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Nanoparticle synthesis based on ripening processes: modeling and optimal control

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Motivation: Chemical engineering

- Increasing need for more effective (bio-)chemical products (cosmetics, medicaments, semiconductors)
- The quality of such a product is not only influenced by its different components, but also by the so-called **disperse** properties (particle size, morphology, etc.)
- Phenomena in the nanometer regime not neglectable

⇒ Necessity of detailed analysis and optimization of synthesis processes

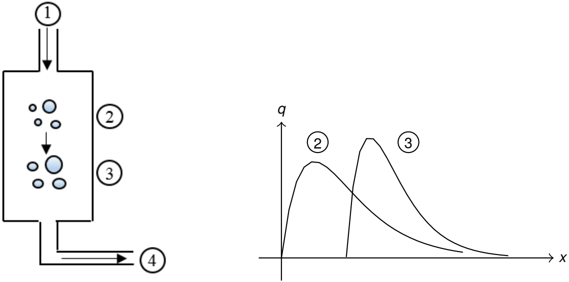

Figure 1: Ripening process in a reactor with particle size distributions at two different points in time (own illustration based on [10, p. 11]).

Outline

A model for ripening processes

Solution theory for starting time parametrized continuity equation

Optimal control of starting time parametrized continuity equation

Conclusion and future research

A model for ripening processes

Ripening process

- Let be $T > 0$. General population balance law:

$$q_t + \frac{\partial}{\partial x}(Rq) + \frac{\partial}{\partial r}(Vq) = B - D$$

Internal coordinate:	$x \in \mathbb{R}$	Spatial coordinate:	$r \in [0, T]$
Particle size distribution (PSD):	$q \equiv q(t,x,r)$	Source terms:	$B - D$
Velocity functions:	$R \equiv R[q](t,x,r)$,	$V \equiv V[q](t,x,r)$	

- By β denoting a coagulation kernel "birth" B and "death" D of x-sized particles can be modeled as

$$B[q](t,x) := \tfrac{1}{2} \int_0^x \beta(x-y,y) q(t,x-y) q(t,y) \mathrm{d}y$$

$$D[q](t,x) := q(t,x) \int_0^\infty \beta(x,y) q(t,y) \mathrm{d}y$$

Nonlocal terms in the ripening velocity term

Nonlocal terms also occur in the ripening velocity function. Reason:

- Due to agglomeration effects the ripening of a particle can occur by the solving of particles in the reaction medium and merging with other particles on their free surface
- The solvability is influenced by the rate of saturation of synthesized particles
- The saturation again depends on the concentration of the product, which yields the nonlocal term.

Examples

Spray granulation process

$$R[q](t) \sim \frac{1}{\int_{x_{\min}}^{\infty} y^2 q(t,y)\,\mathrm{d}y}$$

Ostwald ripening

$$R[q](t) \sim \int_{x_{\min}}^{\infty} y^3 q(t,y)\,\mathrm{d}y$$

Application: Feedback control of nanoparticle synthesis

- Input-PSD $q(t_0, t_0, \cdot)$ as the result of a control in both locations C at the time t_0
- Backflow of $F[q](t_0, x)$ (density of particles on the bottom of the reactor at time t_0) with rate $u(t_0)$ where $u(t_0) \in [0, 1]$
- The other part, namely $1 - u(t_0)$, by a PSD q_0 independent from the process

$$\Rightarrow q(t_0, t_0, x) = u(t_0) F[q](t_0, x) + (1 - u(t_0)) q_0(x)$$

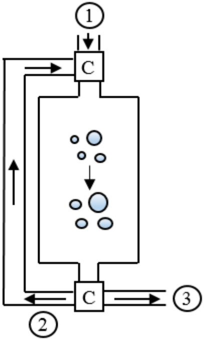

Figure 2: (Convex) control of the ripening in the locations C in the case of a synthesis process with feedback.

Basic assumptions

- $B - D \equiv 0$ (reasonable for slow flow profile)
- $R \equiv R(t, x) \rightarrow$ Reduction of the balance law to a **continuity equation** allowing an easier adjoint approach in the optimization
- Diffusion of particles neglected $\rightarrow$ admits the consideration of the flow (of the fluid) in terms of a **residence time distribution** $\rightarrow$ Consequence: Velocity function V can be neglected (see the next slides)

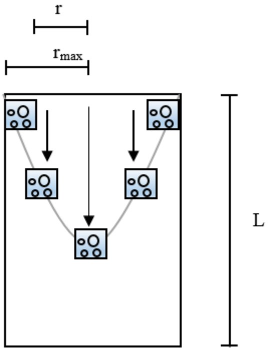

Figure 3: Flow of volume packages in a laminar flow profile.

Poiseuille-flow I

- Association of a residence time distribution k with $\int_0^\infty k(t) = 1$
- Starting at time s the probability to reach the bottom of the reactor in time t_0 is $\int_0^{t_0 - s} k(t)\,\mathrm{d}t$
- $q(s,\cdot,\cdot) \equiv q(s,t,x)$: PSD at the time t with starting time s ($\rightarrow$ upper reactor wall)
  $\Rightarrow$ Amount of particles with radius x at the time t_0 at the bottom of the reactor:

$$F[q](t_0, x) := \int_0^{t_0} k(t_0 - s) q(s, t_0, x)\,\mathrm{d}s$$

Poiseuille-flow II

- Let be $v_{\max}$ the maximal flow velocity in the reactor given by pressure and temperature among others. Then the flow velocity profile reads as:

$$v(r) = v_{max}\left[1 - \left(\frac{r}{r_{\max}}\right)^2\right], \quad r \in [0, r_{\max})$$

- Because of the laminar flow the $v(r) = \frac{L}{t}$ we obtain by setting $t_{\min} := \frac{L}{v_{\max}}$:

$$\Rightarrow r \equiv r(t) = r_{max}\left[1 - \left(\frac{t_{\min}}{t}\right)\right]^{\frac{1}{2}} \text{ for } t > t_{\min}$$

Example: Poiseuille-flow III

- Cumulative residence time distribution $K = \frac{V_t(r)}{V_t(r_{\max})}$ with the volume flow rate $V_t(r) = \int_0^r 2\pi s v(s)\, \mathrm{d}s$
- After integration with upper limit $r = r_{\max}\left[1 - \left(\frac{t_{\min}}{t}\right)\right]^{\frac{1}{2}}$ we obtain with $k = K'$

$$K(t) = 0 \text{ for } \quad t \leq t_{\min}, \quad K(t) = 1 - \left(\frac{t_{\min}}{t}\right)^2 \quad \text{for } t > t_{\min}$$

$$k(t) = 0 \text{ for } \quad t \leq t_{\min}, \quad k(t) = \frac{2t_{\min}^2}{t^3} \quad \text{for } t > t_{\min}$$

Solution theory for starting time parametrized continuity equation

Classical theory I

Method of characteristics

Suitable for solving first order hyperbolic equations. Basic idea: Find differentiable curves $(t, \xi[0,x](t)) \in (0,T) \times \mathbb{R}$ for $(t,x) \in (0,T) \times \mathbb{R}$, parametrized by ξ, such that the solution of the (homogeneous) continuity equation is constant respectively on those.

Example: Consider the homogeneous transport equation

$$\begin{aligned} q_t(t,x) + R(t,x) q_x(t,x) &= 0 && \text{in } (0,T) \times \mathbb{R} \\ q(0,x) &= q_0(x) && \text{on } \mathbb{R} \end{aligned}$$

and assume the data and the solution are sufficiently smooth. By the chain rule and the upper equations

$$\left. \begin{array}{ll} \frac{\mathrm{d}}{\mathrm{d}t} q(t, \xi[0,x](t)) & \equiv 0 \\ q(0,x) & = q_0(x) \end{array} \right\} \Leftrightarrow \left\{ \begin{array}{ll} \dot{\xi}[0,x](t) & = R(t, \xi[0,x](t)) \\ \xi[0,x](0) & = x. \end{array} \right.$$

Classical theory II

Solution of the continuity equation is

$$q(t,x) = q_0(\xi[t,x](0))\partial_2\xi[t,x](0). \tag{1}$$

Starting time parametrized (STP)-continuity equation

Define $D_T := \{(t_0, t) \ : \ 0 < t_0 \leq t < T\}$.

$$\begin{aligned} S_1[q](t_0,t,x) &= 0 & (t_0,t,x) &\in D_T \times \mathbb{R} \\ q(t_0,t_0,x) &= S_2[q](t_0,x) & (t_0,x) &\in (0,T) \times \in \mathbb{R}, \end{aligned}$$

where

$$S_1[q](t_0,t,x) := q_t(t_0,t,x) + \partial_x(R(t,x)q(t_0,t,x))$$

$$S_2[q](t_0,x) := u(t_0)\int_0^{t_0} k(t_0-s)q(s,t_0,x)\,\mathrm{d}s + (1-u(t_0))q_0(x).$$

Solution strategy for the STP-continuity equation

Condition: "t_{min}-property"

It exists a positive minimal residence time, i.e.

$$\exists t_{\text{min}} \in \mathbb{R}_{>0} \forall t \in [0, t_{\text{min}}) : \qquad k(t) = 0.$$

Now use an induction argument and the properties of the solution of the non-parametrized Cauchy-Problem to obtain a solution of the parametrized one on whole $(0, T) \times \mathbb{R}$.
The characteristics are now defined as the solution of

$$\dot{\xi}[t_0, x](t) = R(t, \xi[t_0, x](t)), \quad \xi[t_0, x](t_0) = x.$$

For all $t_0 \in [0, t_{\text{min}})$ we have $q(t_0, t_0, x) = (1 - u(t_0))q_0(x)$ such that we have $q(t_0, t, x) = (1 - u(t_0))q_0(\xi[t, x](t_0))\partial_2\xi[t, x](t_0)$ as a solution.

For all $t_0 \in [t_{\min}, 2t_{\min})$ we have

$$\int_0^{t_0} k(t_0 - s) q(s, t_0, x) \mathrm{d}s = \int_0^{t_0 - t_{\min}} k(t_0 - s) q(s, t_0, x) \mathrm{d}s$$
$$= \int_0^{t_0 - t_{\min}} k(t_0 - s)(1 - u(s)) q_0(\xi[t_0, x](s)) \partial_2 \xi[t_0, x](s) \mathrm{d}s$$

The upper integral term depends only on the given data. Therefore there exists a solution q of the STP-continuity equation. For bigger t_0 the argumentation is similar.
Solution formula:

$$\begin{aligned} q(t_0, t, x) = {} & u(t_0) q(t_0, t_0, \xi[t, x](t_0)) \partial_2 \xi[t, x](t_0) \\ & + (1 - u(t_0)) q_0(\xi[t, x](t_0)) \partial_2 \xi[t, x](t_0). \end{aligned}$$

Main conditions for the weak solution theory

- "$t_{\min}$-property", $k \in L^1((0,\infty))$ and $k|_{[t_{\min},\infty)} \in C([t_{\min},\infty))$.
- $q_0, q_d \in L^2(\mathbb{R})$.
- For $T \in \mathbb{R}_{>0}$:

$$R \in L^1((0,T); H^1_{\mathrm{loc}}(\mathbb{R})), \quad R_x \in L^1((0,T); L^\infty(\mathbb{R}))$$
$$\frac{R}{1+|x|} \in L^1((0,T); L^1(\mathbb{R})) + L^1((0,T); L^\infty(\mathbb{R}))$$

- For $M \in \mathbb{R}_{>0}$:

$$U_{ad} := \{u \in H^1((0,T)) \ : \ ||u||_{H^1((0,T))} \leq M,\ 0 \leq u \leq 1 \text{ a.e.}\}.$$

Well-posedness I

Remark

For the well-posedness of the problem weaker assumptions on k and u are possible, furthermore L^p-Settings with $p \in [1, \infty]$ considerable.

Proposition: Existence, uniqueness, regularity

Let the main conditions hold true. Then the STP-continuity equation has a unique solution q in the weak sense with $q \in L^\infty\big((0,T)^2; L^2(\mathbb{R})\big)$ and

$$q(t_0, \cdot, \cdot) \in C\big([t_0, T]; L^2(\mathbb{R})\big) \quad \textit{a.e. } t_0 \in [0, T]. \tag{2}$$

Sketch of proof:
Using an induction argument like in the smooth case due to the fact of the "$t_{\min}$"-property.

Well-posedness II

Proposition: Stability of a subsequence

$(k, q_{0,n}, R_n, R_{n,x})$ und (k, q_0, R, R_x) fulfill respectively the main conditions and $u_n, u \in U_{ad}$.
$R_{n,x}$ are uniformly bounded in $L^1((0,T); L^\infty(\mathbb{R}))$ and $R_n, R_{n,x}$ converge for $n \to \infty$ to R, R_x respectively in $L^1((0,T); L^1_{\text{loc}}(\mathbb{R}))$.
Let q_n and q be their corresponding weak solution of the STP-continuity equation.
If $u_n \to u$ in $L^2((0,T))$ and $q_{0,n} \to q_0$ in $L^2(\mathbb{R})$, then there exists a subsequence of q_n, which is denoted again by q_n, such that:

$$q_n(t_0,\cdot,\cdot) \to q(t_0,\cdot,\cdot) \text{ in } C([t_0,T]; L^2(\mathbb{R})) \text{ a.e. } t_0 \in [0,T]$$
$$q_n \to q \text{ in } L^2((0,T)^2; L^2(\mathbb{R})).$$

Sketch of proof:
Combining the previous existence and regularity results with stability theorems described exemplarily in [3, p. 38]. Because of the solution formula the pointwise convergence of u_n to u would be required. Since this is in general only possible for subsequences, it will imply the stated stabilty result for a subsequence of $(q_n)_n$.

Optimal control of starting time parametrized continuity equation

Optimal control problem

For $\alpha \in \mathbb{R}_{>0}$ consider the following optimal control problem

$$\left.\begin{aligned}
&\min_{q,u} I(q,u) = \frac{1}{2}||F[q](T,\cdot) - q_d||^2_{L^2(\mathbb{R})} + \frac{\alpha}{2}||u||^2_{L^2((0,T))} \\
&\text{s.t.} \\
&S_1[q](t_0,t,x) = 0 \qquad (t_0,t,x) \in D_T \times \mathbb{R} \\
&q(t_0,t_0,x) = S_2[q](t_0,x) \qquad (t_0,x) \in (0,T) \times \in \mathbb{R},
\end{aligned}\right\} \tag{3}$$

where

$$S_1[q](t_0,t,x) := q_t(t_0,t,x) + \partial_x(R(t,x)q(t_0,t,x))$$

$$S_2[q](t_0,x) := u(t_0)\int_0^{t_0} k(t_0-s)q(s,t_0,x)\,\mathrm{d}s + (1-u(t_0))q_0(x).$$

Existence of optimal controls

Proposition: Existence

If the main conditions hold true, there exists an optimal control u^* with an optimal solution q^*.

Sketch of proof:
Minimizing sequence $(u_n)_n$ bounded in $U_{ad} \subset H^1((0,T))$. Thus, a subsequence converges in $L^2((0,T))$ to a $u^* \in U_{ad}$. The previous stability results imply the convergence of the to u_n associated solution q_n of the STP-continuity equation in $L^2((0,T)^2; L^2(\mathbb{R}))$ to the solution q^* w.r.t. u^*.

Remark: (Non)-uniqueness

For $T \in [0, 2t_{\min}]$ you can easily show uniqueness of the optimal control. The iterative construction method of the solution of the STP-continuity equation yields for $T \gg t_{\min}$ that u is in a polynomial way involved into the solution $q \equiv q[u]$. Therefore the reduced cost functional $u \mapsto I(q[u], u)$ is in general not strictly convex, thus the uniqueness of an optimal control is not garantueed.

First order necessary optimality condition I

Lemma: Uniform Fréchet-differentiability

Let $u \in U_{ad}$ and $f[\cdot](s,x) : U_{ad} \to \mathbb{R}$ be uniformly in $(s,x) \in (0,T) \times \mathbb{R}$ Fréchet-differentiable in u, i.e.

$$\sup_{s,x} \lim_{\|h\|_{H^1((0,T))}} \left| f[u+h](s,x) - f[u](s,x) - f'[u](s,x)h \right| = o(\|h\|_{H^1((0,T))}).$$

Then also $U_{ad} \ni u \mapsto \int_0^s u(\tau) f[u](\tau,x) \mathrm{d}\tau$ is uniformly in $(s,x) \in (0,T) \times \mathbb{R}$ Fréchet-differentiable in u.

Sketch of proof:
Use the very definition of Fréchet-differentiability and use the fact that for $u \in U_{ad}$ we have $\|u\|_{L^\infty((0,T))} \le M$.

First order necessary optimality condition II

Proposition: Optimality

Assume the main conditions and consider the reduced cost-functional $J(u) := I(q[u], u)$. *Then* J *is Fréchet-differentiable and every minimum* u^* *of* J *on* U_{ad} *fulfills the variational inequality*

$$J'[u^*](v - u^*) \geq 0 \quad \forall v \in U_{ad}.$$

Sketch of the proof:
Consider at first the functional

$$U_{ad} \ni u \mapsto F[q[u]](s,x) = \int_0^s k(s-\tau)q[u](\tau,s,x)\mathrm{d}\tau \quad \text{for } (s,x) \in (0,T) \times \mathbb{R}.$$

If $s \in [0, t_{\text{min}})$, then $F[q[u]](s,x) \equiv 0$ independent from $(s,x) \in (0,T) \times \mathbb{R}$.
Therefore this functional is uniformly in $(s,x) \in (0,T) \times \mathbb{R}$ Fréchet-differentiable.

First order necessary optimality condition III

Next, consider

$$F[q[u]](s,x) = \int_0^s k(s-\tau)q[u](\tau,s,x)\mathrm{d}s$$
$$= \int_0^{s-t_{\min}} k(s-\tau)\partial_2\xi[s,x](\tau)\Big(u(\tau)F[q[u]](\tau,\xi[s,x](\tau))$$
$$+(1-u(\tau))q_0(\xi[s,x](\tau))\Big)\mathrm{d}\tau.$$

Because of the "$t_{\min}$"-property of k we obtain by an induction argument that $F[q[\cdot]](s,x)$ is uniformly in $(s,x)\in(0,T)\times\mathbb{R}$ Fréchet-differentiable. Together with the chain rule for Fréchet-differentiable functions we also get that J is Fréchet-differentiable and this implies the validity of the stated variational inequality.

Formal derivation of necessary optimality conditions I

Forward equation (STP-continuity equation):

$$q_t(t_0,t,x) + \partial_x\big(R(t,x)q(t_0,t,x)\big) = 0$$
$$q(t_0,t_0,x) = u(t_0)F[q](t_0,x) + (1-u(t_0))q_0(x)$$

Backward equation (STP-transport equation):

$$p_t(t_0,t,x) + R(t,x)p_x(t_0,t,x) = -u(t)k(t-t_0)p(t,t,x)$$
$$p(t_0,T,x) = -k(T-t_0)\big(F[q](T,x) - q_d(x)\big)$$

Optimality condition: For every $\tilde{u} \in U_{ad}$

$$\int_0^T (\tilde{u}-u)\cdot\left(\alpha u + \int_{\mathbb{R}} p(t_0,t_0,x)\,(q_0(x) - F[q](t_0,x))\,\mathrm{d}x\right)\,\mathrm{d}t_0 \geq 0.$$

Formal derivation of necessary optimality conditions II

Remark: STP-transport equation

- Under the main conditions the previous adjoint equation has a unique solution $p \in L^\infty([0, T]^2; L^2(\mathbb{R}))$ in the weak sense with $p(t_0, \cdot, \cdot) \in C([t_0, T]; L^2(\mathbb{R}))$ for almost every $t_0 \in [0, T]$. Stability results for subsequences similar to those of the STP-continuity equation can be obtained.
- Unfortunately, the upper results don't guarantee that the presented optimality system can be rigorously obtained.

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Conclusion and future research

Summary of previous results

- In a laminar flow: under reasonable assumptions nanoparticle synthesis based on ripening processes can be modeled by using a fluid velocity - residence time distribution relation resulting in a continuum of initial conditions/time delays
  $\rightarrow$ Reduction of the dimension of the spatial variables
- Solution theory for the STP-continuity equation based on the method of characteristics
- Under the main conditions the presented optimal control problem admits an optimal control, which in some cases can be unique. Moreover, a first order necessary optimality condition could be stated and, albeit only formally, formulated by the solution of the adjoint equation

Possible problems to tackle

- Nonlocal term in ripening velocity function
- Right-hand sides
- More general cost functionals
- Multi-dimensional internal variable ($\rightarrow$ consideration of several disperse properties) and systems
- Numerics

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Thanks for listening.

Any questions? Then please, feel free to ask!