Numerical Solutions of Population-Balance Models in Particulate Systems

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1 Motivation
   • Aim
   • Application Areas

2 Mathematical Model
   • General Population Balance Equation (PBE)
   • Reformulation of PBE
   • Preferential Crystallization Model

3 Numerical Procedure
   • Domain Discretization
   • Numerical Method 1: Combination of MOC and FVS
   • Numerical method 2: Semi-Discrete HR-Schemes

4 Numerical Results
Outline

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   • Aim
     • Application Areas

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4 Numerical Results

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Motivation

Aim
To model and simulate nucleation, growth, aggregation and Breakage phenomena in processes engineering by solving population balance equations (PBEs).

Numerical Methods
To solve population balance models we use the high resolution finite volume schemes as well as their combination with the method of characteristics.
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Industrial Applications

Applications

- Pharmaceutical
- Chemical industries
- Biomedical science
- Aerosol formation
- Atmospheric physics
- Food industries
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4 Numerical Results
General Population Balance Equation (PBE)

\[
\frac{\partial f(t, x)}{\partial t} + \frac{\partial [G(t, x)f(t, x)]}{\partial x} = Q_{\text{agg}}^\pm(t, x) + Q_{\text{break}}^\pm(t, x) + Q_{\text{nuc}}^+(t, x)
\]

\[f(0, x) = f_0, \quad x \in \mathbb{R}_+ := ]0, +\infty[ , \quad t \geq 0\]

1. \(f(t, x)\) is the number density function,
2. \(t\) denotes the time and \(x\) is an internal coordinate
3. \(G(t, x)\) is the growth/dissolution rate along \(x\),
4. \(Q_{\alpha}^\pm(t, x)\) are the aggregation, breakage and nucleation terms for \(\alpha = \{\text{agg, break, nuc}\}\).
5. The entities in the population density can be crystals, droplets, molecules, cells, and so on.
Figure: A schematic representation of different particulate processes
Motivation
Mathematical Model
Numerical Procedure
Numerical Results

General Population Balance Equation (PBE)
Reformulation of PBE
 Preferential Crystallization Model

\[ Q_{\text{agg}}^\pm(t, x) = \frac{1}{2} \int_0^x \beta(t, x', x - x') f(t, x') f(t, x' - x) dx' \]
\[ - \int_0^\infty \beta(t, x, x) f(t, x) f(t, x') dx'. \]

Where: \( \beta = \beta(t, x, x') \) is the rate at which the aggregation of two particles with respective volumes \( x \) and \( x' \) produces a particle of volume \( x + x' \) and is a nonnegative symmetric function,

\[ 0 \leq \beta(t, x, x') = \beta(t, x', x), \quad x' \in ]0, x[, \quad (x, x') \in \mathbb{R}_+^2. \]
Mathematical Model

General Population Balance Equation (PBE)

Preferential Crystallization Model

\[ Q_{\text{break}}^{\pm}(t, x) = \int_{x}^{\infty} b(t, x, x') S(x') f(t, x') dx' - S(x) f(t, x). \]

\( b := b(t, x, x') \) is the probability density function for the formation of particles of size \( x \) from particle of size \( x' \). The selection function \( S(x') \) describes the rate at which particles are selected to break.

**Moments:**

\[ \mu_i(t) = \int_{0}^{\infty} x^i f(t, x) dx, \quad i = 0, 1, 2, \ldots, \]

\( \mu_0(T) = \) total number of particles, \( \mu_1(t) = \) total volume of particles
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4. Numerical Results
Reformulation of PBE

Multiply the original PBE with \( x \) and re-arrange the terms, we get

\[
\frac{\partial \tilde{f}(t, x)}{\partial t} + \frac{\partial [(G\tilde{f})(t, x)]}{\partial x} - \frac{(G\tilde{f})(t, x)}{x} = -\frac{\partial \mathcal{F}_{\text{agg}}(t, x)}{\partial x} + \frac{\partial \mathcal{F}_{\text{break}}(t, x)}{\partial x} + \tilde{\mathcal{Q}}_{\text{nuc}},
\]

where \( \tilde{f}(t, x) := xf(t, x) \), \( \tilde{\mathcal{Q}}_{\text{nuc}} = xQ_{\text{nuc}}^+ \) and

\[
\mathcal{F}_{\text{agg}}(t, x) = -\int_0^x \int_{x-u}^\infty u \beta(t, u, v) f(t, u) f(t, v) \, dv \, du \quad (\text{Filbet & Laurencot, 2004})
\]

\[
\mathcal{F}_{\text{break}}(t, x) = \int_0^x \int_x^\infty u b(t, u, v) S(v) f(t, v) \, dv \, du.
\]
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4. Numerical Results

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Amino acid enantiomers
Ternary Phase Diagram

Metastable zone
Equilibrium point

Seeding with $E_1$ seeds

Real trajectories after seeding with $E_1$

Solubility curves

$E_1$
$E_2$
$E_1$
$T_{\text{cryst}} + \Delta T$

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Preferential Batch Crystallizer With Fines Dissolution

\begin{enumerate}
\item Tank A
\item Annular Settling Zone
\item Fines Dissolution Loop
\item preferred crystals (seeded)
\item counter crystals (unseeded)
\item \( F^{(k)}(x, t) \)
\item \( m^{(k)}_{\text{liq}, 1}, m_{\text{w}, 1}, \tau_1, V_1 \)
\item \( m^{(k)}_{\text{liq}, 2}, m_{\text{w}, 2}, \tau_2, V_2 \)
\end{enumerate}
Model for Preferential Crystallization

Balance for solid phase

\[
\frac{\partial f^{(k)}(t, x)}{\partial t} = -G^{(k)}(t) \frac{\partial f^{(k)}(t, x)}{\partial x} - \frac{1}{\tau_1} h(x) f^{(k)}(t, x), \quad k \in [p, c].
\]

Mass balance for liquid phase in crystallizer

\[
\frac{d m^{(k)}(t)}{dt} = \dot{m}_{in}^{(k)}(t) - \dot{m}_{out}^{(k)}(t) - 3 \rho k_v G^{(k)}(t) \int_0^\infty x^2 f^{(k)}(t, x) dx.
\]

\[
f^{(k)}(t, 0) = \frac{B^{(k)}(t)}{G^{(k)}(t)} , \quad w^{(k)}(t) = \frac{m^{(k)}(t)}{m^{(p)}(t) + m^{(c)}(t) + m_W(t)}
\]

\[
S^{(k)}(t) = \frac{w^{(k)}(t)}{w^{(k)}_{eq}} - 1, \quad G^{(k)}(t) = k_g [S^{(k)}(t)]^\alpha , \quad k_g \geq 0, \alpha \geq 1.
\]
Motivation
Mathematical Model
Numerical Procedure
Numerical Results

General Population Balance Equation (PBE)
Reformulation of PBE

Preferential Crystallization Model

\[
B_{0}^{(p)}(t) = k_{b}^{(p)} \left( S^{(p)}(t) \right)^{b^{(p)}} \mu_{3}^{(p)}(t)
\]

\[
B_{0}^{(c)}(t) = k_{b}^{(c)} e^{-\frac{b^{(c)}}{\ln(S^{(c)}(t))^{2}}}
\]

\[
\dot{m}_{out}^{(k)}(t) = w^{(k)}(t) \rho_{liq}(T)
\]

\[
\dot{m}_{in}^{(k)}(t) = \dot{m}_{out}^{(k)}(t - \tau_{2}) + \frac{k_{V} \rho}{\tau_{1}} \int_{0}^{\infty} x^{3} h(x) f^{(k)}(t - \tau_{2}, x) \, dx.
\]
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4 Numerical Results
**Regular/Irregular grid:** Let $N$ be a large integer and denote by $(x_{i-\frac{1}{2}})_{i\in\{1,\ldots,N+1\}}$ a mesh of $[x_{\text{min}}, x_{\text{max}}]$. We set

$$
x_{1/2} = x_{\text{min}}, \quad x_{N+1/2} = x_{\text{max}}, \quad x_{i+1/2} = x_{\text{min}} + i \cdot \Delta x_i, \quad \forall \ i = 1, 2, \ldots, N-1.
$$

Here $x_i = (x_{i-1/2} + x_{i+1/2})/2$, $\Delta x_i = x_{i+1/2} - x_{i-1/2}$. 

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Geometric grid:

\[ x_{1/2} = x_{\text{min}}, \quad x_{i+1/2} = x_{\text{min}} + 2^{(i-N)/q}(x_{\text{max}} - x_{\text{min}}), \quad \forall \ i = 1, 2, \ldots, N \]

where the parameter \( q \) is any positive integer.

Let \( \Omega_i = [x_{i-1/2}, x_{i+1/2}] \) for \( i \geq 0 \). We approximate the initial data \( f_0(x) \) in each grid cell by

\[ f_i = \frac{1}{\Delta x_i} \int_{\Omega_i} f_0(x) \, dx. \]
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Method 1: Combination of MOC and FVS

Let us substitute the growth rate \( G(t, x) \) by

\[
\frac{dx}{dt} := \dot{x}(t) = G(t, x)
\]

Then we have to solve:

\[
\frac{d\tilde{f}_i}{dt} = - \frac{1}{\Delta x_i(t)} \left[ (F_{\text{agg}})_{i+\frac{1}{2}} - (F_{\text{agg}})_{i-\frac{1}{2}} \right] + \frac{1}{\Delta x_i(t)} \left[ (F_{\text{break}})_{i+\frac{1}{2}} - (F_{\text{break}})_{i-\frac{1}{2}} \right] \\
+ \frac{G_{i+\frac{1}{2}} \tilde{f}_i}{x_i(t)} - \left( G_{i+\frac{1}{2}} - G_{i-\frac{1}{2}} \right) \frac{\tilde{f}_i}{\Delta x_i(t)} + \tilde{Q}_i
\]

\[
\frac{dx_{i+\frac{1}{2}}}{dt} = G_{i+\frac{1}{2}}, \quad \forall \; i = 1, 2, \ldots, N \quad \text{with i.c.} \quad \tilde{f}(0, x_i) = \tilde{f}_0(x_i)
\]

where
(F_{agg})_{i+1/2} = \sum_{k=0}^{i} \Delta x_k(t) \tilde{f}_k \left\{ \sum_{j=\alpha_{i,k} \wedge h}^{N} \int_{\Omega_j} \frac{\beta(x', x_k)}{x'} dx' \tilde{f}_j + \int_{x_{i+1/2} - x_k}^{x_{i,k} - 1} \frac{\beta(x', x_k)}{x'} dx' \tilde{f}_{\alpha_{i,k}-1} \right\},

(F_{break})_{i+1/2} = \sum_{k=0}^{i} \int_{\Omega_k} x^* \left( \sum_{j=i+1}^{N} \tilde{f}_j \int_{\Omega_j} b(x^*, x') \frac{S(x')}{x'} dx' \right) dx^* + \mathcal{O}(\Delta x^3).

Here, the integer \(\alpha_{i,k}\) corresponds to the index of the cell such that \(x_{i+1/2}(t) - x_k(t) \in \Omega_{\alpha_{i,k}-1}(t)\).

A standard ODE-solver can be used to solve the above ODEs.
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4 Numerical Results

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Method 2: Semidiscrete HR-schemes

Integration of PBE over the control volume \( \Omega_i = \left[ x_{i-\frac{1}{2}}, x_{i+\frac{1}{2}} \right] \) implies

\[
\int_{\Omega_i} \frac{\partial \tilde{f}(t, x)}{\partial t} \, dx + \int_{\Omega_i} \frac{\partial [G(t, x) \tilde{f}(t, x)]}{\partial x} \, dx - \int_{\Omega_i} \frac{G(t, x) \tilde{f}(t, x)}{x} \, dx \\
= - \int_{\Omega_i} \frac{\partial F_{\text{agg}}(t, x)}{\partial x} \, dx + \int_{\Omega_i} \frac{\partial F_{\text{break}}(t, x)}{\partial x} \, dx + \int_{\Omega_i} \tilde{Q}(t, x) \, dx.
\]

Let \( \tilde{f}_i = \tilde{f}_i(t) \) and \( \tilde{Q}_i = \tilde{Q}_i(t) \) be the averaged values, then we have

\[
\frac{\partial \tilde{f}_i}{\partial t} = - \frac{1}{\Delta x} \left[ F_{i+\frac{1}{2}} - F_{i-\frac{1}{2}} \right] - \frac{1}{\Delta x} \left[ (F_{\text{agg}})_{i+\frac{1}{2}} - (F_{\text{agg}})_{i-\frac{1}{2}} \right] \\
+ \left[ (F_{\text{break}})_{i+\frac{1}{2}} - (F_{\text{break}})_{i-\frac{1}{2}} \right] + \frac{G_{i+\frac{1}{2}} \tilde{f}_i}{x_i} + \tilde{Q}_i,
\]

where \( F_{i+\frac{1}{2}} = \left( G\tilde{f} \right)_{i+\frac{1}{2}} \) and \( (F_{\text{agg}}) \) & \( (F_{\text{break}}) \) are as given in Method 1.
The flux $F_{i+\frac{1}{2}}$ at the right cell interface is given as (Koren, 1993):

$$F_{i+\frac{1}{2}} = \left( F_i + \frac{1}{2} \Phi \left( r_{i+\frac{1}{2}} \right) (F_i - F_{i-1}) \right)$$

and $\Phi$ is defined as:

$$\Phi \left( r_{i+\frac{1}{2}} \right) = \max \left( 0, \min \left( 2r_{i+\frac{1}{2}}, \min \left( \frac{1}{3} + \frac{2}{3}r_{i+\frac{1}{2}}, 2 \right) \right) \right).$$

The argument $r_{i+\frac{1}{2}}$ of the function $\Phi$ is given as

$$r_{i+\frac{1}{2}} = \frac{F_{i+1} - F_i + \varepsilon}{F_i - F_{i-1} + \varepsilon}.$$

Analogously, one can formulate the flux $F_{i-\frac{1}{2}}$. Here, $\varepsilon = 10^{-10}$.

There are several other limiting functions, namely, minmod, superbee and MC limiters, etc. Each of them leads to a different HR-scheme (LeVeque 2002, Koren 1993).
Example 1: All Processes

The initial data:

\[
f(0, x) = \begin{cases} 
100 & \text{for } 0.4 \leq x \leq 0.6, \\
0.01 & \text{elsewhere}.
\end{cases}
\]

B.C.: \( f(t, 0) = 100 + 10^6 \exp(-10^4(t - 0.215)^2) \).

\( G = 1.0, \beta = 1.5 \cdot 10^{-5}, b(t, x, x') = \frac{2}{x'}, \) and \( S(x) = x^2. \) The exact solution in growth and nucleation case is:

\[
f(t, x) = \begin{cases} 
10^2 + 10^6 \exp(-10^4((G't - x) - 0.215)^2) & \text{for } 0 \leq x \leq Gt, \\
10^2 & \text{for } 0.4 \leq x - Gt \leq 0.6, \\
0.01 & \text{elsewhere}.
\end{cases}
\]

\( t_{\text{max}} = 0.5 \) and \( N = 200. \)
Results of Method 1: MOC+FVM

- **Pure Growth and Nucleation**
- **Nucleation + Growth + Aggregation**
- **Nucleation + Growth + Breakage**
- **Nucleation + Growth + Aggregation + Breakage**

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Results of Method 2: FVM

- Pure Growth and Nucleation
- Nucleation + Growth + Aggregation
- Nucleation + Growth + Breakage
- Nucleation + Growth + Aggregation + Breakage

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Example 2: Pure Growth

The initial data are:

\[ f(0, x) = \begin{cases} 
1 \times 10^{10} & \text{if } 10 < x < 20, \\
0 & \text{elsewhere}. 
\end{cases} \]

with \( G = 1.0, \ N = 100, \ t = 60. \)

For mesh adaptation we have used a moving mesh technique of T. Tang et al. (2003)
Preferential Crystallization

**Isothermal Case**

\[ \text{Temperature} = 33 \degree C. \]

**Non-isothermal Case**

\[
T(t)[C^0] = -1.24074e^{-7}t^3 + 4.50926e^{-5}t^2 - 0.0040556t + 33. 
\]
Example 3: Preferential Crystallization

The initial data:

\[ f^{(p)}(0, x) = \frac{1}{\sqrt{2\pi}\sigma l_a} \cdot \frac{1}{x} \cdot \exp \left[ -\frac{1}{2} \cdot \left( \frac{\ln(x) - \mu}{\sigma} \right)^2 \right], \]

\[ f^{(c)}(0, x) = 0, \quad \text{with} \quad l_a = \frac{k_v \cdot \rho_s M_s}{\mu_3^{(p)}(0)}. \]

Here \( M_s = 2.5 \cdot 10^{-3} \text{kg} \) is the mass of initial seeds. The maximum crystal size is \( x_{\text{max}} = 0.005 \text{ m} \) with \( N = 500 \) for \( t = 600 \text{ min} \).
Example 3: Preferential Crystallization

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Example 3: Preferential Crystallization

Isothermal Case

Non-isothermal Case

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Example 3: Mass Preservation in the Schemes

Table: Percentage errors in mass preservation without fines dissolution.

<table>
<thead>
<tr>
<th>Method</th>
<th>Isothermal</th>
<th>Non-isothermal</th>
<th>CPU time (s) (isothermal)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N=500</td>
<td>N=1000</td>
<td>N=500</td>
</tr>
<tr>
<td>First order</td>
<td>3.737</td>
<td>3.775</td>
<td>4.460</td>
</tr>
<tr>
<td>HR-$\kappa = -1$</td>
<td>3.811</td>
<td>3.813</td>
<td>4.733</td>
</tr>
<tr>
<td>HR-$\kappa = 1/3$</td>
<td>3.813</td>
<td>3.814</td>
<td>4.736</td>
</tr>
<tr>
<td>MOC</td>
<td>2.604</td>
<td>1.844</td>
<td>3.792</td>
</tr>
</tbody>
</table>

Table: Percentage errors in mass preservation with fines dissolution.

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<tbody>
<tr>
<td></td>
<td>N=500</td>
<td>N=1000</td>
<td>N=500</td>
</tr>
<tr>
<td>First order</td>
<td>2.801</td>
<td>2.838</td>
<td>2.841</td>
</tr>
<tr>
<td>HR-$\kappa = -1$</td>
<td>2.873</td>
<td>2.875</td>
<td>2.962</td>
</tr>
<tr>
<td>HR-$\kappa = 1/3$</td>
<td>2.875</td>
<td>2.876</td>
<td>2.965</td>
</tr>
<tr>
<td>MOC</td>
<td>1.823</td>
<td>1.30</td>
<td>2.055</td>
</tr>
</tbody>
</table>
Results of isothermal (30 °C) seeded growth experiments with mandelic acid in water. Left: without counter enantiomer; Right: with counter-enantiomer (Lorenz et al., 2006).
For Further Reading

S. Qamar, M. Elsner, I. Angelov, G. Warnecke and A. Seidel-Morgenstern
A comparative study of high resolution schemes for solving population balances in crystallization.

S. Qamar, and G. Warnecke
Solving population balance equations for two-component aggregation by a finite volume scheme.

S. Qamar, and G. Warnecke
Numerical solution of population balance equations for nucleation growth and aggregation processes.
Thanks for your Attention