Using a hybrid particle-number and particle model to study high-rate aerosol synthesis

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Industrial aerosol synthesis is challenging to study

- Fast growth dynamics
- Complex reactor geometry
- High particle number density
- Non-spherical particles

Reactants introduced
Particles form and grow
Precursor

O₂
Complex morphology requires detailed particle models

Typical product particle

- Non-spherical particles
- Overall size $\mathcal{O}(1) \, \mu m$
- Multiple primary particles
- Primary size $\mathcal{O}(100) \, nm$
- Varying degrees of primary particle cohesion/bonding

$\Rightarrow$ Need a particle model that can account for particle morphology
Complex morphology requires detailed particle models

Typical product particle

- Non-spherical particles
- **Overall size** $\mathcal{O}(1) \, \mu m$
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⇒ Need a particle model that can account for particle morphology

SEM provided by Venator
A detailed particle model\textsuperscript{1,2,3}

\[ P_i = (p_1, \ldots, p_n, C) \]

\[ p_j = \text{(number of units)} \]

\[ C_{a,b} = \text{(shared surface)} \]

Gas phase and particle mechanisms describe the system.

\[ \text{TiCl}_4 + \text{O}_2 \rightarrow \text{Ti}_x\text{O}_y\text{Cl}_z \]

- Gas phase model
- Population balance model
Gas phase and particle mechanisms describe the system

Gas: **66 reactions** for **29 species** with thermodata from DFT$^{1,2,3}$

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Gas phase and particle mechanisms describe the system

Particle: **PBE** describes evolution of particles of type $x \in \mathcal{X}$

$$\frac{d}{dt} n(t, x) = I(x) + \mathcal{K}(n)(t, x) + S(n)(t, x) + \mathcal{F}(n)(t, x)$$
Gas phase and particle mechanisms describe the system

Operator-splitting: couples gas phase system advanced by ODE method and particle system advanced by Monte Carlo solver\(^1\)

This allows study of evolving particle structure

Titania industrial reactor

Reactor network model

Dosing \( x = 0.2L \)  
Reactor \( x = L \)  
Cooler \( x = 7L \)

TEM-style images from simulation


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Large ensembles are required to resolve the PSD

PRE-DEFINED ENSEMBLE CAPACITY

Number of particles

Time

Ensemble
Large ensembles are required to resolve the PSD

1. Use a smaller sample volume
2. Pre-define a larger ensemble

PRE-DEFINED ENSEMBLE CAPACITY

Number of particles vs Time
Particle complexity varies...

\[ P_i = (x_i, w_i) \]

- Spherical
- Detailed

Real system

Model system

\[ V_{real} \]
\[ V_{smp} \]

Particle type space

Particle model

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Particle complexity varies...

\[ P_i = (x_i, w_i) \]

Real system

Model system

Particle type space

Aggregate

Particle model

\[ V_{\text{real}} \]

\[ V_{\text{smp}} \]

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Particle complexity varies...

$V_{\text{real}}$  

$V_{\text{smp}}$  

$P_i = (x_i, w_i)$  

Model system  

Particle type space  

Particle model  

Aggregate  

Crystal  

Real system
... we can exploit this by splitting the type space
i.e. use a hybrid particle-number and detailed particle model\(^1\)

For a particle \(P\):

\[ P \in \mathcal{M} \quad \bullet \text{small particles} \]

\[ P \in \mathcal{X} \quad \bullet \text{particles above a threshold size} \]
\[ \quad \bullet \text{structurally complex particles} \]

... we can exploit this by splitting the type space i.e. use a hybrid **particle-number** and **detailed particle** model\(^1\)

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Adapting DSA to allow particle-number and particle models

Hybrid approach is \textbf{exact} for a univariate primary particle model

\textit{Convergence study}

\textbf{Particle size distribution (KDE)}


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Hybrid method reduces ensemble size requirements

1. Use a smaller sample volume
2. Pre-define a larger ensemble

PRE-DEFINED ENSEMBLE CAPACITY

Number of particles

Time

Ensemble


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Hybrid method reduces ensemble size requirements

1. Use a smaller sample volume
2. Pre-define a larger ensemble
3. Use hybrid particle model

PRE-DEFINED ENSEMBLE CAPACITY

Number of particles using hybrid type space model


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Hybrid method reduces error for a given cost

- Pre-defined space exceeded
- Use a smaller sample volume
- Use hybrid particle model

More efficient loading facilitates simulating high-rate conditions

A small reactor network with representative industrial conditions:

![Diagram of reactor network]

- CSTR 1
- CSTR 2
- CSTR 3
- CSTR 4
- PFR

**Loading**

- **CSTR1**: Loading over time
- **CSTR2**: Loading over time
- **CSTR3**: Loading over time
- **CSTR4**: Loading over time
- **PFR**: Loading over distance

**Time, t/τ**

0 5 10

**Distance, x/L**

0.0 0.5 1.0

**Number List**

- **N_max**
- **Ensemble**
More efficient loading facilitates simulating high-rate conditions

A small reactor network with representative industrial conditions:
More efficient loading facilitates simulating high-rate conditions

A small reactor network with representative industrial conditions:

Efficient, robust treatment of particles

Permits complex structures
More efficient loading facilitates simulating high-rate conditions

A small reactor network with representative industrial conditions:

![Diagram of reactor network]

CSTR 1 → CSTR 2 → CSTR 3 → CSTR 4 → PFR

- \( f_0 \)
- \( f_1 \)
- \( f_2 \)
- \( f_3 \)
- \( f_4 \)

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We can start to explore developed particle morphology

- Typical primary PSD?
- Aggregate polydispersity?
- Level of primary cohesion?
- Aggregate size?
Process conditions have different effects on polydispersity*

\[ \text{CoV} (d) := \frac{\sigma(d)}{d} \]

*10% increase in labelled condition *cf.* base case for one CSTR
Conclusions

A hybrid particle-number and particle model was introduced to address numerical challenges in the Monte Carlo algorithm.

It improves efficiency of industrially representative simulations:

▶ simpler description of small particles
▶ detailed resolution of aggregate structure when required

It facilitates more robust and flexible simulations.

This allows studying particle growth under high-rate conditions.
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