Finite-time breakdown of chemical precipitation patterns

Potsdam, April 4, 2019

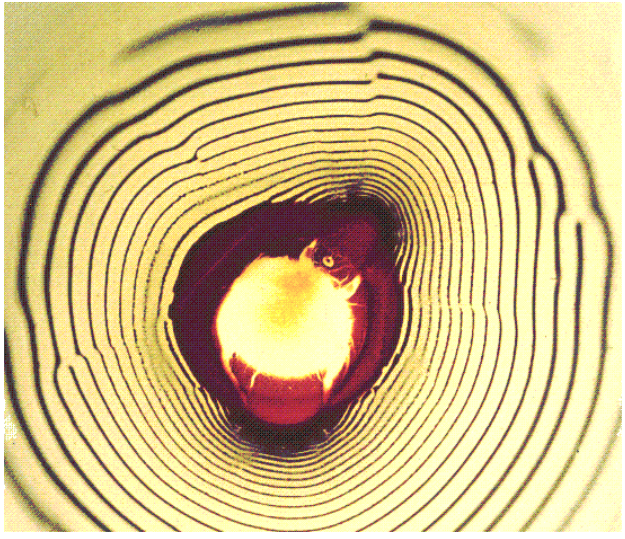
Marcel Oliver

Joint work with Zymantas Darbenas and Rein van der Hout

Plan

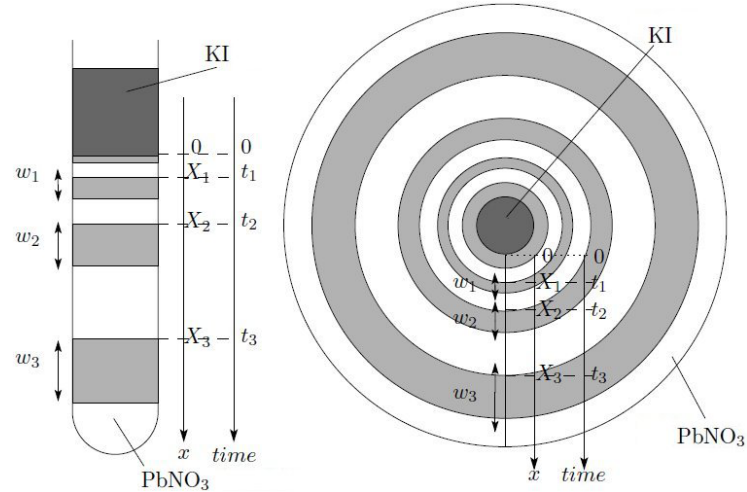
1. Liesegang rings
2. The Keller–Rubinow model in the fast reaction limit
3. Self-similar solution
4. Breakdown of solutions to a simplified model
5. On the uniqueness of the full model
6. Long-time asymptotics

1. Liesegang rings



http://upload.wikimedia.org/wikipedia/commons/6/66/Liesegangrings.jpg
http://facstaff.elon.edu/jkarty/researchinterests.htm

2. Scaling laws



(From Hilhorst, van der Hout, Mimura, and Ohnishi, 2009)

$$\frac{X_{n+1}}{X_n} \to 1 + p \text{ with } p > 0 \qquad X_n \sim \sqrt{t_n} \qquad w_n \sim X_n^{\alpha} \text{ with } \alpha > 0$$

(spacing law) (time law) (width law)

3. Modeling

Post-nucleation theories – not considered here

- Structures develop through competitive growth, similar to Ostwald ripening
- Spurious spiral patterns in 2D

Pre-nucleation theories (e.g. Keller–Rubinow, 1981)

$$A + B \to C \to D$$

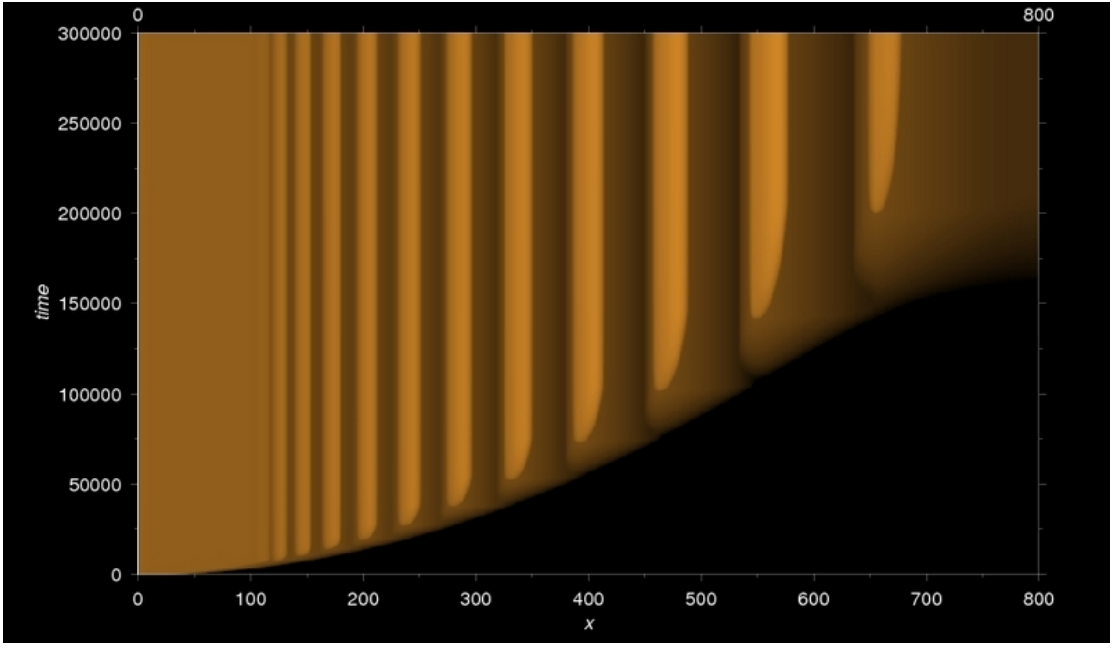
leads to a system of reaction-diffusion equations

$$\begin{aligned} a_t &= \nu_a \, \Delta a - k \, ab \\ b_t &= \nu_b \, \Delta b - k \, ab \\ c_t &= \nu_c \, \Delta c + k \, ab - P(c, d) \\ d_t &= P(c, d) \end{aligned}$$

Supersaturation function

$$P(c, d) = \begin{cases} 0 & \text{if } d = 0 \text{ and } c < c^{\top} \\ \lambda \, (c - c^{\perp})_+ & \text{if } d > 0 \text{ or } c \geq c^{\top} \end{cases}$$

4. Space-time visualization



Numerical simulation by András Büki

http://www.insilico.hu/liesegang/scaling/scaling.html

5. Fast reaction limit

Simplifying assumptions

- $\nu_b = 0$ (in experiments, $\nu_a \gg \nu_b$)
- $c^\perp = 0$
- Domain is half-line
- reaction rate k is large

Theorem (Hilhorst, van der Hout, Mimura, and Ohnishi, 2009). *As $k \to \infty$,*

$$k\, a_k\, b_k \rightharpoonup \frac{\alpha\beta}{2\sqrt{t}}\, \delta(x - \alpha\sqrt{t})$$

weakly in measure.

Resulting simplified model

$$c_t = \nu_c\, \Delta c + \frac{\alpha\beta}{2\sqrt{t}}\, \delta(x - \alpha\sqrt{t}) - \lambda\, p[x,t;u]u$$

where

$$p[x,t;c] = \begin{cases} 1 & \text{if } c(x,s) \geq c^\top \text{ for some } 0 \leq s \leq t \\ 0 & \text{otherwise} \end{cases}$$

6. Weak formulation

$$(u-\psi)_t = (u-\psi)_{xx} - p[x,t;u]\,u$$

with $u_x(0,t) = 0$ for $t \geq 0$ and $u(x,0) = 0$ for $x > 0$, and

$$p[x,t;u] \in \begin{cases} 0 & \text{if } \sup_{s\in[0,t]} u(x,s) < u^* \\ [0,1] & \text{if } \sup_{s\in[0,t]} u(x,s) = u^* \\ 1 & \text{if } \sup_{s\in[0,t]} u(x,s) > u^* \end{cases}$$

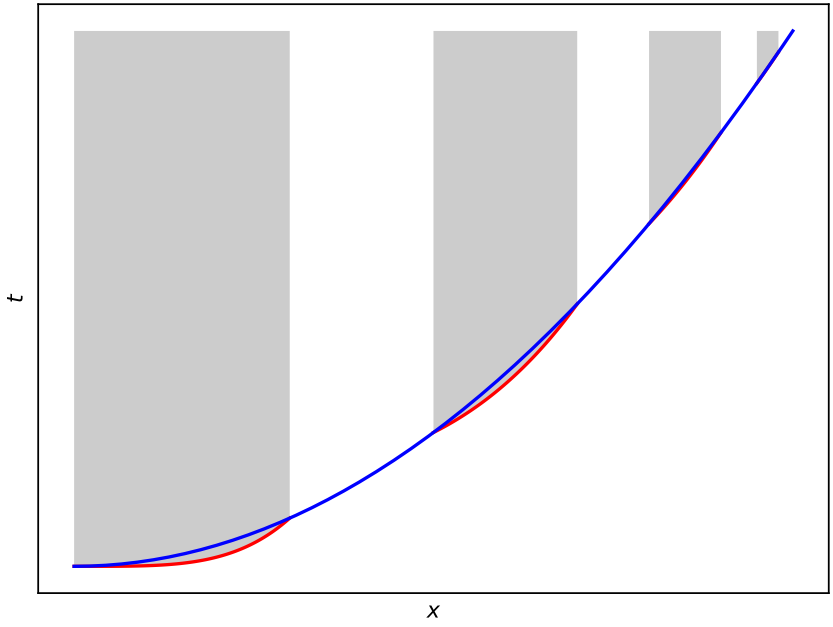
Key points

- Subtract out precipitation-less solution ψ to remove singular forcing
- Equation is satisfied in an integral sense
- Precipitation function p may take fractional values at criticality

What was known?

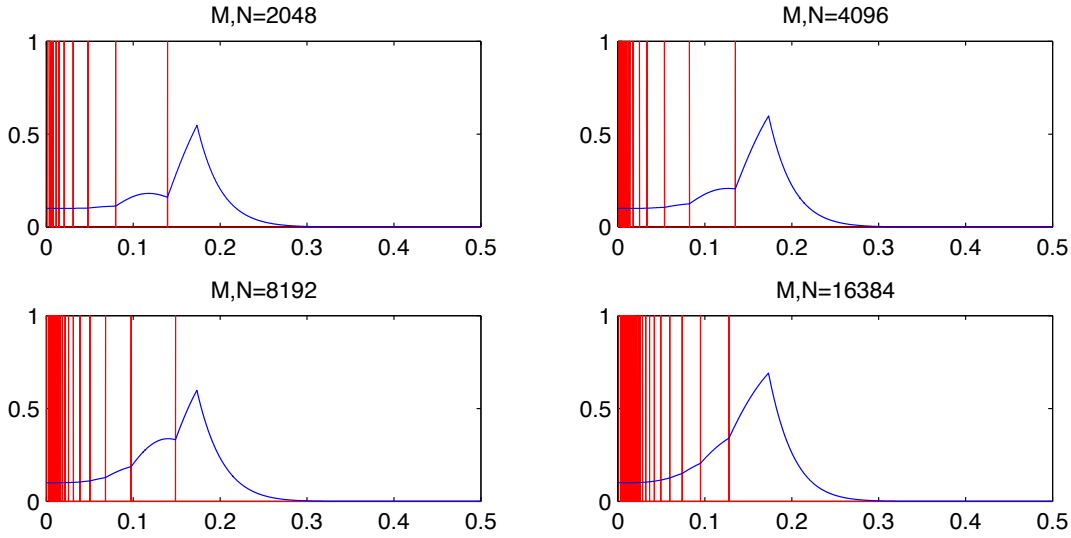
✓ Existence (Hilhorst, van der Hout, Mimura, and Ohnishi, 2009)
✗ Uniqueness?
✗ Binary p?

7. Artist's impression of the HHMO-dynamics



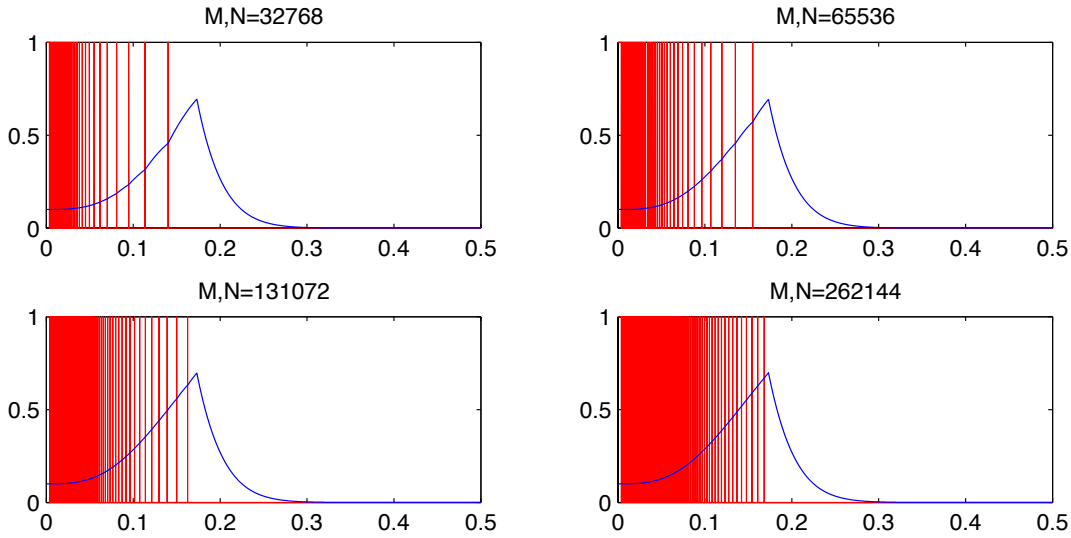
8. Numerical Solution (I)

Naive numerics...



9. Numerical Solution (II)

...under grid refinement



10. Self-similar solution

Introduce parabolic scaling

Setting $\eta = x/\sqrt{t}$ and $s = \sqrt{t}$, we obtain

$$s\, v_s - \eta\, v_\eta = 2\, v_{\eta\eta} + \alpha\beta\, \delta_\alpha - 2\, s^2\, q[\eta, s; v]\, v$$

Enforce a self-similar precipitation density function

$$q(\eta, s) = \frac{\gamma}{s^2\, \eta^2}\, H(\alpha - \eta) \qquad \text{or} \qquad p(x,t) = \frac{\gamma}{x^2}\, H(\alpha\sqrt{t} - x)$$

Look for stationary solutions in η-s-variables

$$\phi_\mathrm{l}'' + \frac{\eta}{2}\, \phi_\mathrm{l}' - \frac{\gamma}{\eta^2}\, \phi_\mathrm{l} = 0 \qquad \text{with } \phi_\mathrm{l}'(0) = 0 \qquad \text{for } \eta \in [0, \alpha)$$

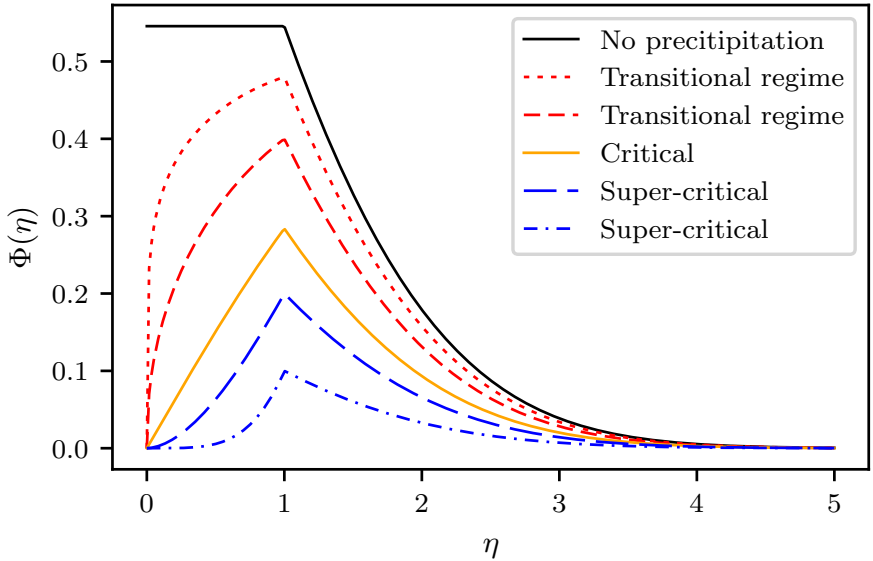
$$\phi_\mathrm{r}'' + \frac{\eta}{2}\, \phi_\mathrm{r}' = 0 \qquad \text{with } \phi_\mathrm{r}(\eta) \to 0 \text{ as } \eta \to \infty \qquad \text{for } \eta \in (\alpha, \infty)$$

Matching conditions

$$\phi(\alpha) = u^* \qquad \text{and} \qquad [\phi'(\alpha)] = -\frac{\alpha\beta}{2}$$

11. Self-similar solution (ctd.)

$$\Phi(\eta;\kappa) = \begin{cases} \dfrac{u_\kappa^* \, \eta^\kappa \, M\left(\frac{\kappa}{2}, \kappa + \frac{1}{2}, -\frac{\eta^2}{4}\right)}{\alpha^\kappa \, M\left(\frac{\kappa}{2}, \kappa + \frac{1}{2}, -\frac{\alpha^2}{4}\right)} & \text{if } \eta < \alpha \\ \dfrac{u_\kappa^*}{\operatorname{erfc}(\frac{\alpha}{2})} \operatorname{erfc}\left(\dfrac{\eta}{2}\right) & \text{if } \eta \geq \alpha \end{cases}$$



12. Theorems

Long-time asymptotics (Darbenas, van der Hout, O., 2018)

Let (u, p) be a weak solution s.t. there exists a measurable function $p^* \neq 0$ s.t. for a.e. $x \in \mathbb{R}_+$,

$$p(x,t) = p^*(x) \quad \text{for} \quad t > x^2/\alpha^2 \,.$$

Then the following are equivalent.

(i) $h(x) \equiv \dfrac{1}{x}\displaystyle\int_0^x \xi^2\, p^*(\xi)\, \mathrm{d}\xi \to \gamma$ as $x \to \infty$
(“**precipitation function is asymptotically self-similar**”)

(ii) u converges to some limit profile V pointwise a.e. in η-s coordinates
(“**concentration converges to some profile**”)

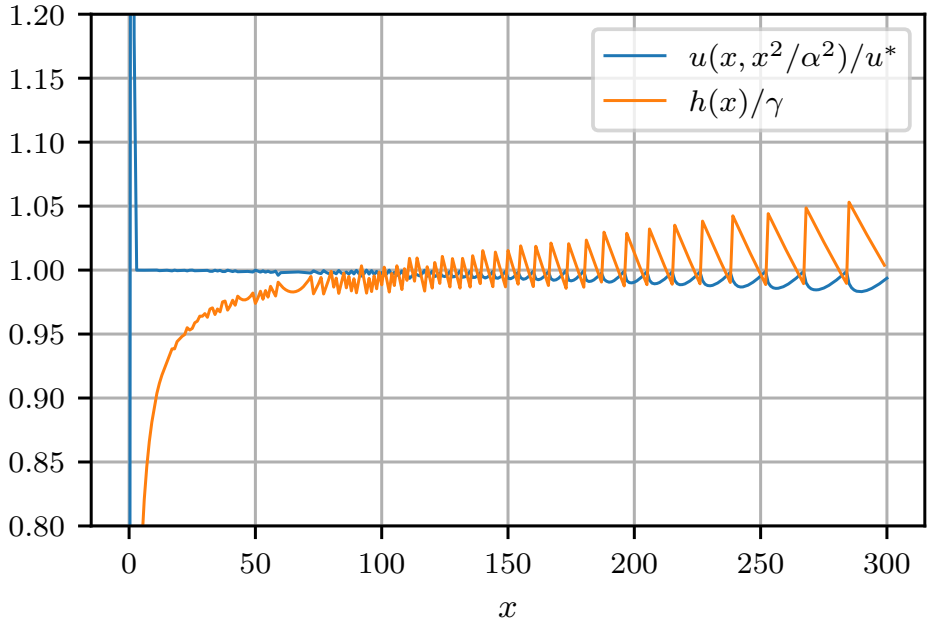
(iii) u converges to Φ_γ uniformly in η-s coordinates
(“**concentration converges to self-similar profile**”)

Further, $\Phi_\gamma(\alpha) = u^*$ if $\gamma > 0$ and $0 < \Phi_\gamma(\alpha) \leq u^*$ if $\gamma = 0$.

Uniqueness (Darbenas, O., 2018)

- Solution is unique for a short time
- Solution remains unique subject to a transversality condition

13. Numerical illustration



Note: We see "rattling", cf. Gurevich and Tikhomirov (2017, 2018)

14. Simplified HHMO-model

Change to difference variable $w \equiv u - \phi$:

$$w_t - w_{xx} + p\,w = \left(\frac{\gamma}{x^2}\,H\!\left(\alpha - \frac{x}{\sqrt{t}}\right) - p\right)\phi\!\left(\frac{x}{\sqrt{t}}\right)$$

- Drop damping term pw
- Replace p by $H(w(x, x^2/\alpha^2))$
- Apply Duhamel's principle and set $\omega(x) = w(x, x^2/\alpha^2)$

Scalar functional equation for ω

$$\omega(x) = \Gamma - x^2 \int_0^1 K(\theta)\,H(\omega(x\theta))\,\mathrm{d}\theta$$

with constant Γ and weakly degenerate kernel K

Definition: non-degenerate solution

Let x_i denote the maximal finite or infinite increasing sequence such that

- $\omega > 0$ on (x_i, x_{i+1}) for i even ("ring")
- $\omega < 0$ on (x_i, x_{i+1}) for i odd ("interring")

Set $x^* \equiv \sup x_i$.

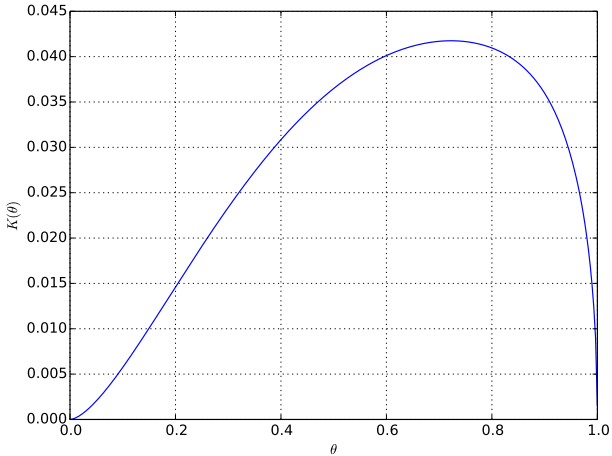
15. Properties of the kernel K

K is continuous on $[0,1]$ and smooth on $[0,1)$ with

(i) $K(0) = K'(0) = 0$,

(ii) $K(\theta) \sim k\sqrt{1-\theta}$ as $\theta \to 1$ for some $k > 0$,

(iii) $K(\theta)$ is non-negative and unimodal, i.e., there exists $\theta^* \in (0,1)$ such that $K''(\theta) > 0$ for $\theta \in (0,\theta^*)$ and $K''(\theta) < 0$ for $\theta \in (\theta^*, 1)$.



16. Theorems (Darbenas, O., 2018)

Breakdown of ring domain for the simplified model

- A non-degenerate solution has an infinite number of rings,
- ring widths bounded by geometric progression, **hence, x^* is finite**

Existence of kernels with degenerate solutions

- There exist (open sets of) weakly degenerate kernels such that ω is degenerate
- So finite-length finite-ring breakdown is possible

Extended solutions

(ω, ρ) is an *extended solution* if

$$\omega(x) = \Gamma - x^2 \int_0^1 K(\theta)\, \rho(x\theta)\, \mathrm{d}\theta \quad \text{with} \quad \rho(y) \in \begin{cases} 0 & \text{if } \omega(y) < 0 \\ [0,1] & \text{if } \omega(y) = 0 \\ 1 & \text{if } \omega(y) > 0 \end{cases}$$

It is *regularly extended* if $\omega = 0$ on some right-neighborhood of x^*.

- When $K \in C([0,1])$, extended solutions exist
- Regularly extended solutions are unique

17. Simplified model as MLCP

Set $\omega = \omega_+ - \omega_-$, $\sigma = 1 - \rho$, and

$$V = \begin{pmatrix} \sigma \\ \rho \end{pmatrix}, \qquad W = \begin{pmatrix} \omega_+ \\ \omega_- \end{pmatrix}, \quad \text{and} \quad \langle V, W \rangle = \int_0^a \omega_+(x)\,\sigma(x)\,\mathrm{d}x + \int_0^a \omega_-(x)\,\rho(x)\,\mathrm{d}x$$

Then extended solutions can be formulated as the following mixed linear complementarity problem:

Find $V \geq 0$, $W \geq 0$ such that

$$\mathcal{L}V + \mathcal{M}W + B = 0$$

subject to

$$\langle V, W \rangle = 0$$

where $\mathcal{L}$ and $\mathcal{M}$ are linear operators defined by

$$\mathcal{L}V = \begin{pmatrix} x^2 \int_0^1 K(\theta)\,\rho(x\theta)\,\mathrm{d}\theta \\ \rho + \sigma \end{pmatrix}, \qquad \mathcal{M}W = \begin{pmatrix} \omega_+ - \omega_- \\ 0 \end{pmatrix}, \quad \textit{and} \quad B = \begin{pmatrix} \Gamma \\ -1 \end{pmatrix}.$$

18. Outlook

1. Theory for the MLCP?
2. Full proofs of uniqueness, breakdown, asymptotics
3. Numerical Analysis?
4. Coarse-grained modeling?