Prediction of Polymers Particles Morphology Development: Models and Methods

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Outline

- Motivation and Process Description
- Modelling Approaches
  1. Individual-based Methods
  2. Population-based Methods
- Results and Comparison
- Conclusions
Multiphase Polymers

- **Multiphase polymers**: comprise phase-separated domains

- **Morphology**: pattern of phases domains. Defines the material’s performance

- **Great practical interest**: multiphase polymers provide performance advantages over particles with uniform compositions

- **Applications**: synthetic rubber, paints, cosmetics, diagnostic tests, drug delivery

- **Current status**:
  - synthesis of new morphologies is time and resources consuming: largely relies on heuristic knowledge
  - no general morphology predicting methodology for multiphase system

- **Objective**: to develop a computationally feasible modeling approach for prediction of the particle morphology development in multiphase systems
Process Description

Production of Composite Latex Particles
Seeded emulsion polymerization

Monomer(s) 1
Inorganic
Water
Emulsifier

SEED (Polymer 2)
Initial Charge
Composite particles
Final Product

Stage I
Monomer swollen particle \( P_1 \)

Stage II
Monomer converts to polymer \( P_2 \)
Non-equilibrium morphology
Equilibrium morphology

process time

Simone Rusconi  BCAM
Mathematical Modelling

**Individual-based Methods**
- Deterministic
  - Molecular Dynamics
  - Langevin Dynamics
  - Hybrid Monte Carlo
- Stochastic

**Population-based Methods**
- Deterministic
  - Reaction Diffusion Equations
  - Population Balance Equations
- Stochastic
  - Stochastic Simulation Algorithm
  - Chemical Langevin Dynamics
Individual-Based Approach: Challenges

1. **Large size systems**: particles of 200 nm in diameter surrounded by water

2. **Slow (rare event) processes**: take hours

3. **Dynamic is important**: non-equilibrium morphologies are governed by kinetics

4. **Mimicking technological process**: complex multivariate
Individual-Based Approach: Model

**Objective:** Simulate a single composite polymer particle consisting of phase beads and surrounded by water beads

1. **A single bead:** a polymer chain
2. **A water bead:** water molecules packed into a particle with size of the phase bead
3. **Number of beads** \( \approx 5 \times 10^3 \)
4. **Simulation sphere:** surrounded by impenetrable structureless wall
   - keeps phases within a polymer particle
   - mimics aqueous phase out of the sphere
5. **Interaction:** Lennard-Jones potential
   \[
   U_{LJ}(r_{ij}) = 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^{6} \right]
   \]
6. **Dynamics:** Langevin Dynamics
7. **Pressure** is imitated by moving the impenetrable wall
8. **Conversion of monomers to polymers** is reproduced by a gradual change of parameters of interaction potentials
   ✓ on exit: predicted equilibrium morphologies vs. technological conditions (TC) AND refined modeling parameters. Limited kinetic information

2. Langevin Dynamics Equations (Brünger, Brooks and Karplus, BBK integrator)
   ✓ on exit: monitoring of non-equilibrium morphologies vs. TC

\[ m \frac{d^2 r}{dt^2} = -\nabla U(r) - \gamma m \frac{dr}{dt} + \sqrt{2\gamma k_B T} m W(t) \]

- r: position, m: mass, \( \gamma \): friction factor, \( k_B \): Boltzmann constant, T: temperature, U: potential energy, t: time, W(t): Wiener processes
Individual-Based Approach: Results

- Predictions are in excellent agreement with experimental evidences
- Computation is very demanding (weeks of simulations on HPC)
- System description does not go beyond a single particle behaviour


Population-based Methods

- **Challenges:**
  1. Description of particles population
  2. Efficient algorithms implemented on high performance computers
  3. On-the-fly recommendations for polymerization processes

- **Model to solve:** Population Balance Equations (PBE)

- **Two families of approaches:**
  - **Deterministic**
    - Finite-Elements methods
    - Pivots Techniques
    - Method of Moments
  - **Stochastic**
    - Generalized Method of Characteristics
    - Monte Carlo based Simulation Algorithm
    - Stochastic Simulation Algorithm
Population Balance Equations: Introduction

Let \( m_{NE}(v, t) \) and \( m_E(v, t) \) be **density functions** for *non-equilibrium (NE)* and *equilibrium (E)* polymers agglomerates respectively.

\( m_{E,NE}(v, t) \) describe the evolution in **time** \( t \) of the **expected distribution** of **volumes** \( v \) of polymers agglomerates within each formed morphology.

**Expected number** of agglomerates with volume \( v \in [\alpha, \beta] \):

\[
\int_{\alpha}^{\beta} m_{E,NE}(v, t) \, dv
\]

**The Population Balance Equations (PBE)** for modelling time evolution of the density functions \( m_{E,NE}(v, t) \) can be written in the terms of the **reaction rates**
Population Balance Equations: Formulation

\[
\frac{\partial m_{E,NE}(v, t)}{\partial t} = - \frac{\partial (g(v, t)m_{E,NE}(v, t))}{\partial v} \pm k_{\text{moving}} m_{NE}(v, t)
\]

growth transport

\[
+ \frac{1}{2} \mathbb{1}_{\{v \geq 2v_{\text{min}}\}} \int_{v_{\text{min}}}^{v-v_{\text{min}}} k_{\text{aggr}}(v - u, u, t)m_{E,NE}(v - u, t)m_{E,NE}(u, t)du
\]

aggregation produces agglomerates with volume \(v\)

\[
- m_{E,NE}(v, t) \int_{v_{\text{min}}}^{+\infty} k_{\text{aggr}}(v, u, t)m_{E,NE}(u, t)du
\]

aggregation between volume \(v\) and \(u\) agglomerates

\(g(v, t)\): expected volume increase per unit time of volume \(v\) agglomerates

\(k_{\text{moving}}\): constant expected proportion of agglomerates moving from \(NE\) to \(E\) per unit time

\(k_{\text{aggr}}(v, u, t)\): expected proportion of volumes \(v\) and \(u\) agglomerates aggregating per unit time

**Aggregation terms:** Smoluchowski coagulation equation

Boundary and Initial Conditions

▶ **Initial Conditions (IC):**

\[ m_{E,NE}(v, 0) = 0 \quad \forall v \in [v_{\text{min}}, +\infty) \]

▶ **Boundary Conditions (BC):**

\[ m_{NE}(v_{\text{min}}, t) = \frac{k_{\text{form}}(t)}{g(v_{\text{min}}, t)} \quad \forall t \in \mathbb{R}^+ \]

\[ m_{E}(v_{\text{min}}, t) = 0 \quad \forall t \in \mathbb{R}^+ \]

▶ \( k_{\text{form}}(t) \): expected number of \( NE \) agglomerates with volume \( v_{\text{min}} \) formed per unit time
## Proposed Approaches: Deterministic & Stochastic

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<tr>
<th>Challenge</th>
<th>Deterministic Approach</th>
<th>Stochastic Approach</th>
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<tr>
<td><strong>Choice of Building Units</strong></td>
<td>Generalized Characteristics</td>
<td>Reaction Rates</td>
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<td><strong>Computationally Intractable Orders of Magnitude</strong></td>
<td>Optimal Scaling</td>
<td>Coarse Model</td>
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<tr>
<td><strong>Accuracy</strong></td>
<td>Numerical Stability?</td>
<td>Numerical Stability!</td>
</tr>
<tr>
<td><strong>Efficiency</strong></td>
<td>Fast Integration</td>
<td>Slow Sampling</td>
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</tbody>
</table>

**Generalized Method of Stochastic Simulation (GMOC)**

**Stochastic Simulation Algorithm (SSA)**
Generalized Method of Characteristics: Introduction

- **Main Goal**: to transform the PBE system into an ODE system

- **Existing Methods**: to evaluate PBE system on $N$ curves $\{v = \varphi_k(t)\}_{k=1}^N$
  
  1. **Method of Lines (ML)**: to use constant lines, $\{\varphi_k(t) = \bar{\varphi}_k\}_{k=1}^N$
  2. **Method of Characteristics (MOC)**: given the growth rate $g(v, t)$, to define
     
     \[
     \left\{ \frac{d\varphi_k(t)}{dt} = +g(\varphi_k(t), t), \quad \varphi_k(0) = \bar{\varphi}_k \right\}_{k=1}^N
     \]

- **GMOC**: to keep general curves $\{v = \varphi_k(t)\}_{k=1}^N$ (generalized characteristics)

  ✓ **Main Advantage**: freedom in choice of curves $\{v = \varphi_k(t)\}_{k=1}^N$
  
  ✓ **Preferred Strategy**: to make curves $\varphi_k(t)$ more dense where $m_{E, NE}(v, t)$ steeply change

  ✓ **Open Question**: how to define the curves $\varphi_k(t)$?

- **In this study**: Method of Lines, $\bar{\varphi}_k = kh + v_{\min}, \; h > 0, \; \forall k = 1, .., N$

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GMOC: Formulation

1. Define $N$ curves $\nu = \varphi_k(t)$: $\varphi_k(t) > \varphi_{k-1}(t) \geq \nu_{\text{min}}$, $\forall t \in \mathbb{R}^+$, $\forall k = 1, .., N$

2. Given $m_{E,NE}^k(t) := m_{E,NE}(\nu, t)|_{\nu=\varphi_k(t)}$, evaluate the PBE system on $\nu = \varphi_k(t)$:

\[
\frac{dm_{E,NE}^k(t)}{dt} = + \frac{\partial m_{E,NE}(\nu, t)}{\partial \nu} \bigg|_{\nu=\varphi_k(t)} \frac{d\varphi_k(t)}{dt} - \frac{\partial (g(\nu, t)m_{E,NE}(\nu, t))}{\partial \nu} \bigg|_{\nu=\varphi_k(t)} \pm k_{\text{moving}} m_{NE}^k(t) \\
+ \frac{1}{2} \mathbb{1}\{\varphi_k(t) \geq 2\nu_{\text{min}}\} \int_{\nu_{\text{min}}}^{\varphi_k(t) - \nu_{\text{min}}} k_{\text{aggr}}(\varphi_k(t) - u, u, t)m_{E,NE}(\varphi_k(t) - u, t)m_{E,NE}(u, t)du \\
- m_{E,NE}^k(t) \int_{\nu_{\text{min}}}^{+\infty} k_{\text{aggr}}(\varphi_k(t), u, t)m_{E,NE}(u, t)du, \quad \forall t \in \mathbb{R}^+, \forall k = 1, .., N
\]

3. Impose PBE IC: $m_{E,NE}^k(0) = m_{E,NE}(\varphi_k(0), 0) = 0$, $\forall k = 1, .., N$

4. Impose PBE BC: define $\varphi_0(t) := \nu_{\text{min}}$ s.t. $m_{E,NE}^0(t) = m_{E,NE}(\nu_{\text{min}}, t)$, $\forall t \in \mathbb{R}^+$

5. Given $\{\varphi_k(t), m_{E,NE}^k(t)\}_{k=0}^N$, numerically approximate:

- volume $\nu$ partial derivatives by using finite difference schemes
- integral terms by using quadrature rules (composite Simpson)

6. Solve the resulting ODE system by using an ODE solver (Runge-Kutta) to provide a numerical approximation of PBE system solution
GMOC: Scaling Experimental Orders of Magnitude

- **Challenge**: to deal with computationally *intractable* experimental orders of magnitude, e.g. $m_{E,NE} \approx 10^{+38} \, \text{L}^{-1}$, $v_{\text{min}} = 2.5 \times 10^{-22} \, \text{L}$

- **Change of Variables**:
  
  \[
  \tilde{t} := \frac{t}{t_0}, \quad \tilde{v} := \frac{v}{v_0}, \quad \tilde{m}_{E,NE}(\tilde{v}, \tilde{t}) := \frac{m_{E,NE}(v,t)}{m_0},
  \]

  \[
  \tilde{k}_{\text{form}}(\tilde{t}) := \frac{k_{\text{form}}(t)}{\Gamma_f}, \quad \tilde{g}(\tilde{v}, \tilde{t}) := \frac{g(v,t)}{\Gamma_g}, \quad \tilde{k}_{\text{aggr}}(\tilde{v}, \tilde{u}, \tilde{t}) := \frac{k_{\text{aggr}}(v,u,t)}{\Gamma_a}
  \]

- **Optimal Scaling**: to search for $\theta := \log_{10} \{t_0, v_0, m_0, \Gamma_f, \Gamma_g, \Gamma_a\}$ as minimizer of the cost function
  
  \[
  C(\theta) := \sum 1_{\lambda_i(\theta)>0} [\log_{10}(\lambda_i(\theta)) - \Theta_i]^2,
  \]

  weighting the orders of dimensionless model parameters $\lambda_i(\theta)$ against desired orders $\Theta_i$, e.g. $\Theta_i = 0$

- **Simulated Annealing Optimization Method**:
  - ✓ not to get trapped into local minima
  - ✓ to deal with non smooth cost functions

- **Result**: the scaled model handles computationally *tractable* orders of magnitude, e.g. $\tilde{m}_{E,NE} \approx 1$, $\tilde{v}_{\text{min}} := v_{\text{min}}/v_0 = 2.5 \times 10^{-2}$

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Stochastic Simulation Algorithm: Introduction

- Stochastic Simulation Algorithm (SSA) is a popular method for simulation of polymerization processes

- Hypothesis of **well-mixed systems**: mixing is faster than reactions, information on positions of reactants can be neglected

- Hypothesis of **Markovian dynamics**: memoryless kinetics, each state depends only upon the previous state

- **Monte Carlo (MC) algorithm**: draws multiple realizations of the process and computes statistics on them

- The proper sampling guarantees **convergence** to the solutions of the chemical master equations (PBE)

SSA: Initialization

- Introduce a space discretization: \( v_k = kh + v_{\text{min}}, \ h > 0, \ \forall k = 0, \ldots, N \)
- Define \( X^k_E(t) \) and \( X^k_{NE}(t) \) as the numbers of \( E \) and \( NE \) agglomerates with volume \( v_k \) at time \( t \) respectively
- Polymerization can be seen as a stochastic process driven by the following reactions and corresponding rates functions

<table>
<thead>
<tr>
<th>Event</th>
<th>Reaction</th>
<th>Rate Function</th>
<th>( \lambda_i(t) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formation ( NE )</td>
<td>( X^0_{NE} \rightarrow X^0_{NE} + 1 )</td>
<td>( k_{\text{form}}(t) )</td>
<td></td>
</tr>
<tr>
<td>Moving ( NE \rightarrow E )</td>
<td>( X^k_{NE} \rightarrow X^k_{NE} - 1 ) ( X^k_E \rightarrow X_{E} + 1 )</td>
<td>( k_{\text{moving}}X^k_{NE}(t) )</td>
<td></td>
</tr>
<tr>
<td>Growth ( E, NE )</td>
<td>( X^k_{E,NE} \rightarrow X^k_{E,NE} - 1 ) ( X^{k+1}<em>{E,NE} \rightarrow X^{k+1}</em>{E,NE} + 1 )</td>
<td>( g(v_k, t) \frac{X^k_{E,NE}(t)}{h} )</td>
<td></td>
</tr>
<tr>
<td>Aggregation ( E, NE )</td>
<td>( X^k_{E,NE} \rightarrow X^k_{E,NE} + 1 ) ( X^i,j_{E,NE} \rightarrow X^i,j_{E,NE} - 1 )</td>
<td>( k_{\text{aggr}}(v_i, v_j, t)X^i_{E,NE}(t)X^j_{E,NE}(t) )</td>
<td></td>
</tr>
</tbody>
</table>

- REM: rates functions have similar forms as the terms in the PBE equations!
SSA: Formulation

- **Stochastic Dynamics**: given $X_{E,NE}^k(t)$, $k = 0, ..., N$

  1. Compute the rates functions $\lambda_l(t)$
  2. Draw $\tau \sim \text{Exp} \left( \sum_l \lambda_l(t) \right)$
  3. Update $t \leftarrow t + \tau$
  4. Choose the reaction $l$ with probability proportional to $\lambda_l(t)$
  5. Update $X_{E,NE}^k(t + \tau) = X_{E,NE}^k(t) + \nu_l$, where $\nu_l = \{-1, 0, +1\}$ is given by the chosen reaction $l$

- **Initial Conditions**: $X_{E,NE}^k(0) = 0$, $\forall k = 0, ..., N$

- **Sample**: draw $G$ independent realizations of the random process defined by the variables $X_{E,NE}^k(t)$

- **Estimations**:

  ✓ $M_{NE}(v, t)|_{v=v_k} = \mathbb{E} \left[ X_{NE}^k(t) \right]$: the mean numbers of $NE$ agglomerates with volume $v_k$ at time $t$

  ✓ $M_E(v, t)|_{v=v_k} = \mathbb{E} \left[ X_E^k(t) \right]$: the mean numbers of $E$ agglomerates with volume $v_k$ at time $t$
SSA: Scaling Experimental Orders of Magnitude

- **Challenge:** to deal with computationally *intractable* experimental orders of magnitude, e.g. $X_{E,NE}^k \approx 10^{+17}$, $v_{\text{min}} = 2.5 \times 10^{-22}$ L
- **Coarse Model:** quantize the polymers agglomerates into packages, given by $K$ polymers agglomerates with the same volume $v_k$
- **Variables Scaling:** $\tilde{v}_k = K v_k$, $\tilde{X}_{E,NE} = X_{E,NE}/K$
- **Rates Scaling:** recompute the rates functions to be the expected number of times each reaction fires for $K$ agglomerates, instead of one agglomerate per unit of time
- **Example:**
  - $k_{\text{form}}(t) = \text{expected number of times one single polymers agglomerate with volume $v_{\text{min}}$ is formed per unit of time}$
  - $k_{\text{form}}(t)/K = \text{expected number of times one package of $K$ polymers agglomerates with volume $v_{\text{min}}$ is formed per unit of time}$
- **Open Questions:**
  - is the quantized system equivalent to the original one?
  - given dimensionless PBE (optimal scaling), how to define corresponding reactions and rate functions?
The approximated **density function** $m_{NE}(v, t)$ of non-equilibrium polymers agglomerates, provided by the **Method of Lines**

The estimated **mean number** $M_{NE}(v, t)$ of non-equilibrium polymers agglomerates, provided by the **Stochastic Simulation Algorithm**
The approximated **density function** \( m_E(v, t) \) of equilibrium polymers agglomerates, provided by the **Method of Lines**

The estimated **mean number** \( M_E(v, t) \) of equilibrium polymers agglomerates, provided by the **Stochastic Simulation Algorithm**
The two proposed approaches demonstrate the same resulting trends for the unknown distributions.

ML finds the irregular structure of $m_{E,NE}(v, t)$ for small volumes and times, which is not confirmed by SSA.

SSA returns broader distributions of volumes.

ML is faster than SSA: minutes vs. hours on 2.7 GHz Intel Core i5 processor running a Linux environment.

SSA is not affected by numerical instabilities, but big sample sizes are required to provide accurate estimations.
Conclusions

- Our objective is to develop the methodology which ultimately will contribute in guiding the synthesis of high performance polymers.
- This requires fast and accurate predictions of polymerization processes.
- We present three approaches which are potentially promising tools for being used individually or/and jointly in the rational design of new materials:
  1. **Individual-based method** provides accurate description of a single particle, but computationally is very demanding.
  2. **ML** allows for particles ensemble description and it provides the required computational speed, but often at the price of accuracy for prediction.
  3. **SSA** provides description of particles ensemble, it shows numerical stability, but computationally is rather demanding.

- **Future Developments**: to look for answers to open questions.
Thank you

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