

Part 2. Asymptotic behaviour for large time: The Ostwald ripening phenomenon (Díaz–Gómez (2008, 2012)).

Part 1. Some periodic processes:

a) The *Belousov-Zhabotinski* reaction.



1930

Boris Pavlovich **Belousov** (1893 –1970)

Anatol Zhabotinsky (1938 –2008),

(Ph.D. student of S.E. Schnoll,
(Puschino, Rusia)

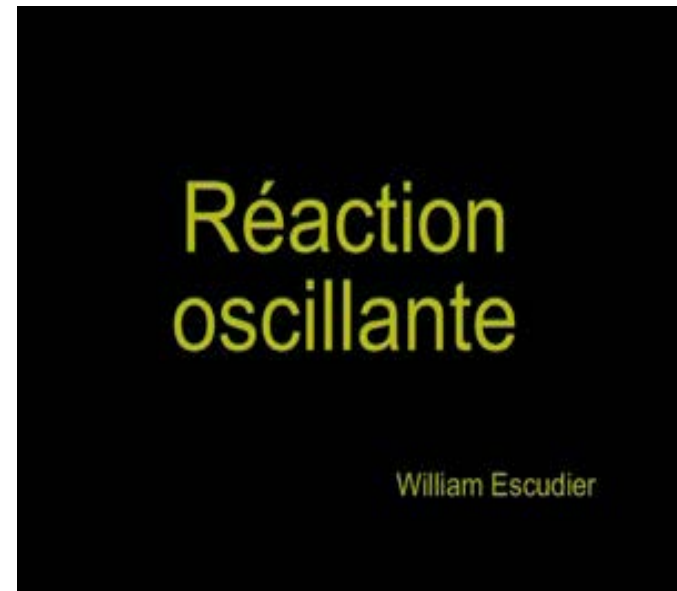


The Belousov-Zhabotinskii (BZ) reaction is an intriguing experiment that displays unexpected behavior. When certain reactants are combined, an “induction” period of inactivity is followed by sudden oscillations in color from red to blue. In spatially nonhomogeneous systems (such as a simple petri dish), the red and blue oscillations propagate as spiral wave fronts. The oscillations last about one minute and are repeated over a long period of time. Eventually, the reaction stops oscillating and approaches an equilibrium state. We now know

that the color changes are caused by alternating oxidation-reductions in which cerium changes its oxidation state from Ce(III) (producing a magenta solution) to Ce(IV) (producing a blue solution) or vice versa. Because of this, we call the BZ reaction an “oscillating reaction”; this simply means a reaction in which there is a regular, periodic change in the concentration of one or more reactants. Because this reaction is well understood, it is considered the prototype oscillator. An excellent, accessible reference for this material is [15].

- [15] S.K. Scott, *Oscillations, Waves, and Chaos in Chemical Kinetics*, Oxford Science Publications, Oxford, 1994.

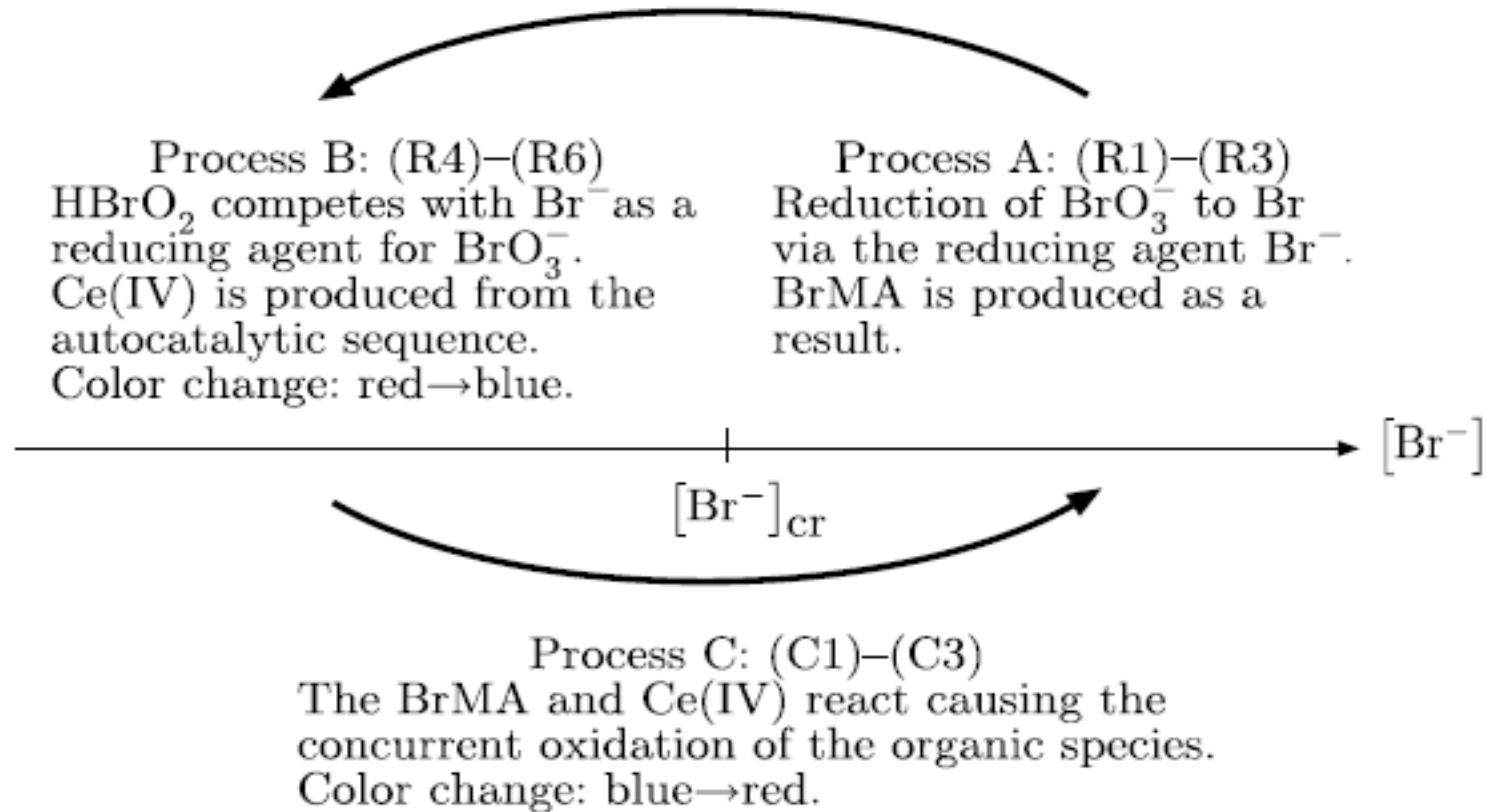
Some movies from Internet



Chemical processes

Table 2: Abbreviated FKN mechanism governing the BZ reaction.

	Reaction	Rate constant
(R1)	$\text{Br}^- + \text{HOBr} + \text{H}^+ \rightarrow \text{Br}_2 + \text{H}_2\text{O}$	$k_{\text{R1}} = 8 \times 10^9 \text{ M}^{-2} \text{ s}^{-1}$
(R2)	$\text{HBrO}_2 + \text{Br}^- + \text{H}^+ \rightarrow 2\text{HOBr}$	$k_{\text{R2}} = 10^6 \text{ M}^{-2} \text{ s}^{-1}$
(R3)	$\text{BrO}_3^- + \text{Br}^- + 2\text{H}^+ \rightarrow \text{HBrO}_2 + \text{HOBr}$	$k_{\text{R3}} = 2 \text{ M}^{-3} \text{ s}^{-1}$
(R4)	$2\text{HBrO}_2 \rightarrow \text{BrO}_3^-$	$k_{\text{R4}} = 2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$
(R5)	$\text{BrO}_3^- + \text{HBrO}_2 + \text{H}^+ \rightarrow 2\text{BrO}_2 \cdot + \text{H}_2\text{O}$	$k_{\text{R5}} = 10 \text{ M}^{-2} \text{ s}^{-1}$
(R6)	$\text{BrO}_2 \cdot + \text{Ce(III)} + \text{H}^+ \rightarrow \text{HBrO}_2 + \text{Ce(IV)}$	$k_{\text{R6}} = 6 \times 10^5 \text{ M}^{-2} \text{ s}^{-1}$
(C1)	$\text{CH}_2(\text{COOH})_2 \rightleftharpoons (\text{HO})_2\text{C} = \text{CHCOOH}$	see [7]
(C2)	$(\text{HO})_2\text{C} = \text{CHCOOH} + \text{Br}_2$ $\rightarrow \text{BrCH}(\text{COOH})_2 + \text{H}^+ + \text{Br}^-$	see [7]
(C3)	$2\text{Ce(IV)} + \text{CH}_2(\text{COOH})_2 + \text{BrCH}(\text{COOH})_2$ $\rightarrow f\text{Br}^- + \text{other products}$	see [7]



Mathematical modelling

$X = [\text{HBrO}_2]$ (hypobromous acid),
 $Y = [\text{Br}^-]$ (bromide)
 $Z = [\text{Ce(IV)}]$ (cerium-4)
 $A = [\text{BrO}_3^-]$ (bromate)
 $B = [\text{Org}]$ (organic species)
 $P = [\text{HOBr}]$.

	Reaction	Rate
(O1)	$A + Y \rightarrow X + P$	$k_3 = k_{R3}[\text{H}^+]^2 AY$
(O2)	$X + Y \rightarrow 2P$	$k_2 = k_{R2}[\text{H}^+]XY$
(O3)	$A + X \rightarrow 2X + 2Z$	$k_5 = k_{R5}[\text{H}^+]AX$
(O4)	$2X \rightarrow A + P$	$k_4 = k_{R4}X^2$
(O5)	$B + Z \rightarrow \frac{1}{2}fY$	k_0BZ

Nonlinear kinetics:

$$\begin{aligned}\frac{dX}{dt} &= k_3AY - k_2XY + k_5AX - 2k_4X^2, \\ \frac{dY}{dt} &= -k_3AY - k_2XY + \frac{1}{2}fk_0BZ, \\ \frac{dZ}{dt} &= 2k_5AX - k_0BZ.\end{aligned}$$

Dimensional analysis:

$$\begin{aligned}x &= \frac{X}{X_0}, & y &= \frac{Y}{Y_0}, & z &= \frac{Z}{Z_0}, & \tau &= \frac{t}{T_0}, \\ X_0 &= \frac{k_5A}{2k_4}, & Y_0 &= \frac{k_5A}{k_2}, & Z_0 &= \frac{(k_5A)^2}{k_4k_0B}, & T_0 &= \frac{1}{k_0B}.\end{aligned}$$

$$\varepsilon \frac{dx}{d\tau} = qy - xy + x(1 - x),$$

$$\delta \frac{dy}{d\tau} = -qy - xy + fz,$$

$$\frac{dz}{d\tau} = x - z,$$

Delta is the smaller parameter

$$y \approx \frac{fz}{q + x}.$$

$$\varepsilon \frac{dx}{d\tau} = x(1 - x) + \frac{f(q - x)}{q + x}z \equiv g(x, z),$$

$$\frac{dz}{d\tau} = x - z \equiv h(x, z).$$

$$\varepsilon = \frac{k_0 B}{k_5 A}, \quad \delta = \frac{2k_0 k_4 B}{k_2 k_5 A}, \quad q = \frac{2k_3 k_4}{k_2 k_5}.$$

In particular, if $[\text{H}^+] = 0.8 \text{ M}$ (pH = 0.097)

$$k_2 = 8 \times 10^5 \text{ M}^{-1} \text{ s}^{-1},$$

$$k_3 = 1.28 \text{ M}^{-1} \text{ s}^{-1},$$

$$k_4 = 2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1},$$

$$k_5 = 8.0 \text{ M}^{-1} \text{ s}^{-1}.$$

Initial data

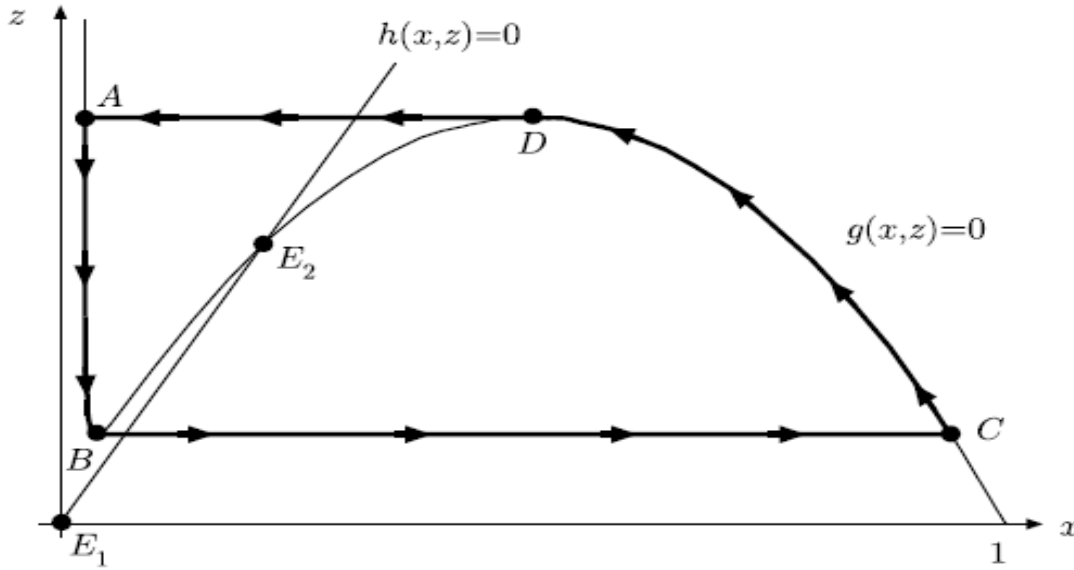
$$A_0 = [\text{BrO}_3^-](t=0) = 0.06 \text{ M}, \quad B_0 = [\text{Org}](t=0) = 0.02 \text{ M}, \\ k_0 = 1 \text{ M}^{-1} \text{ s}^{-1}.$$

$$\varepsilon = 4 \times 10^{-2}, \quad \delta = 4 \times 10^{-4}, \quad q = 8 \times 10^{-4}.$$

Equilibrium points

$$g(x, z) = 0 \iff z = x(1 - x) \frac{x + q}{(x - q)f}, \quad (10)$$

$$h(x, z) = 0 \iff z = x. \quad (11)$$

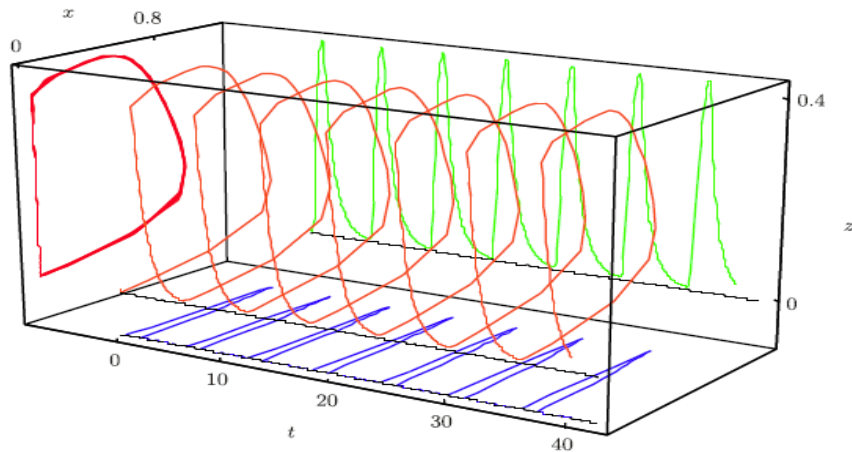


$$B: \quad x_B = (1 + \sqrt{2})q, \quad z_B = \frac{(1 + \sqrt{2})^2 q}{f}, \quad y_B = 1 + \frac{1}{\sqrt{2}},$$

$$D: \quad x_D = \frac{1}{2} - q, \quad z_D = \frac{1 + 4q}{4f}, \quad y_D = \frac{1}{2} + 2q,$$

$$A: \quad x_A = (1 + 8q)q, \quad z_A = \frac{1 + 4q}{4f}, \quad y_A = \frac{1}{8q},$$

$$C: \quad x_C = 1 - 6q, \quad z_C = \frac{(1 + \sqrt{2})^2 q}{f}, \quad y_C = (1 + \sqrt{2})^2 q.$$



$$f = 2/3, \quad \varepsilon = 4 \times 10^{-2},$$

$$q = 8 \times 10^{-4}.$$

It is (rigorously) shown that the system oscillates if

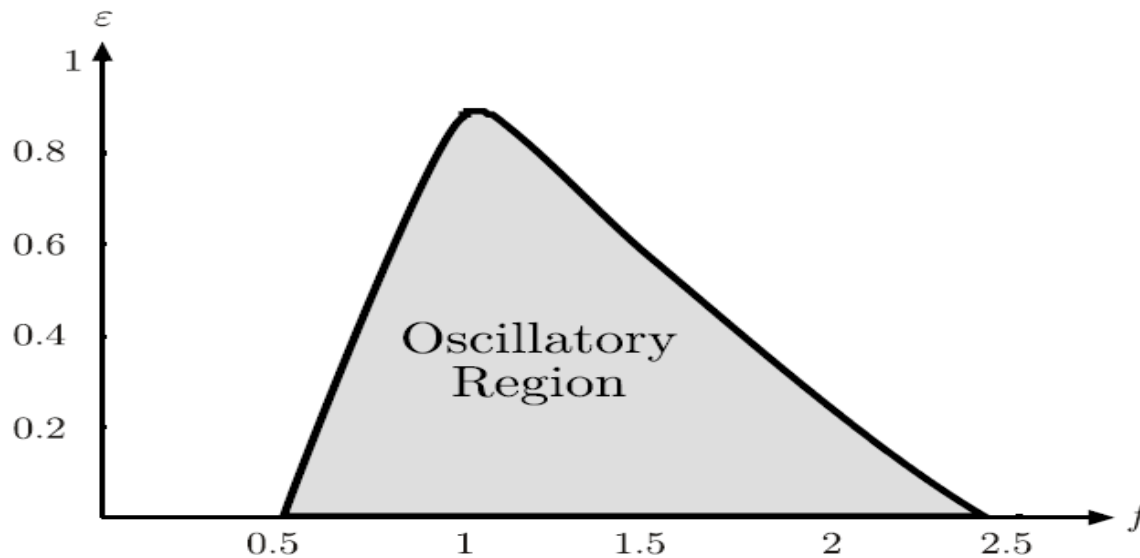
$$\frac{1 + 2q}{2 - 8q} < f < 1 + \sqrt{2} - (3 + 2\sqrt{2})q.$$

Hopf Bifurcation if

$$\varepsilon = 1 - 2x^* - \frac{2fqx^*}{(q + x^*)^2}.$$

Equilibrium (x^*, z^*)

$$(1 - x^*)(q + x^*) + f(q - x^*) = 0.$$



Numerical results: experiments

	Calculated	Experimental
Period	210 s	110 s
$[\text{Br}^-]_B = [\text{Br}^-]_{\text{cr}}$	$(1.71 \times 10^{-5})[\text{BrO}_3^-]$	$(2 \times 10^{-5})[\text{BrO}_3^-]$
$[\text{Br}^-]_A = [\text{Br}^-]_{\text{max}}$	$(1.6 \times 10^{-3})[\text{BrO}_3^-]$	$(6 \times 10^{-5})[\text{BrO}_3^-]$

A posterior stage (much harder) modern research focuses on the propagation of traveling waves and spirals for spatially inhomogeneous systems



A reference by the author, ...

C. Casal, J. I. Díaz and M. Stich, Control of turbulence in oscillatory reaction-diffusion systems through a combination of global and local feedback,

Physical Review E **76**, 1-9, 2007.

Part 1. Some periodic processes:

b. Periodic “dead cores”

M. Badii (†) and J.I. Díaz, On the time periodic free boundary associated to some nonlinear parabolic equations. *Boundary Value Problems*, Volume 2010, Article ID 147301,

$$(P) \begin{cases} u_t - \Delta_p u + \lambda f(u) = g & \text{in } Q := \Omega \times \mathbb{R}, \\ u(x, t) = h(x, t) & \text{on } \Sigma := \partial\Omega \times \mathbb{R}, \\ u(x, t + T) = u(x, t) & \text{in } Q. \end{cases}$$

(H_f) : $f \in C(\mathbb{R})$, $f(0) = 0$ and there exist two nondecreasing continuous functions f_1, f_2 such that $f_2(0) = f_1(0) = 0$ and

$$f_2(s) \leq f(s) \leq f_1(s), \forall s \in \mathbb{R},$$

(H_g) : $g \in C(\mathbb{R}; L^\infty(\Omega))$ and g is T -periodic,

(H_h) : $h \in C(\Sigma)$ and h is T -periodic.

Analogously, we can consider the doubly nonlinear diffusion-absorption equation

$$(P_b) \begin{cases} b(u)_t - \Delta_p u + \lambda f(u) = g & \text{in } Q := \Omega \times \mathbb{R}, \\ u(x, t) = h(x, t) & \text{on } \Sigma := \partial\Omega \times \mathbb{R}, \\ u(x, t + T) = u(x, t) & \text{in } Q, \end{cases}$$

$b \in C(\mathbb{R})$ is a nondecreasing function such that $b(0) = 0$

Sufficient conditions for the existence of a periodic free boundary

Together with problem (P) we consider the following stationary problems

$$(\underline{SP}) \begin{cases} -\Delta_p v + \lambda f_1(v) = g_1 & \text{in } \Omega, \\ v = h_1 & \text{on } \partial\Omega, \end{cases}$$

$$(\overline{SP}) \begin{cases} -\Delta_p w + \lambda f_2(w) = g_2 & \text{in } \Omega, \\ w = h_2 & \text{on } \partial\Omega, \end{cases}$$

$$g_1(x) \leq g(x, t) \leq g_2(x), \quad \forall t \in \mathbb{R}, \text{ a.e. } x \in \Omega,$$

$$h_1(x) \leq h(x, t) \leq h_2(x), \quad \forall (x, t) \in \Sigma.$$

Existence and uniqueness of weak solutions of (P)

$$W_{T\text{-per}} := \{u - h \in L^p(0, T; W_0^{1,p}(\Omega)), u_t - h_t \in L^q(0, T; W^{-1,p'}(\Omega)) \text{ and } u(., t + T) = u(., t) \forall t \in \mathbb{R} \}$$

Suitable modifications for (P_b): [Badii-Díaz \(2010\)](#).

Some previous general notations: Given $\varphi : Q \rightarrow \mathbb{R}$, $\varphi \in C([0, T] : L_{loc}^1(\Omega))$,
 $S(\varphi(., t)) = \text{support } \varphi(., t)$,
 $N(\varphi(., t)) = \overline{\Omega} - S(\varphi(., t))$ null set $\varphi(., t)$

Theorem 1. *Assume (H_f) , (H_g) , (H_h) and let $g_1, h_1 \geq 0$. Let $F_i(s) = \int_0^s f_i(s)ds$ and assume that*

$$\int_{0+} \frac{ds}{F_i(s)^{1/p}} < +\infty, i = 1, 2.$$

Then, if $u(x, t)$ denotes the unique periodic solution of problem (P) we have that $N(u_1) \supset N(u(., t)) \supset N(u_2) \forall t \in \mathbb{R}$. In particular, $N(u(., t))$ contains, at least, the set of $x \in N(h_2) \cup N(g_2)$ such that

$$d(x, \partial(N(h_2) \cup N(g_2))) > \Psi_{2,N}(\|u_2\|_{L^\infty(\Omega)})$$

where

$$\Psi_{2,N}(\tau) = \left(\frac{N(p-1)}{p} \right)^{1/p} \int_0^\tau \frac{ds}{F_2(s)^{1/p}}.$$

Nevertheless, if $\min_{\partial\Omega} h_1 \geq k > 0$ and if

$$R < \Psi_{1,1}(k),$$

then $N(u(\cdot, t))$ is empty since we have $0 < u_1(x) \leq u(x, t) \forall t \in \mathbb{R}$ and a.e. $x \in \Omega$. Here R is the radius of the smaller ball containing Ω and

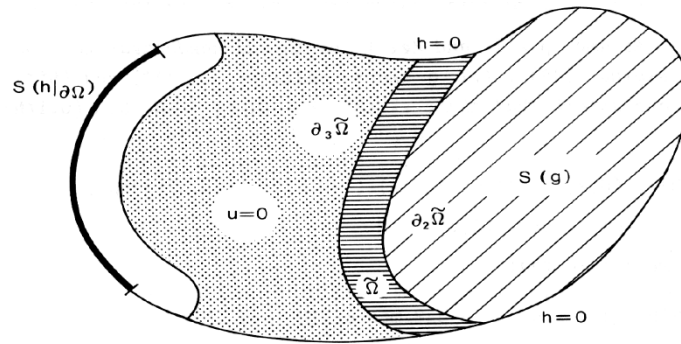
$$\Psi_{1,1}(\tau) = \left(\frac{(p-1)}{p} \right)^{1/p} \int_0^\tau \frac{ds}{F_1(s)^{1/p}}.$$

- Balance between the size of the domain and the « size » of the data.
- A different negative criterion (Vázquez 1986):

Theorem 2. Under assumptions (H_f) , (H_g) and (H_h) , if $g_1, h_1 \geq 0$ and

$$\int_{0+} \frac{ds}{F_1(s)^{1/p}} = +\infty,$$

then $N(u(\cdot, t))$ is empty.

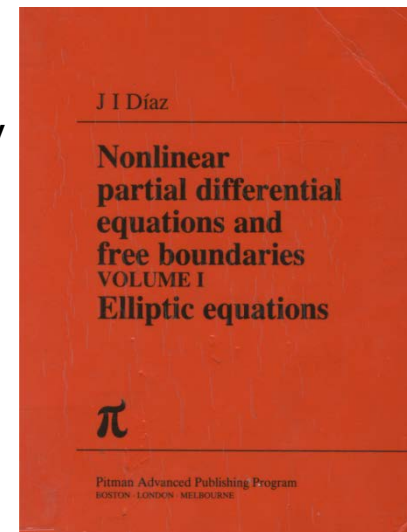
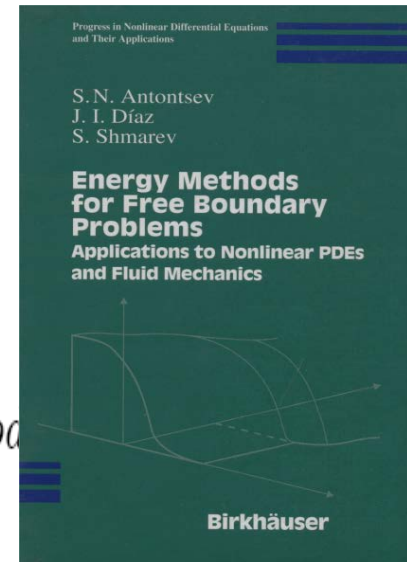


Lemma 1. Assume (H_f) , (H_g) and (H_h) . Let $u(x, t)$ be the unique periodic solution of (P) . Then

$$u_1(x) \leq u(x, t) \leq u_2(x), \forall t \in \mathbb{R} \text{ and a.e. } x \in \Omega.$$

Remarks

1. The above results apply to some ill-posed problems since they are established under a great generality which does not require a complete information on the equation neither on the type of boundary condition (for instance, it is enough to know some L^∞ estimates outside the support of the data). Neumann problem,...
2. Application under non-uniqueness of solutions (D-Hernández (1999), (2009),...



Remark 3.

The above energy method applies to suitable higher order equations of Cahn-Hilliard type (see details for the associated initial BVP in [Antontsev-Diaz-Shmarev \(2002\)](#)).

Periodical time connection between stationary episodes and on disconnected free boundaries (Díaz-Ramos (2012)).

It is possible to connect (in a finite time) two different solutions of the stationary problem

$$(SP) \begin{cases} -\Delta_p v + \lambda f(v) = g^* & \text{in } \Omega, \\ u = h^* & \text{on } \partial\Omega, \end{cases}$$

by means of a transient periodic solution of the associated parabolic problem (P) .

As example we have:

Theorem 4. Let $n = 1$, $\Omega = (-L, L)$ and $f(s) = |s|^{q-1} s$ with $q < p - 1$. Then the function

$$u(x, t) = C [|x| - \tau(t)]_+^{p/(p-1-q)}$$

with

$$\tau(t) = \begin{cases} l_0 + \frac{(l_1 - l_0)t}{t_1} & \text{if } 0 \leq t \leq t_1, \\ l_1 & \text{if } t_1 \leq t \leq t_2, \\ l_1 + \frac{(l_0 - l_1)(t - t_2)}{T - t_2} & \text{if } t_2 \leq t \leq T, \end{cases} \quad (1)$$

for some l_0, l_1 nonnegative given constants, $0 \leq t_1 \leq t_2 \leq T$, such that

$$\max\left\{\frac{(l_1 - l_0)}{t_1}, \frac{(l_0 - l_1)}{T - t_2}\right\} \leq \frac{C^{q-1}(\lambda - C^{(p-1-q)})(p - 1 - q)}{p},$$

is a T -periodic solution of problem (P) with $h(\pm L, t) = C(L - \tau(t))^{p/p-1-q} > 0$ and

$$g(x, t) = \left(\lambda C^q - \frac{p}{(p - 1 - q)} C \tau'(t) - C^{p-1} \right) [|x| - \tau(t)]_+^{pq/(p-1-q)}.$$

In particular, it connects the stationary solutions corresponding to the data

$$\begin{cases} g^*(x) = \left(\lambda C^q - \frac{p}{(p-1-q)} C \frac{(l_1-l_0)}{t_1} - C^{p-1} \right) [|x| - l_0]_+^{pq/(p-1-q)}, \\ h^*(\pm L) = C(L - l_0)^{p/p-1-q}, \end{cases}$$

and

$$\begin{cases} g^*(x) = (\lambda C^q - C^{p-1}) [|x| - l_1]_+^{pq/(p-1-q)}, \\ h^*(\pm L) = C(L - l_1)^{p/p-1-q}. \end{cases}$$

Exponent of the non-diffusion of the support, waiting time

[Álvarez-Díaz \(1993, 2003\)](#).

Remark. This behavior (heteroclinic connection in a finite time) is very exceptional: for instance it cannot hold in the case of linear parabolic problems. In particular, this solution can be used for different purposes in the study of controllability problems (see, e.g., Coron 2002).

We shall end this section by showing that it is possible to construct nonnegative periodic solutions of (P_b) giving rise to *disconnected free boundaries*, i.e. with free boundaries given by closed hypersurfaces of the space \mathbb{R}^{n+1} .

For instance, we have

Theorem 5. *Assume $\Omega = (-L, L)$, $f(s) = |s|^{q-1} s$ with $q < \min(1, p - 1)$. Let $u(x, t)$ be the unique T -periodic solution of problem (P) corresponding to data $h(\pm L, t)$ and $g(x, t)$*

$$0 \leq U(t) \leq h(\pm L, t) \leq C(L - \tau(t))^{p/(p-1-q)} + U(t)$$

and

$$G(t) \leq g(x, t) \leq \left(\frac{\lambda}{2} C^q - \frac{p}{(p-1-q)} C \tau'(t) - C^{p-1} \right) [|x| - \tau(t)]_+^{pq/(p-1-q)} + G(t),$$

with $\tau(t)$ given as before, with $0 \leq l_0 < l_1 = L$, $0 < t_1 < t_2 < T$, and $C > 0$ such that

$$\frac{(l_1 - l_0)}{t_1} \leq C^q \left(\frac{\lambda}{2} - C^{(p-1-q)} \right).$$

where $U(t)$ is given by

$$U(t) = \begin{cases} \underline{w}(t) & \text{if } t \in [0, t^*], \\ w(t; \varsigma, t^*) & \text{if } t \in [t^*, T], \end{cases} \quad (2)$$

with $\underline{w} \in C([0, t^*])$ such that $\underline{w}' \in L^1(0, t^*)$, $\underline{w} \geq 0$, $\underline{w}'(t) + \frac{\lambda}{2} f(\underline{w}) \geq 0$ on $(0, t^*)$, $\underline{w}(0) = 0$, $\underline{w}(t^*) = \varsigma$, (for some $\varsigma > 0$) and $w(t : \varsigma, t^*)$ the unique solution of the Cauchy problem

$$\begin{cases} w'(t) + \frac{\lambda}{2} f(w) = 0 & t > t^*, \\ w(t^*) = \varsigma, \end{cases}$$

for some $t^* \in (t_1, t_2)$. Here

$$G(t) = \begin{cases} 0 & \text{if } t \in [0, t_1], \\ \underline{w}'(t) + \frac{\lambda}{2} f(\underline{w}) & \text{if } t \in [t_1, t^*], \\ 0 & \text{if } t \in [t^*, t_2], \\ 0 & \text{if } t \in [t_2, T]. \end{cases}$$

Finally take $t_2 = t^* + \frac{2\Psi(\varsigma)}{\lambda}$, with

$$\Psi(\tau) := \int_0^\tau \frac{ds}{f(s)} \text{ for any } \tau > 0.$$

Then $U(t) \leq u(x, t) \leq C [|x| - \tau(t)]_+^{p/(p-1-q)} + U(t)$ on $\Omega \times \mathbb{R}$. In particular the null set $\cup_{t \in [0, T]} N(u(\cdot, t))$ has at least two connected components since it contains the set

$$\{(x, t) \in (-L, L) \times [0, t_1] : |x| \leq l_0 - \frac{l_0 t}{t_1}\} \cup \{(x, t) \in (-L, L) \times [t_2, T] : |x| \leq \frac{l_1}{T - t_2} (t - t_2)\},$$

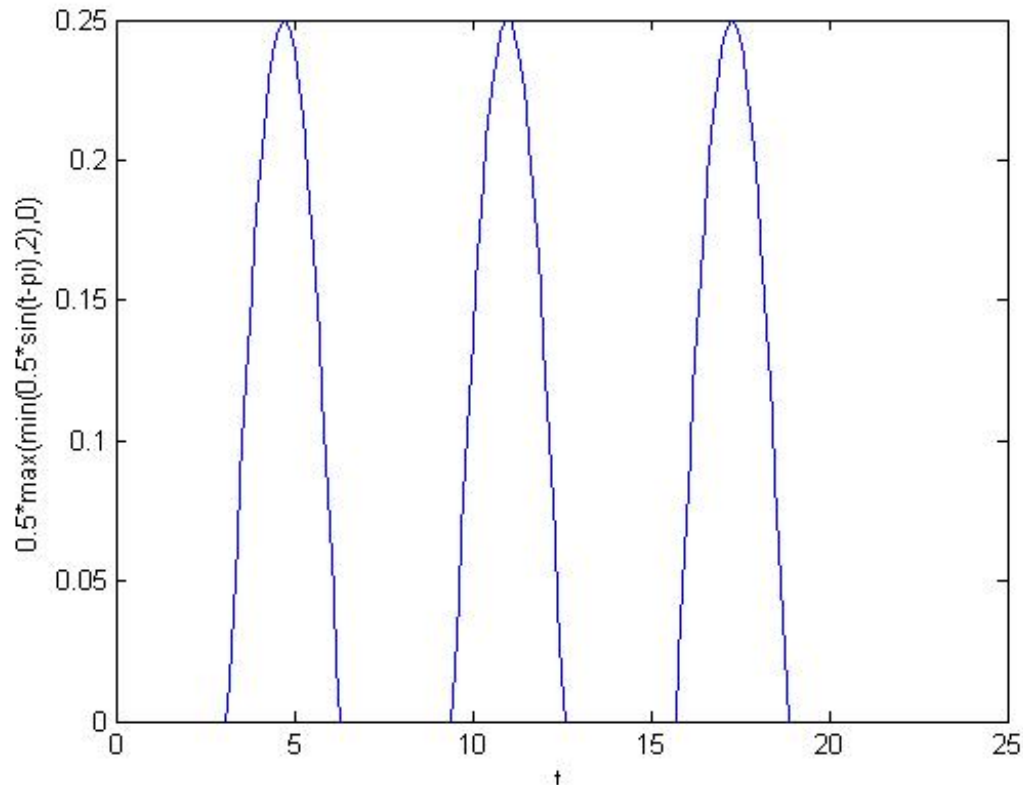
and $u(x, t) > 0$ on the set $(-L, L) \times (t_1, t_2)$.

Some numerical experiences

Disconnected support and reproductive periodic phenomena:

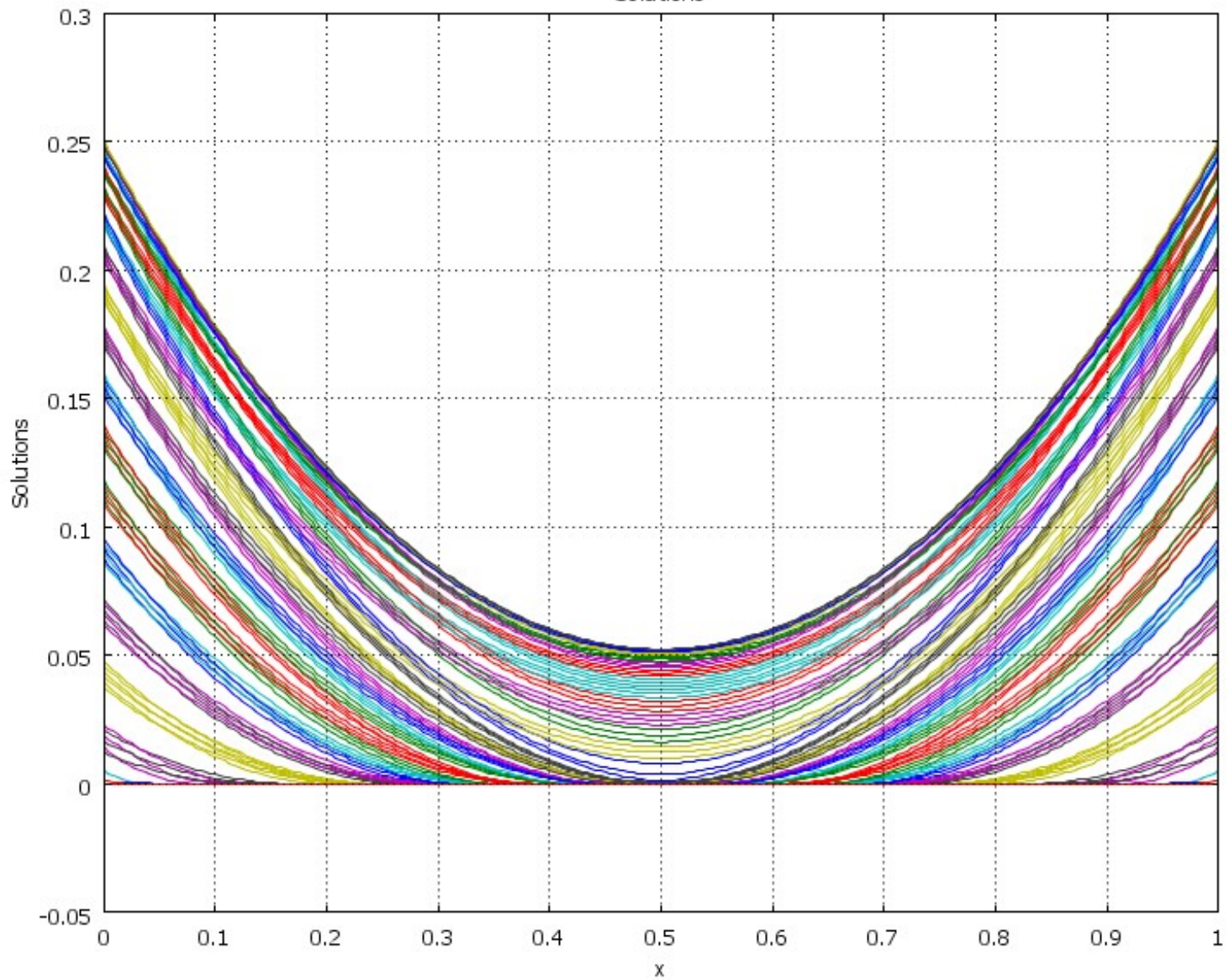
D-Ramos (2012).

Motivation: **Food Engineering** (intermittent heat treatment to reduce the period of maturation of beef: Valin-Koop (1978),..., Grajales-Ruiz (2004))

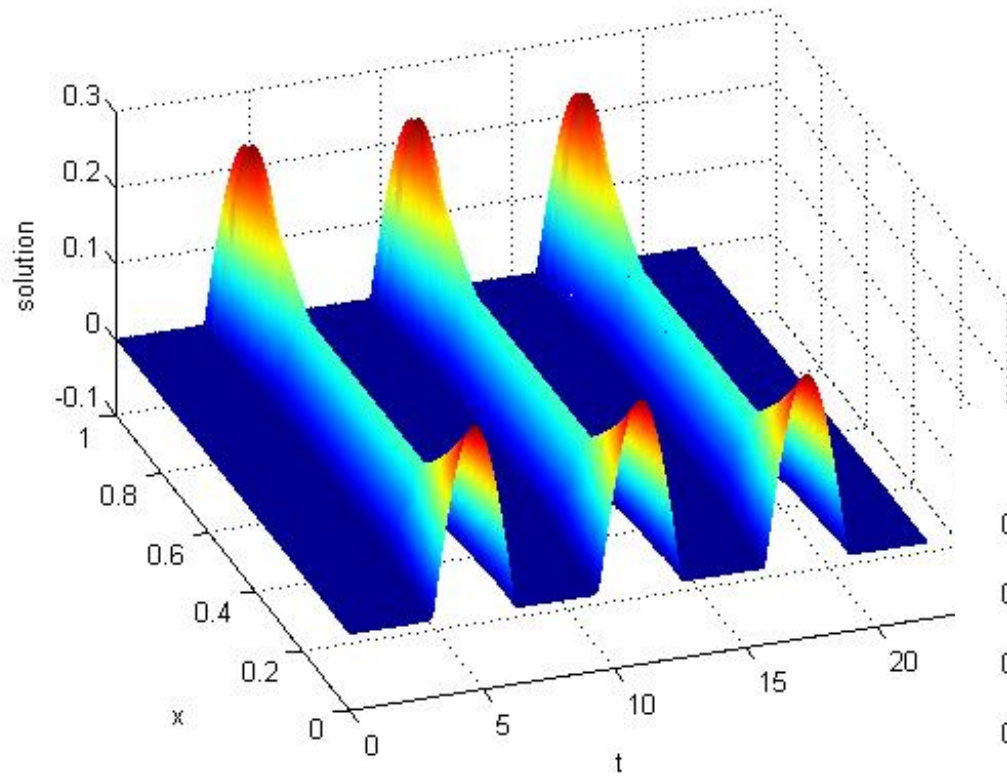


$g(t,x)=0$ and $f'(0) \uparrow \infty$

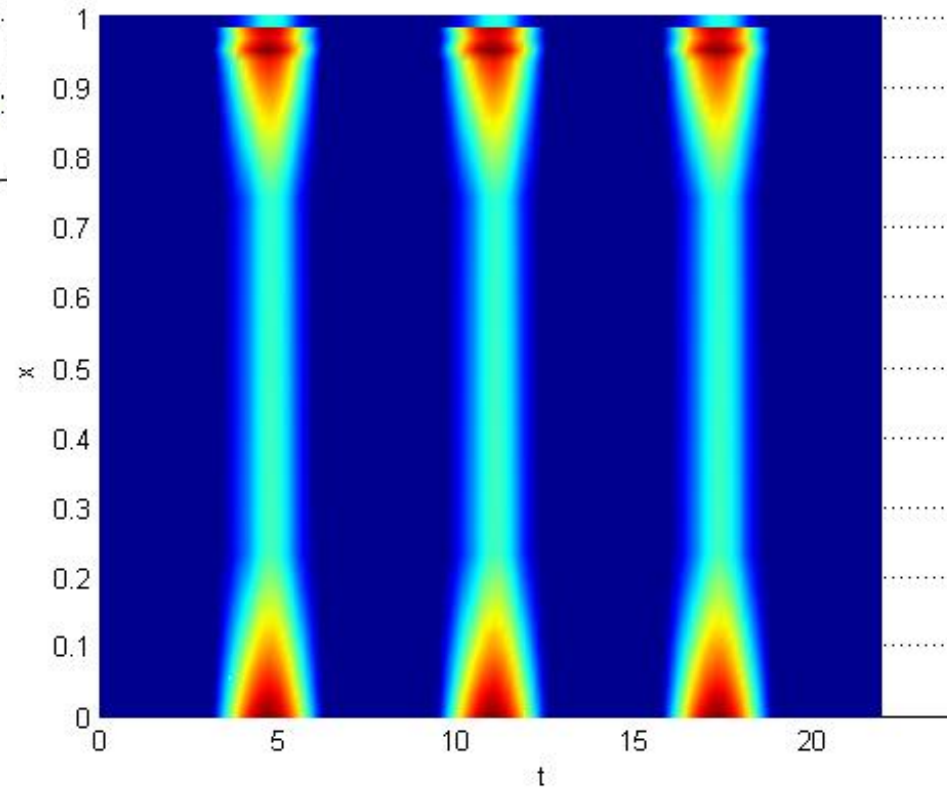
Solutions



Periodic solution: **reproductive phenomenon**



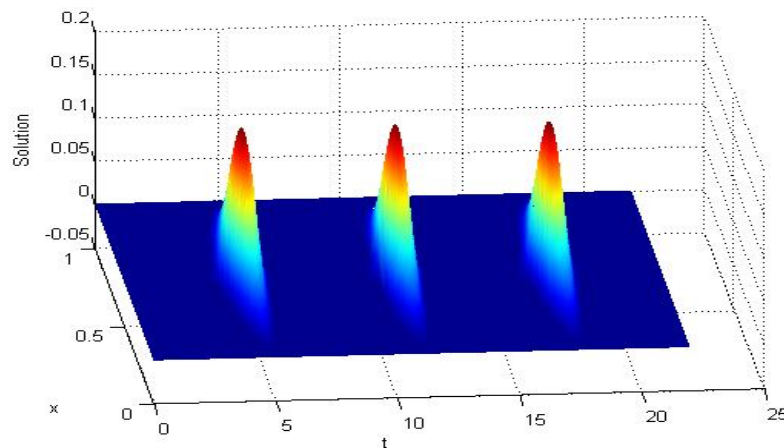
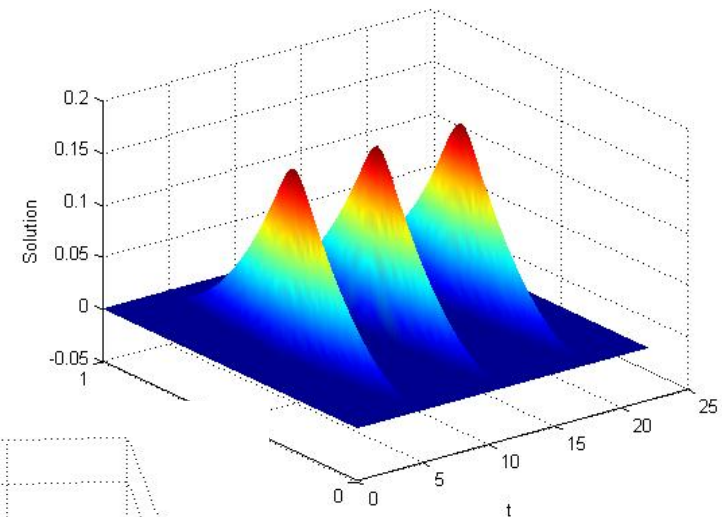
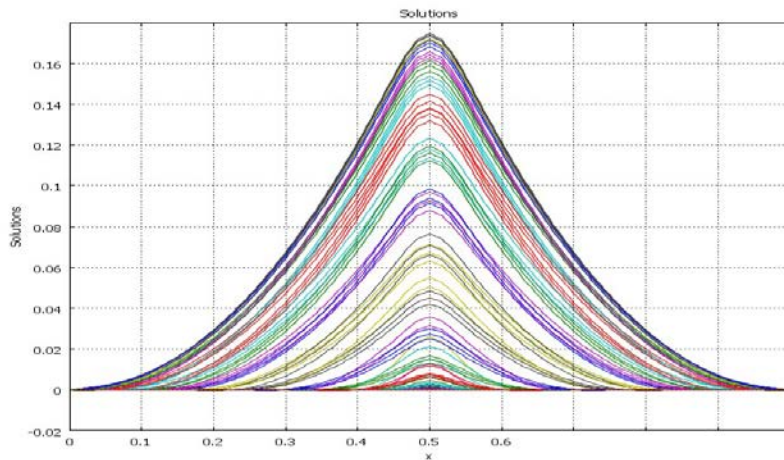
Disconnected support



Case of homogeneous boundary conditions and $g(t, \cdot)$ periodic and with compact support

$$g(x, t) = \max\left\{0, h(t) - k \left|x - \frac{1}{2}\right|\right\} \quad h(t) = 0.5 \max(0.5 \sin(t - \pi), 0).$$

$$\text{soporteg}(\cdot, t) = \left[\frac{1}{2} - \max\left(h(t) - \frac{k}{2}, 0\right), \frac{1}{2} + \max\left(h(t) - \frac{k}{2}, 0\right)\right] \subsetneq (0, 1)$$



Part 2. Asymptotic behaviour for large time: The Ostwald ripening phenomenon.

The study of the precipitation of crystals is a central issue in chemical engineering that has attracted the attention of specialists in many disciplines (including mathematics), especially after the pioneering work of the 1909 Nobel Prize F.W. Ostwald.

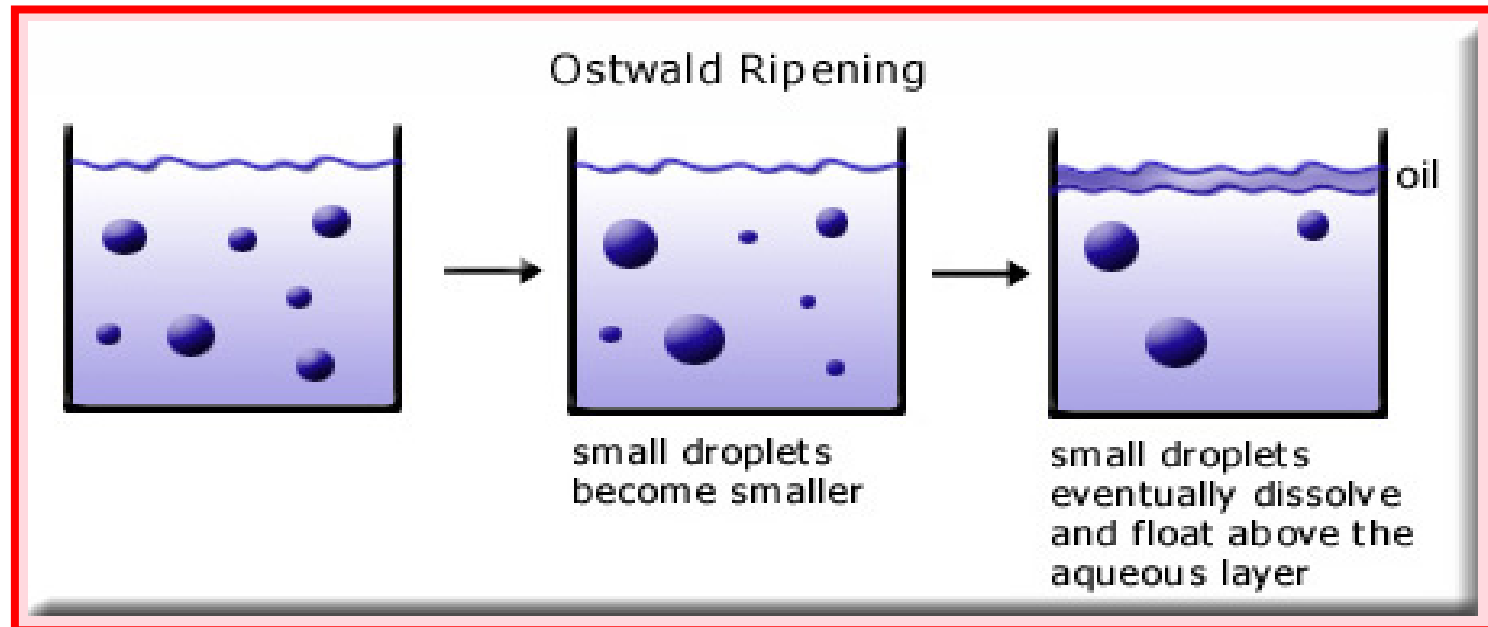
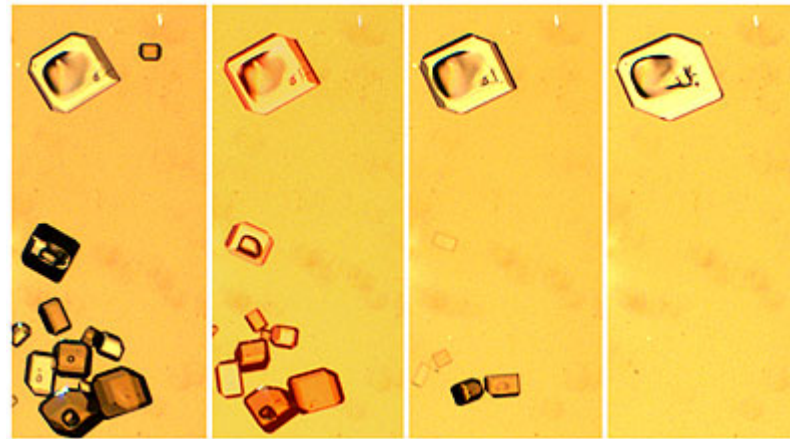


Friedrich Wilhelm **Ostwald** (1853-1932)

- Riga (Russian Empire, now capital of Letonia), Baltic German family.
- University of Dorpat (now Tartu University) until 1881.
- Riga Polytechnic Institute (1881-1887)
- University of Leipzig (1887-retirement 1906), professor of physical chemistry.

Painter, writer, philosopher, defender of the Esperanto

The so-called Ostwald ripening in crystallizing agents (persistence of a single crystal size as time goes on solutions that initially contain crystals of many other sizes).



Everyday examples:

- recrystallization in ice water (sandy texture, crunchy: larger ice crystals grow at the expense of smaller ice cream, creating a thicker texture), ...
- gastronomy: emulsions, ...
- Geology: megacrysts of feldspar (orthoclase), ...
- chemistry: the smaller crystals act as fuel for the growth of large crystals. solution synthesis of quantum dots, gravimetric analysis, ...
- manufacture of photographic film, ...

Several mathematical models can be introduced in this regard.

N.S. Tavaré, Simulation of Ostwald Ripening in a Reactive Batch Crystallizer, *AlchE J.* 33, (1985), 152-156.

L. Ratke and P.W. Voorhees, *Growth and Coarsening: Ostwald Ripening in Material Processing*. Springer. Berlin. 2002

A. Friedman, B. Ou and D.S. Ross, Crystal Precipitation with Discrete Initial Data, *J. Math. Anal. Appl.* 137, (1989), 576-590.

J.I. Díaz, R. Gómez, Measure-valued solutions to a nonlocal conservation law arising in crystal precipitation, *CEDyA*, 2008.

Simplified mathematical model: the number of crystals, is fixed. As we shall see; system of nonlinear ordinary differential equations.

A more realistic model leads to a problem in partial differential equations of first order (hyperbolic, nonlinear and nonlocal) in which the solution is given by the Dirac delta (worse than discontinuous functions): mathematics very sophisticated, more than initially expected.

Very opposite dynamics to the B-Z reaction:

the Ostwald ripening process ends (equilibrium is reached) completely or almost completely in a finite time (and not only asymptotically as $t \rightarrow +\infty$).

On Tavare's model with a prescribed number of crystals.

Given a volume of *solute* (a fluid containing an amount of dissolved matter), we denote by c^* the maximum solute saturation concentration (per unit volume of fluid in equilibrium) that the system can hold. If for some t the concentration $c(t)$ exceeds c^* , then the excess precipitates out in solid form, i.e., in crystal form.

We denote the edge of crystal grains by L (we assume that all crystal grains have the same shape and that they differ only in size). To simplify the modelling, we assume that all the grains are cubes with variable diameter and variable orientation. So, we assume that the distribution of grains of edge L is roughly uniform throughout the solution but that there are only a finite number of sizes grains L .

In fact, to get precipitation, $c(t)$ must be larger than a different quantity c_L ($c_L > c^*$), which also depends on the size L of the grain, and which is given by the Gibbs-Thomson relation,

$$c_L = c^* e^{\Gamma/L}$$

where Γ is a physical quantity that depends on the shape of the crystals, on its material properties, and on the temperature (which here is assumed fixed).

If $c(t) > c_L$, then material will come out of the solution and deposit onto the crystals characterized by L , but if $c(t) < c_L$ then material will dissolve from the crystals. It will be useful to introduce

$$L^*(t) = \frac{\Gamma}{\log \frac{c(t)}{c^*}}.$$

As usual in chemical engineering, the crystal size L will grow or dissolve according to some semi-empirical law, which here we assume given by the kinetics rate law

$$\frac{dL}{dt}(t) = G(L(t), c(t)) \quad (1)$$

where

$$G(L(t), c(t)) = \begin{cases} k_{\gamma}(c(t) - c^* e^{\Gamma/L(t)})^{\gamma} & \text{if } L(t) > L^*(t), \\ -k_{\delta}(c^* e^{\Gamma/L(t)} - c(t))^{\delta} & \text{if } L(t) < L^*(t). \end{cases} \quad (2)$$

Let us mention that here, we are assuming merely that $\gamma > 0$ and $\delta > 0$ (in contrast with some other previous studies where it is supposed that $\gamma \geq 1$ and $\delta \geq 1$: see, e.g. [Friedman-Hu-Ross 1989])

We mention that it is well known (see, e.g. [Aris 1975]) that in many chemical reactions the kinetics leads to exponents $\gamma \in (0, 1)$ and $\delta \in (0, 1)$. As a matter of fact, the limit cases $\gamma = 0$ and $\delta = 0$ are also relevant in the applications [Aris 1975] but they must be suitably formulated in terms of multivalued maximal monotone graphs [Díaz 1985] but we shall not discuss them here. On the rest of parameters, k_γ , k_δ , Γ and c^* , we assume that they are given positive numbers.

So, we recall that

if $c(t) > c_L$ (or, equivalently, $L(t) > L^*(t)$) then $\frac{dL}{dt}(t) > 0$, i.e. the crystal

if $c(t) < c_L$ (or, equivalently, $L(t) < L^*(t)$) then $\frac{dL}{dt}(t) < 0$, i.e. the crystal

As mentioned before, we assume that initially there are N different sizes of crystals which are characterized by their sizes $L = x_j^*$, and in numbers μ_j^* per unit volume. We assume that

$$0 < x_1^* < x_2^* < \dots < x_N^*.$$

These crystal sizes will then evolve in time to $x_1(t) < x_2(t) < \dots < x_N(t)$, according to the above rate law (1), but we rewrite now as

$$\frac{dx_j}{dt}(t) = G(x_j(t), c(t)). \quad (3)$$

Thus, the solute concentration $c(t)$, at time t , is given by

$$c(t) := c_0 + \rho k_v \sum_{j=1}^N \mu_j^*(x_j^*)^3 - \rho k_v \sum_{j=1}^N \mu_j^*(x_j(t))^3,$$

where c_0 denotes the initial concentration, k_v is a geometric parameter connecting L^3 to the crystal volume (in the case of cubic crystals, $k_v = 1$), and ρ is the mass density of the solid phase.

If we substitute $c(t)$ into (3), we obtain a self-contained system of differential equations (i.e. without the $c(t)$ dependence)

$$\frac{dx_j}{dt}(t) = G_j(x_1(t), \dots, x_N(t)), \quad j = 1, \dots, N.$$

We recall that we are denoting the initial conditions as $x_j(0) = x_j^*$. For the sake of the notation it is useful to introduce

Note that \widehat{c}_0 represents the total amount of concentration per unit volume in either crystal or solution form.

It turns out that some typical physical constants are $c^* = 4 \times 10^{-6} \text{ kmol/m}^3$, $\Gamma = 4 \times 10^{-9} \text{ m}$, $\rho = 6473 \text{ kg/m}^3$, $k_\gamma = k_\delta = 5 \times 10^{-2}$, and $c_0 = 1.05c^*$, $x^* = 10^{-7} \text{ m}$ or 10^{-8} m and $\mu = 10^{19}$ or 10^{16} ([Tavare 1985]).

Note also that for $N = 2$ the problem can be reformulated as the nonlinear ODEs system

$$\begin{cases} \frac{dx_1}{dt} + |f_1(x_1, x_2)|^{\delta-1} f_1(x_1, x_2) = 0 \\ \frac{dx_2}{dt} + |f_2(x_1, x_2)|^{\delta-1} f_2(x_1, x_2) = 0 \\ x_1(0) = x_{0,1} \\ x_2(0) = x_{0,2} \end{cases}$$

where $\delta > 0$ (here we are assuming $\gamma = \delta$ for simplicity) and

$f_i(x_1, x_2) = \mu_1 x_1^3 + \mu_2 x_2^3 + e^{\Gamma/x_i} - \widehat{c}$ for $i = 1, 2$ and for some positive constants μ_1, μ_2, Γ and \widehat{c}

Crystals of single size

Let us start by considering the situation when all crystal grains have initially the same size x^* . Thus, $N = 1$ and we get

$$\frac{dx}{dt}(t) = G(x(t)), \quad (4)$$

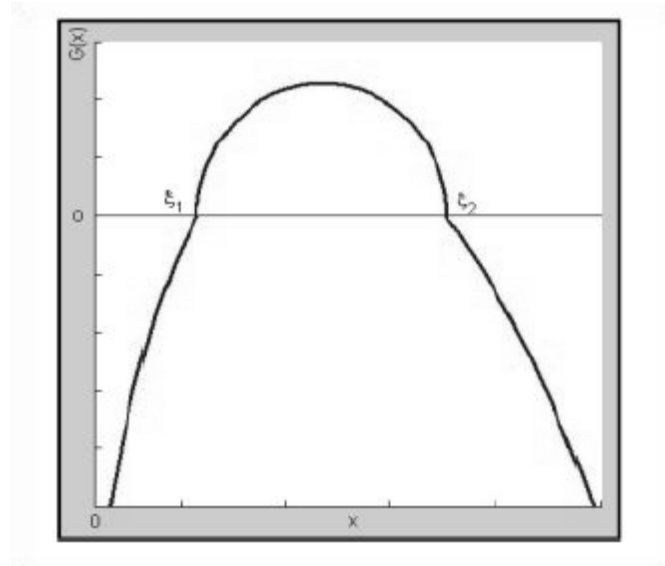
$$G(x) = \begin{cases} k_\gamma(\hat{c}_0 - \mu x^3 - c^* e^{\Gamma/x})^\gamma & \text{if } \hat{c}_0 - \mu x^3 > c^* e^{\Gamma/x}, \\ -k_\delta(c^* e^{\Gamma/x} - (\hat{c}_0 - \mu x^3))^\delta & \text{if } \hat{c}_0 - \mu x^3 < c^* e^{\Gamma/x}. \end{cases} \quad (5)$$

The values of x where G changes sign will play a crucial role. They are given through the equation

$$\mu x^3 + c^* e^{\Gamma/x} = \hat{c}_0. \quad (6)$$

Lemma 1. *There exist at most two positive solutions $\tilde{\zeta}_1$ and $\tilde{\zeta}_2$ (with $\tilde{\zeta}_1 \leq \tilde{\zeta}_2$) of (6).*

Proof. It is enough to check that function $f(x) := \mu x^3 + c^* e^{\Gamma/x}$ has a positive second derivative for $x > 0$, and that $f(x) \rightarrow \infty$ if $x \rightarrow 0$ and if $x \rightarrow \infty$.



Equation (6) may have no positive solutions, but for definiteness we concentrate in the rest of this lecture on the case where there are two distinct positive solutions. The following results can be obtained

- Theorem 1.** *i) If $x^* = \zeta_2$ then the solution of (4) is $x(t) = x^*$. If $x^* = \zeta_1$ then $x(t) = x^*$ is a solution of (4) (which, in fact, it is the only one if $\gamma \geq 1$ and $\delta \geq 1$).*
- ii) If $x^* > \zeta_2$ then $x(t)$ is strictly decreasing and $\lim_{t \rightarrow \infty} x(t) = \zeta_2$ (with $x(t) = \zeta_2$ after a finite time if $\delta \in (0, 1)$).*
- ii) If $x^* \in (\zeta_1, \zeta_2)$ then $x(t)$ is strictly increasing and $\lim_{t \rightarrow \infty} x(t) = \zeta_2$ (with $x(t) = \zeta_2$ after a finite time if $\gamma \in (0, 1)$).*
- iii) If $x^* \in (0, \zeta_1)$ then $x(t)$ is strictly decreasing for some interval $[0, t_0]$ and then $x(t_0) = 0$ with $\lim_{t \rightarrow t_0} \frac{dx}{dt}(t) = -\infty$.*

Remarks 1. Note that part iii) of Theorem 1 asserts that the crystal's size will decrease to zero in a finite time t_0 . So, it means that the crystal is entirely dissolved in the solution (note that there is no differential equation once that $x(t) = 0$).

2. The proof of the existence and uniqueness (for $x^* \neq \zeta_1$) of the solution uses the decomposition of G as a locally Lipschitz function + monotone function and the different sign of $\frac{dx}{dt}(t)$ according the initial condition x^* (see, e.g. [Di-Thelin 1994] for some related results).

3. A singularity on $\frac{dx}{dt}(t)$ arises at the extinction time t_0

$$t_0 = \int_0^{x^*} \frac{ds}{G(s)}.$$

Crystals of several (prescribed) sizes

We consider now the general case of many crystals but with only N different sizes. We shall always assume that the initial concentration is larger than the critical concentration c^*

$$c_0 > c^*. \quad (7)$$

Lemma 2. *Assumption (7) implies that $c(t) > c^*$ for any $t > 0$.*

Proof. Indeed, if for some t_1 we have $c(t_1) = c^*$ then $\frac{dc}{dt}(t_1) \leq 0$. But, on the other hand,

$$\frac{dc}{dt}(t) = -3 \sum_{j=1}^N \mu_j(x_j(t))^2 \frac{dx_j}{dt}(t) = -3 \sum_{j=1}^N \mu_j(x_j(t))^2 G(x_j(t), c(t)) > 0, \quad (8)$$

which leads to a contradiction at $t = t_1$.

Lemma 3. We $c(t) < \hat{c}_0 := c_0 + \rho k_v \sum_{j=1}^N \mu_j^* (x_j^*)^3$ for any $t > 0$.

Moreover $x_N(t) \leq \left(\frac{\hat{c}_0}{\mu_N}\right)^{1/3}$ for any $t > 0$.

Proof. Use the definition of $c(t)$.

Lemma 4. The ordering size among the crystals $x_1(t), \dots, x_N(t)$ remains to hold as long they are positive.

Proof. From the equations, we get that

$$\frac{d}{dt}(x_{j+1}(t) - x_j(t)) = G(x_{j+1}(t), c(t)) - G(x_j(t), c(t)) > 0,$$

and so $x_{j+1}(t) - x_j(t)$ is a strictly monotone increasing function.

Remark. As mentioned before, the curve $x = L^*(t) := \frac{\Gamma}{\log \frac{c(t)}{c^*}}$ determines whether a crystal grows or shrinks ($x_j(t) > L^*(t)$ implies that $x_j(t)$ is growing, whereas if $x_j(t) < L^*(t)$ then $L^*(t)$ is shrinking).

We denote by $k = k(t)$ the maximal number of crystal sizes that have disappeared in finite time (obviously it will change with the time t). So if we for a given time $t^* > 0$, for $t > t^*$ it remains only crystal grains with sizes $x_{k+1}(t), x_{k+2}(t), \dots, x_N(t)$.

Theorem 2. *All crystals, except at most $x_N(t)$, will dissolve in finite time, i. e., $k + 1 \geq N$ for t large enough.*

Proof. We argue by contradiction: assume, that $k + 1 < N$. We start by proving that $x_N(t)$ can intersect the curve $x = L^*(t)$ at most once. Indeed, let $t = t_N$ the first instant in which $x_N(t) = L^*(t)$. Then

$$\frac{dx_N}{dt}(t_N) = G(x_N(t_N), c(t_N)) = 0,$$

whereas, from (8)

$$\frac{dL^*}{dt}(t_N) < 0 \text{ since } \frac{dc}{dt}(t_N) < 0.$$

Thus, for some $t_N > t^*$ either

$$x_N(t) > L^*(t) \text{ for all } t > t_N \tag{9}$$

or

$$x_N(t) < L^*(t) \text{ for all } t > t_N. \tag{10}$$

In the last case (10) $\frac{dx_N}{dt}(t_N) < 0$ for all $t > t_N$ whereas in the first case (9) $\frac{dx_N}{dt}(t_N) > 0$ for all $t > t_N$.

In both cases $\lim_{t \rightarrow \infty} x_N(t)$ exists ($x_N(t)$ is bounded, by Lemma 3).

Moreover, from Lemma 4, with $j + 1 = N$, it follows that $\lim_{t \rightarrow \infty} x_{N-1}(t)$ also exists, and similarly $\lim_{t \rightarrow \infty} x_j(t)$ exists for all $N > j > k + 1$.

From the definition of $c(t)$ it also follows that the limit $\lim_{t \rightarrow \infty} c(t)$ exists.

We can define

$$x_j(\infty) = \lim_{t \rightarrow \infty} x_j(t) \text{ and } c(\infty) = \lim_{t \rightarrow \infty} c(t).$$

Again, by Lemma 4 we know that

$$x_{k+1}(\infty) < x_N(\infty).$$

Hence

$$G(x_{k+1}(\infty), c(\infty)) < G(x_N(\infty), c(\infty)).$$

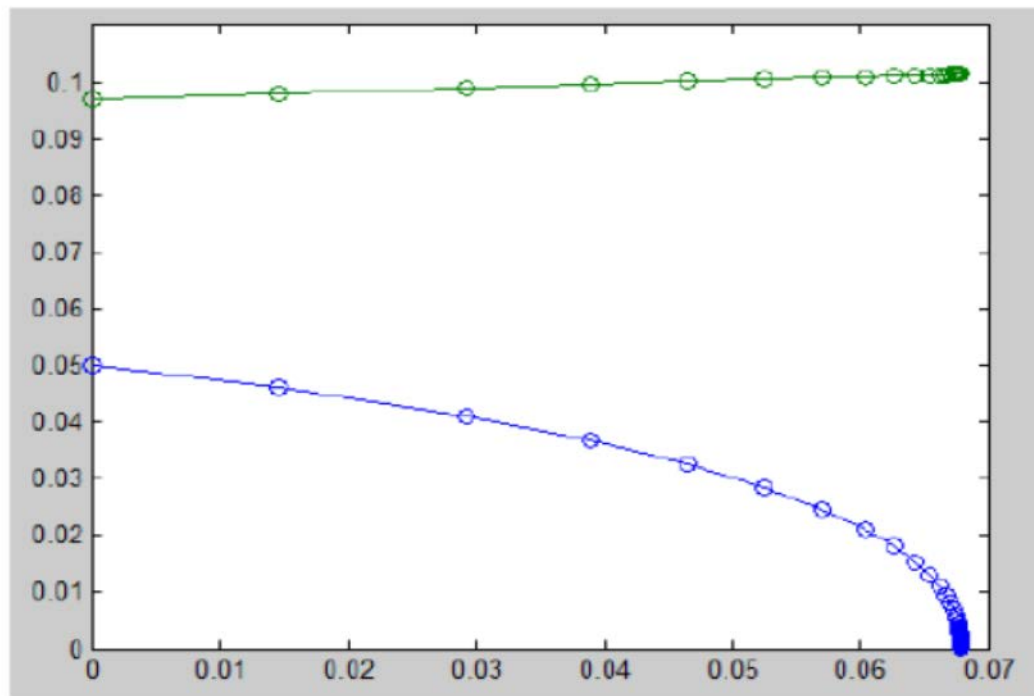
Assume that $\eta := G(x_{k+1}(\infty), c(\infty)) \neq 0$ (the same argument can be reproduced if $G(x_N(\infty), c(\infty)) \neq 0$). Thus, for large values of t

$$\frac{dx_{k+1}}{dt}(t_N) = G(x_{k+1}(t), c(t)) \sim \eta,$$

and thus we deduce that $\lim_{t \rightarrow \infty} x_{k+1}(t)$ does not exist, which is a

contradiction.

As conclusion, we now know that $x_1(t)$ dissolves in time τ_1 , $x_2(t)$ dissolves in time τ_2 , ..., $x_{N-1}(t)$ dissolves in time τ_{N-1} . For $t > \tau_{N-1}$ we are back into the one-size crystals situation studied before. Moreover $x_N(t)$ attains its asymptotic value in *a finite time* if $\delta \in (0, 1)$ or $\gamma \in (0, 1)$ according if $\frac{dx_N}{dt}(t)$ is negative or positive after τ_{N-1} . Numerical methods allow us to compute the limiting size of the crystals.



**Thanks for
your attention**