Multi-phase Particles: comprise phase-separated polymers

Morphology: pattern of phase-separated domains. It defines the material’s performance

Practical Interest: multi-phase polymers provide performance advantages over particles with uniform composition

Applications: synthetic rubber, latex, cosmetics, drug delivery

Examples of particle morphologies: the white and black areas indicate phase-separated domains
State-of-the-art & Our Objective

Current Status:

✔ synthesis of multi-phase particles is time and resources consuming
✔ it largely relies on heuristic knowledge
✔ no general methodology for prediction of morphology formation

Objective: to develop a computationally efficient modelling approach for prediction of multi-phase particles morphology formation
Multi-phase Particles Morphology Formation

**Morphology Formation** \(\equiv\) dynamics of phase-separated polymers clusters

**Reaction Mechanisms** driving polymers clusters within a single particle [●]:

(a) **Polymerization**: conversion of monomers [●] into polymers chains [▪▪]

(b) **Nucleation**: polymers chains [▪▪] agglomerate into clusters [●]

(c) **Growth**: clusters [●] increase their volume

(d) **Aggregation**: clusters, with sizes \(v\) and \(u\), merge into a newly formed cluster with size \(v+u\)

(e) **Migration**: transition of clusters from a phase [●] to another phase [●]
Multi-phase Particles Morphology Formation

- **Morphology Formation** ≡ dynamics of phase-separated polymers clusters
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(d) **Aggregation**: clusters, with sizes \( v \) and \( u \), merge into a newly formed cluster with size \( v+u \)
(e) **Migration**: transition of clusters from a phase [●] to another phase [●]

**Idea**: morphology formation can be described through time \( t \) evolution of the size \( v \) distribution \( m(v,t) \) of clusters belonging to a given phase
Population Balance Equation (PBE) for Multi-phase Particles Morphology (MPM)

Polymers clusters in MPM development are subjected to: **Nucleation, Growth, Aggregation** and **Migration**

The distribution \( m(v,t) \) of clusters size \( v \) satisfies the PBE system

\[
\frac{\partial m(v,t)}{\partial t} = - \frac{\partial (g(v,t) m(v,t))}{\partial v} + n(v,t) - \mu(v,t) m(v,t) - m(v,t) \int_0^\infty a(v,u,t) m(u,t) \, du
\]

\[
+ \frac{1}{2} \int_0^v a(v-u,u,t) m(v-u,t) m(u,t) \, du, \quad \forall v, t \in \mathbb{R}^+,
\]

\[
m(v,0) = \omega_0(v) \geq 0, \quad \forall v \in \mathbb{R}^+, \quad g(0,t) m(0,t) = 0, \quad \forall t \in \mathbb{R}^+.
\]

Population Balance Equation (PBE): Outcome & Difficulties

**Outcome**

Well defined PBE based model for prediction of Multi-phase Particles Morphology Formation

**Difficulties**

- Experimental Parameters
- Critical Nucleation Size
- Transport Term
- Integral Terms

- Computationally Intractable Orders of Magnitude
- $n(v,t)$ proportional to $\delta(v-v_0)$, with $v_0 > 0$ and $\delta(x)$ the Dirac delta
- Steep Moving Fronts
- Non-Local Terms
- Unbounded Support of $m(v,t)$

Highly aggregating processes may lead to:
(a) numerical inaccuracies
(b) domain errors
Experimental Parameters: Computationally Intractable Variables

**Problem:** Experimental Values of Parameters $p$ lead to Computationally Intractable Orders of Magnitude

**Strategy:** Scale Variables $x = \{v, t, m\}$ to Computationally Tractable Values

$\nu \approx 10^{-21} L, m \approx 10^{36} L^{-1}$

**General Problem Formulation:** scale to dimensionless and computationally tractable variables the equation $f(x; p) = 0$ with

- Independent and Unknown Variables $x \equiv \{x_1, .., x_{N_x}\}$ in Physical Units
- Parameters $p \equiv \{p_1, .., p_{N_p}\}$ with Experimental Values in Physical Units

**Change of Variables:** $x \rightarrow \tilde{x}$ with

- Scaling Factors $\theta \equiv \{\theta_1, .., \theta_{N_x}\} \in (0, \infty)^{N_x}$ with Dimensions as $x$
- Dimensionless Variables $\tilde{x} \equiv \{\tilde{x}_1 = x_1/\theta_1, .., \tilde{x}_{N_x} = x_{N_x}/\theta_{N_x}\}$

**Plug the Change of Variables** $x \rightarrow \tilde{x}$ in $f(x; p) = 0$

**Rewrite** $f(x; p) = 0$ in Dimensionless Form $\tilde{f}(\tilde{x}; \lambda) = 0$ with

- Dimensionless Coefficients $\lambda(\theta; p) \equiv \{\lambda_1(\theta; p), .., \lambda_{N_d}(\theta; p)\} \in (0, \infty)^{N_d}$

**Question:** How to Set $\theta$ for Ensuring Tractable Values?
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**State-of-the-art:**

- Impose as Many $\lambda$ as Possible Equal to 1

**Holmes. Springer, 2009.**

- If $N_d \leq N_x$, solve $N_d$ equations with $N_x$ unknowns,

  $$\exists \theta \in (0, \infty)^{N_x} \quad \text{s.t.} \quad \lambda_i(\theta; p) = 1, \ \forall i = 1, .., N_d$$

- If $N_d > N_x$, it is possible to ensure at most $N_x$ coefficients $\lambda$ equal to 1, while there is no control on the remaining $N_d - N_x > 0$ coefficients
**Optimal Scaling Factors** $\theta_{\text{opt}} \in (0, \infty)^{N_x}$: find $\theta = \theta_{\text{opt}}$ such that all coefficients $\lambda$ have magnitude $\approx 10^0$,

$$\theta_{\text{opt}} \equiv \arg\min_{\theta \in (0, \infty)^{N_x}} C(\theta), \quad C(\theta) \equiv \sum_{i=1}^{N_d} \left[ \log_{10}(\lambda_i(\theta; p)) - \log_{10}(10^0) \right]^2,$$

where $C(\theta)$ measures the distance of the magnitudes of $\lambda$ from $10^0$.
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where $C(\theta)$ measures the distance of the magnitudes of $\lambda$ from $10^0$.

1. The Buckingham $\Pi$-theorem ensures $\forall i = 1, \ldots, N_d$ and $\forall j = 1, \ldots, N_x$ 

$$
\lambda_i(\theta) = \kappa_i \theta_1^{\alpha_i^1} \cdots \theta_{N_x}^{\alpha_i^{N_x}}, \quad \kappa_i > 0, \quad \alpha_i^j \in \mathbb{R}
$$

2. Imposing $\nabla C(\theta) = 0$, one obtains a symmetric linear system,

$$
\left( \sum_{i=1}^{N_d} \alpha_i^1 \alpha_j^i \right) \rho_1 + \cdots + \left( \sum_{i=1}^{N_d} \alpha_i^{N_x} \alpha_j^i \right) \rho_{N_x} = \log_{10}(\hat{\kappa}_j), \quad \forall j = 1, \ldots, N_x,
$$

whose solution provides $\theta_{\text{opt}} = \{10^{\rho_j}\}_{j=1}^{N_x}$, given $\hat{\kappa}_j = \prod_{i=1}^{N_d} \kappa_i^{-\alpha_j^i}$

S. Rusconi, D. Dutykh, A. Zarnescu, D. Sokolovski, E. Akhmatskaya, An optimal scaling to computationally tractable dimensionless models: Study of latex particles morphology formation, submitted to Journal of Computational Physics, 2018
**Our Strategy:** Optimal Scaling

**Analytical Solution for Optimal Scaling Factors**

**Benefits:**
(a) save computational resources  
b) possible insight for further analysis

---

**Optimal Scaling Factors** $\theta_{\text{opt}} \in (0, \infty)^{N_x}$: find $\theta = \theta_{\text{opt}}$ such that all coefficients $\lambda$ have magnitude $\approx 10^0$,

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Numerical Study of Latex Particles Morphology
Data provided by POLYMAT research group led by Prof. Asua

\[ v \approx 10^{-21} \, \text{L}, \quad t \approx 10^2 \, \text{s}, \quad m \approx 10^{36} \, \text{L}^{-1} \]

Range of Orders of Magnitude \( \approx 10^{57} \)

Original Model

Dimensionless Model

Range of Orders of Magnitude
\[ \max_i \lambda_i / \min_i \lambda_i \approx 10^5 \]

Well Defined & Computationally Tractable PBE System

S. Rusconi, Ph.D. thesis, UPV/EHU, 2018
Optimal Scaling: Computationally Tractable Variables

Results

Numerical Study of Latex Particles Morphology
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Dimensionless Model

Range of Orders of Magnitude
\[ \max_i \lambda_i / \min_i \lambda_i \approx 10^5 \]

Well Defined & Computationally Tractable PBE System

Question

Accurate and Efficient Solution of PBE System?
Given PBE

$$\frac{\partial m(v, t)}{\partial t} = -\frac{\partial (g(v, t) m(v, t))}{\partial v} + n(v, t) - \mu(v, t) m(v, t) - m(v, t) \int_0^\infty a(v, u, t) m(u, t) \, du$$

$$+ \frac{1}{2} \int_0^v a(v - u, u, t) m(v - u, t) m(u, t) \, du, \quad \forall v, t \in \mathbb{R}^+,$$

and assumptions, with $\delta(x)$ the Dirac delta and $a_0, \mu_0, g_0, n_0, v_0, \bar{M} > 0$:

<table>
<thead>
<tr>
<th>Model I</th>
<th>Model II</th>
<th>Model III</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a(v, u, t) = a_0$</td>
<td>$a_0$</td>
<td>$a_0$</td>
</tr>
<tr>
<td>$\mu(v, t) = \mu_0$</td>
<td>$\mu_0$</td>
<td>$\mu_0$</td>
</tr>
<tr>
<td>$g(v, t) = g_0$</td>
<td>$g_0 v$</td>
<td>$g_0$</td>
</tr>
<tr>
<td>$n(v, t) = n_0 \delta(v - v_0)$</td>
<td>$0$</td>
<td>$0$</td>
</tr>
<tr>
<td>$\int m(v, 0) , dv = \bar{M}(a_0, \mu_0, n_0)$</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

We found the solution for the Laplace Transform $\hat{m}(\lambda, t) = \int_0^\infty e^{-\lambda v} m(v, t) \, dv$, that satisfies, under assumptions of Model $X = \{I, II, III\}$:

$$\frac{\partial \hat{m}(\lambda, t)}{\partial t} + \hat{g}_x(\lambda) \frac{\partial \hat{m}(\lambda, t)}{\partial \lambda} = \hat{a}_x(\lambda) + \hat{b}_x(\lambda, t) \hat{m}(\lambda, t) + \hat{c}_x \hat{m}^2(\lambda, t), \quad \forall \lambda \in \mathbb{C}, \forall t \in \mathbb{R}^+$$

The numerical inverse of $\hat{m}(\lambda, t)$ provides the solution $m(v, t)$ of PBE.
Laplace Transform Technique (LTT): Benefits & Drawback

**Benefits**

- High Level of Efficiency and Accuracy for tested Models I, II, III
  - Few Seconds of Running Time
  - Baselines for Validation and Evaluation of Other Methods

**Accuracy** of solution $m(v, t)$ provided by any Numerical Method is quantified by

$$\varepsilon(v, t) \equiv \frac{|m_{LTT}(v, t) - m(v, t)|}{\left[ \int_0^{v_{\text{max}}} m_{LTT}(v, t)^2 \, dv \right]^{1/2}}, \quad \forall v \in [0, v_{\text{max}}], \forall t \in [0, T_{\text{max}}],$$

with $m_{LTT}(v, t)$ the LTT solution, $[0, v_{\text{max}}]$ and $[0, T_{\text{max}}]$ the integration domains

**Drawback**

- Limited Description of Reaction Physics
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**Drawback**
- Limited Description of Reaction Physics

**Question:** How to Extend Applicability?
Generalised Method Of Characteristics (GMOC)

- **MOC:** Evaluate PBE along the Curves \( v = \varphi_k(t) \), with \( \varphi'_k(t) = g(\varphi_k(t), t), \forall t \in \mathbb{R}^+, k = 1, \ldots, N \), and integrate in time the resulting ODE system.

- **GMOC:** Shape of Curves \( v = \varphi_k(t) \) is not Prescribed in Advance

- **System State** \( m_k(t) \equiv m(v, t)\bigg|_{v=\varphi_k(t)}, \forall t \in \mathbb{R}^+, k = 1, \ldots, N: \)

\[
\frac{dm_k(t)}{dt} = \left[ \frac{d\varphi_k(t)}{dt} - g(\varphi_k(t), t) \right] \frac{\partial m(v, t)}{\partial v} \bigg|_{v=\varphi_k(t)} - \left[ \frac{\partial g(v, t)}{\partial v} \bigg|_{v=\varphi_k(t)} + \mu(\varphi_k(t), t) \right] m_k(t) + 
\]

\[
+ n(\varphi_k(t), t) + A^+(\varphi_k(t), t; m(\cdot, t)) - A^-(\varphi_k(t), t; m(\cdot, t)),
\]

where \( A^\pm(\varphi_k(t), t; m(\cdot, t)) \) are the Integral Terms of PBE evaluated on \( v = \varphi_k(t) \).

- **Impulsive Nucleation:** \( n(v, t) \propto \delta(v - v_0) \approx \mathcal{N}(v; v_0, \sigma_0), \) with \( 0 < \sigma_0 \ll v_0 \) and \( \mathcal{N}(x; \mu, \sigma) \) the Gaussian distribution with mean \( \mu \) and std. dev. \( \sigma \)

- **Boundary Condition:** Impose \( g(0, t) m_0(t) = 0 \), with \( m_0(t) \equiv m(0, t) \)

- **Partial Derivative** \( \partial_v m(v, t)\bigg|_{v=\varphi_k(t)} \approx \) Fourth-Order Finite Difference Scheme

- **Integral Terms** \( A^\pm(\varphi_k(t), t; m(\cdot, t)) \approx \) Fourth-Order Simpson’s Rule

- **Time Evolution:** Fourth-Order Runge-Kutta Method (RK4)
Generalised Method Of Characteristics (GMOC)

**Novel Implementation of Known Method Of Characteristics (MOC)**

**System State** $m_k(t) \equiv m(v, t)|_{v=\varphi_k(t)}$, $\forall t \in \mathbb{R}^+$, $k = 1, \ldots, N$:

$$\frac{dm_k(t)}{dt} = \left[ \frac{d\varphi_k(t)}{dt} - g(\varphi_k(t), t) \right] \frac{\partial m(v, t)}{\partial v} \bigg|_{v=\varphi_k(t)} - \left[ \frac{\partial g(v, t)}{\partial v} \right]_{v=\varphi_k(t)} + \mu(\varphi_k(t), t) \right] m_k(t) +$$

$$+ n(\varphi_k(t), t) + A^+(\varphi_k(t), t; m(\cdot, t)) - A^-(\varphi_k(t), t; m(\cdot, t)),$$

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**Impulsive Nucleation**: $n(v, t) \propto \delta(v - v_0) \approx \mathcal{N}(v; v_0, \sigma_0)$, with $0 < \sigma_0 < v_0$ and $\mathcal{N}(x; \mu, \sigma)$ the Gaussian distribution with mean $\mu$ and std. dev. $\sigma$

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**Integral Terms** $A^\pm(\varphi_k(t), t; m(\cdot, t)) \approx$ Fourth-Order Simpson’s Rule

**Time Evolution**: Fourth-Order Runge-Kutta Method (RK4)

**Benefit**: GMOC is Applicable to a **Broader Range** of Rate Functions than LTT
Generalised Method Of Characteristics (GMOC): Drawbacks

**Drawbacks**

Numerical Oscillations due to Moving Fronts (Model I)

Targeted Accuracy: \( \max \varepsilon \approx 10^{-1} \)

CPU time GMOC: \( 7.5 \times 10^3 \) sec

![Graph showing m(v,t) and \( \varepsilon(v,t) \) over v with different GMOC times]
Generalised Method Of Characteristics (GMOC): Drawbacks

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Generalised Method Of Characteristics (GMOC): Drawbacks

**Drawbacks**

Numerical Oscillations due to Moving Fronts (Model I)

Non-Trivial Choice of Curves $v=\varphi_k(t)$: We use $\varphi_k(t)=kh$, $h>0$, since Beneficial for $A^\pm$

Approximation of $\delta(v-v_0)$ leads to $h\ll\sigma_0\ll v_0$

Inefficient Treatment of Small Nucleation Size $v_0$ and Large Volume Domains

![Graph showing model predictions and accuracy](image)
Generalised Method Of Characteristics (GMOC): Drawbacks

**Drawbacks**

- **Numerical Oscillations** due to Moving Fronts (Model I)
- Non-Trivial Choice of Curves $v=\varphi_k(t)$:
  We use $\varphi_k(t)=kh$, $h>0$, since Beneficial for $A^\pm$
- Approximation of $\delta(v-v_0)$ leads to $h\ll\sigma\ll v_0$

**Inefficient Treatment of**
Small Nucleation Size $v_0$ and Large Volume Domains

**Next Task:** Address GMOC Problems

Targeted Accuracy: $\text{max } \varepsilon \approx 10^{-1}$
CPU time GMOC: $7.5 \times 10^3$ sec
**Laplace Induced Splitting Method (LISM)**

**Conceptually New Methodology for PBE Systems**

S. Rusconi, Ph.D. thesis, UPV/EHU, 2018

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**Decompose** PBE into sum of differential and integral operators:

\[
\partial_t m(v, t) = Dm(v, t) + Im(v, t), \quad \forall v, t \in \mathbb{R}^+,
\]

where

\[
\begin{align*}
Dm(v, t) &\equiv -\frac{\partial(g(v, t) m(v, t))}{\partial v} + n(v, t) - \mu(v, t) m(v, t) \\
Im(v, t) &\equiv \frac{1}{2} \int_0^v a(v - u, u, t) m(v - u, t) m(u, t) \, du - m(v, t) \int_0^\infty a(v, u, t) m(u, t) \, du
\end{align*}
\]

**By means of Laplace Transform** \( \hat{m}(\lambda, t) \) of \( m(v, t) \), find the **explicit expression** \( m_X(v, t; \omega_0(\cdot)) \) of solution of sub-problem \( X = A, B, C \) for any \( m(v, 0) = \omega_0(v) \):

**A:** \( \partial_t m(v, t) = Dm(v, t), \quad g(v, t) = g_0 v, \quad n(v, t) = n_0 \delta(v - v_0), \quad \mu(v, t) = \mu_0 \)

**B:** \( \partial_t m(v, t) = Dm(v, t), \quad g(v, t) = g_0, \quad n(v, t) = n_0 \delta(v - v_0), \quad \mu(v, t) = \mu_0 \)

**C:** \( \partial_t m(v, t) = Im(v, t), \quad a(v, u, t) = a_0 \)

**Define operator** \( L_X : [0, \infty)^{N+2} \rightarrow [0, \infty)^{N+1} \) as the element-wise application of \( m_X(\cdot, \tau; \omega_0(\cdot)) \), \( X = A, B, C \), to a vector \( y_i \in [0, \infty)^{N+1} \), with \( i \in \mathbb{N} \):

\[
L_X(y_i, \tau) \equiv m_X(v, \tau; \omega_0(v)), \quad \omega_0(v) \equiv y_i, \quad \tau > 0,
\]

where \( m_X \) and \( \omega_0 \) are computed for each element of grid \( v \equiv \{0 = \varphi_0 < \ldots < \varphi_N\} \)

**The solution values** \( y_i \equiv \{m(\varphi_k, t_i)\}_{k=0}^N \), with \( t_i = i\tau \), of Models I-III can be updated according to the **Symmetrized Strang Splitting Method**:

\[
y_{i+1/2} = L_X(y_i, \tau/2), \quad \bar{y}_{i+1} = L_Y(y_{i+1/2}, \tau), \quad y_{i+1} = L_X(\bar{y}_{i+1}, \tau/2),
\]

with

\[
\begin{align*}
X = B, \quad Y = C & \quad \text{for Model I} \\
X = A, \quad Y = C, \quad n_0 = 0 & \quad \text{for Model II} \\
X = B, \quad Y = C, \quad n_0 = 0 & \quad \text{for Model III}
\end{align*}
\]

---

Laplace Induced Splitting Method (LISM): Drawback

📍 **Remark:** sub-problems must be solved for generic choice of initial data \( \omega_0(v) \)

📍 **Drawback:** LISM relies on availability of analytical solutions for any \( \omega_0(v) \)

📍 **Remark:** despite the simplicity of tested Models I-III, it is not straightforward to solve the sub-problems relative to integral terms for generic initial data

📍 **Consequence:** integral terms are accounted by using numerical schemes
Laplace Induced Splitting Method (LISM): Accurate

LISM does not Suffer from Oscillations as GMOC (Model I)

Targeted Accuracy: max $\varepsilon \approx 10^{-1}$
CPU time GMOC: $7.5 \times 10^3$ sec
CPU time LISM: $10^3$ sec

GMOC: Model I  →  LISM: Model I
Laplace Induced Splitting Method (LISM): Accurate

LISM does not Suffer from Oscillations as GMOC (Model I)

Targeted Accuracy: $\max \varepsilon \approx 10^{-1}$
CPU time GMOC: $7.5 \times 10^3$ sec
CPU time LISM: $10^3$ sec
Laplace Induced Splitting Method (LISM): Efficient

LISM is faster than GMOC by up to $10^2$ times

Targeted Accuracy for Model I: $\max \epsilon \approx 10^{-1}$
Targeted Accuracy for Models II-III: $\max \epsilon \approx 10^{-2}$
Laplace Induced Splitting Method (LISM): Accurate & Efficient

**Benefits**

LISM efficiently Deals with *Small* Nucleation Sizes and *Large* Volume Domains

**Model I**

Nucleation Size $v_0 = 2.7 \times 10^{-2}$
Volume Domain = $[0, 10^3]$
Targeted Accuracy: $\max \varepsilon \approx 10^{-2}$
Estimated CPU time GMOC $\gg 10^6$ sec
CPU time LISM: $1.3 \times 10^3$ sec

*Divide et Impera*

Splitting of PBE into Simpler Sub-Problems should Support *Complex Physical Rate Functions*
Conclusions & Possible Future Developments

- **Our Objective**: to develop a computationally efficient modelling approach for prediction of multi-phase particles morphology formation

1. **PBE Model** captures the time evolution of the size distribution of polymers clusters composing the morphology of interest
2. **Optimal Scaling**: rational definition of dimensionless PBE model, allowing for parameters with experimental values
3. **LISM**: potentially promising methodology for accurate and efficient solution of dimensionless PBE model

- **Possible Future Developments**:

1. **Extension of LISM Applicability**: address PBE models with rate functions dependent on powers of size $v$ and/or time $t$ (physical motivations)
2. **Tuning of LISM**: choice of appropriate numerical schemes for time splitting and/or non-solvable terms, such as integral terms
3. **Comparison with State-of-the-art Solvers for PBE**: Pivot Technique (Kumar and Ramkrishna, 1996, 1997), Monte Carlo methods (Meimaroglou et al., 2006) and Finite Elements methods (Mahoney and Ramkrishna, 2002)
4. **Comparison with Experimental Data**