Topology-Based Parameter Identification for Decoupling Material Structure-Process-Property Relationships

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**Scattering Overview**

- **Scattering Angle** $2\theta$

  - Incident beam (wavelength = $\lambda$)
  - Sample
  - Scattered Radiation
  - Detector

- **Azimuthal Angle**

  - Dark areas: High Intensity
  - Light areas: Low Intensity

- **Scattering Vector**:
  
  $$ q = \frac{4\pi \sin \theta}{\lambda} $$

- Complementary Scattering Techniques:
  - X-Ray (SAXS, WAXS)
  - Light (SALS)
  - Neutron (SANS)

- Take an Azimuthal slice from the center to the edge and plot the intensity as a function of $2\theta$ or $q$
Structure Determination

Bragg’s Law

\[ d = \frac{\lambda}{2 \sin \theta} \]

• When X-rays are scattered only slightly, at small angle \( \theta \), this corresponds to large period of repetition \( d \) by Bragg’s Law.

• X-rays scattered at large angles correspond to a small period of repetition \( d \).

Example: Polymeric structures at multiple length scales characterized by several scattering techniques

- Spherulite
- Lamellae
- Unit Cell

Combining data produces a unique material signature

- Microscale
  - 1 - 100 \( \mu \)m
  - SALS, USAXS

- Nanoscale
  - \( \ell \sim 10 - 20 \) nm, \( L >> 10 \)nm
  - SAXS

- Nanoscale
  - < 1 nm
  - WAXS

Increasing \( q \)

Decreasing Length Scale

(Inverse relationship)
Motivation

• How do we extract this structural information from scattering data?

• Direct Methods: assume a model and fit the data.

More structural complexity may exist in non-lamellar regions

$$I(q) = I_b + J_d(q) + J_l(q)/q^2$$

- Ex: Observed SAXS intensity $I(q)$ which is separated into:
  - $I_b$ (background intensity)
  - $I_d$ (central diffuse scattering)
  - $I_l$ (lamellar stack)

Motivation

• **GOAL**: Obtain all possible morphological contributions to the overall scattering curve across multiple length scales without assuming a specific model

• **Approach**: Model-Free Analysis - Extract different contributions to the overall scattering data signature directly from experimental data
Test System - Branched Copolymers

• Effect of crystallization temperature and short chain branch length
• Samples were prepared by melting at T=160°C in one chamber and then quickly transferred to a second chamber at the desired crystallization temperature (T_c = 83°C, 86°C, 89°C, 92°C, 95°C)
• Time-resolved, simultaneous synchrotron SAXS/WAXS data collected
• Analysis using intensity measured after ~1 hr cooling time

<table>
<thead>
<tr>
<th>Comonomer</th>
<th>CH_2CH_3</th>
<th>CH_2CH_2CH_3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene/1-Butene:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethylene/1-Hexene:</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>M_w</th>
<th>M_w/M_n</th>
<th>Comonomer Content (mol %)</th>
<th>ρ (g/cm³)</th>
<th>T_m nominal</th>
</tr>
</thead>
<tbody>
<tr>
<td>70K</td>
<td>2.0</td>
<td>5.9 %</td>
<td>0.900</td>
<td>95 °C</td>
</tr>
<tr>
<td>70K</td>
<td>2.0</td>
<td>6.4 %</td>
<td>0.900</td>
<td>95 °C</td>
</tr>
</tbody>
</table>

Ethylene/1-Hexene (SAXS/WAXS)

Normalize WAXS data w.r.t. amorphous halo

Important:
- Relative WAXS $I(q)$
- Absolute SAXS $I(q)$

WAXS Peak corresponds to the distance, $d$, between crystallographic planes

$q \sim \frac{1}{d}$
As $T_c \uparrow$, peaks corresponding to (1 1 0) and (2 0 0) crystallographic planes decrease.
Ethylene/1-Hexene (SAXS detail)

Peak position: \( q \sim \frac{1}{L} \)

Peak intensity: \( I(q) \sim N \cdot \langle \Delta \rho \rangle^2 \)

\( N = \) number of lamellae

\( L = \) Long Period
Ethylene/1-Butene (SAXS detail)

SAXS Intensity increases and peak position shifts to left as $T_c = 83^\circ \rightarrow 92^\circ$

- Corresponds to increasing $L$

At $T_c = 95^\circ$, crystals are far apart and scattering is characteristic of dilute particulate system
Network Materials Analysis

Determine:
- **Number of parameters which account for the variance between signatures**
- **Their physical meaning**
- **The network topology**

Assumption: Bipartite Network Topology

Topological Parameter 1

Composite 1

(Signature 1)

Topological Parameter 2

Composite 2

(Signature 2)

Topological Parameter 3

Composite 3

(Signature 3)

Topological Parameter L

Composite M

(Signature M)
Network Materials Analysis

- We construct the linear decomposition:

\[ E_{(M \times N)} = A_{(M \times L)} \cdot P_{(L \times N)} \]

**E** is composed of \( M \) row vectors \( e \), where \( e_i = I(q_i) \)

**P** is composed of \( L \) row vectors \( p \), generated by this decomposition

Elements of **A** represent the connectivity between **e** and **p**

\[ a \neq 0 \Rightarrow \text{Connection Exists} \]

\[ a = 0 \Rightarrow \text{No Connection} \]

**Sample 1**

\[
E = \begin{bmatrix}
q_1 & \cdots & q_N \\
e_{1,1} & \cdots & e_{1,N} \\
\vdots & \ddots & \vdots \\
e_{M,1} & \cdots & e_{M,N}
\end{bmatrix}
\]

**Sample M**

\[
A = \begin{bmatrix}
TP_1 & \cdots & TP_L \\
a_{1,1} & \cdots & a_{1,L} \\
\vdots & \ddots & \vdots \\
a_{M,1} & \cdots & a_{M,L}
\end{bmatrix}
\]

**Sample 1**

\[
P = \begin{bmatrix}
q_1 & \cdots & q_N \\
p_{1,1} & \cdots & p_{1,N} \\
\vdots & \ddots & \vdots \\
p_{L,1} & \cdots & p_{L,N}
\end{bmatrix}
\]

- Based On Network Component Analysis (NCA)


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NMA - Procedure

• Require partial knowledge of the connectivity matrix $A$, most importantly the location of zeroes, in order to decompose $E$ simultaneously into a unique $A$ and $P$, up to a scaling factor.

• Minimize the objective function:

$$\min ||E - A \cdot P||^2$$

s.t. $A \in Z$

$Z$ is a vector of sequences that defines the topological connectivity

$$\dim(Z) \geq L \cdot (L - 1)$$

**No prior knowledge of $P$ is required**

- Carried out using AMPL platform and SNOPT solver
- NEOS Server for Optimization
NMA - Procedure

• Require partial knowledge of the connectivity matrix \( A \), most importantly the location of zeroes, in order to decompose \( E \) simultaneously into a unique \( A \) and \( P \), up to a scaling factor

• Minimize the objective function:

\[
\min_{A} ||E - A \cdot P||^2
\]

s.t. \( A \in Z \)

Network Identifiability Criteria:

- \( A \) must have full-column rank, \( P \) must have full-row rank

Number of Topological Parameters \( L \leq M \) (# of samples)

Each column of \( A \) must have at least \( L-1 \) zeroes
Principal Component Analysis

• Compare NMA to the linear decomposition generated by PCA

• Orthogonality assumption for row vectors \( p \), no topological basis for matrix \( A \), leads to poor reconstruction of original data

• One useful result - generates the % of the variance explained by each parameter. 3 Parameters account for 99.7%

% Explained:  

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Variance Explained</th>
</tr>
</thead>
<tbody>
<tr>
<td>EB83</td>
<td>91.6417</td>
</tr>
<tr>
<td>EB86</td>
<td>6.2735</td>
</tr>
<tr>
<td>EB89</td>
<td>1.7739</td>
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<tr>
<td>EB92</td>
<td>0.167</td>
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<tr>
<td>EB95</td>
<td>0.0551</td>
</tr>
<tr>
<td>EH83</td>
<td>0.0397</td>
</tr>
<tr>
<td>EH86</td>
<td>0.0159</td>
</tr>
<tr>
<td>EH89</td>
<td>0.015</td>
</tr>
<tr>
<td>EH92</td>
<td>0.0112</td>
</tr>
<tr>
<td>EH95</td>
<td>0.007</td>
</tr>
</tbody>
</table>

Reconstruction:

Blue = Original  
Red = Reconstructed

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NMA Topology - Optimal Mapping

Topological Parameters (TP)

• Minimize the objective function while iterating through all possible starting topologies \( Z \), for 1, 2 and 3 TP’s. The global minimum will produce the best decomposition and subsequent reconstruction.
NMA Connectivity Results

- The fit of the reconstruction to the original data improves with the addition of parameters

\[
\Lambda_o = \begin{bmatrix}
    EB-83 & 1 \\
    EB-86 & 1 \\
    EB-89 & 1 \\
    EB-92 & 1 \\
    EB-95 & 1 \\
    EH-83 & 1 \\
    EH-86 & 1 \\
    EH-89 & 1 \\
    EH-92 & 1 \\
    EH-95 & 1 \\
\end{bmatrix}
\]

\[
\Lambda = \begin{bmatrix}
    EB-83 & 5.57 \\
    EB-86 & 6.33 \\
    EB-89 & 6.37 \\
    EB-92 & 5.99 \\
    EB-95 & 3.70 \\
    EH-83 & 5.82 \\
    EH-86 & 6.11 \\
    EH-89 & 4.98 \\
    EH-92 & 4.41 \\
    EH-95 & 3.70 \\
\end{bmatrix}
\]
NMA Connectivity Results

• The fit of the reconstruction to the original data improves with the addition of parameters

$$\Lambda = \begin{bmatrix} TP1 & TP2 \\ EB-83 & 1 & 1 \\ EB-86 & 1 & 1 \\ EB-89 & 1 & 0 \\ EB-92 & 1 & 1 \\ EB-95 & 0 & 1 \\ EH-83 & 1 & 1 \\ EH-86 & 1 & 1 \\ EH-89 & 1 & 1 \\ EH-92 & 1 & 1 \\ EH-95 & 0 & 1 \end{bmatrix}$$

$$\Lambda^* = \begin{bmatrix} TP1 & TP2 \\ EB-83 & 3.89 & 3.28 \\ EB-86 & 6.18 & 1.20 \\ EB-89 & 7.08 & 0 \\ EB-92 & 6.25 & 0.70 \\ EB-95 & 0 & 5.99 \\ EH-83 & 5.34 & 1.61 \\ EH-86 & 6.49 & 0.45 \\ EH-89 & 3.22 & 3.39 \\ EH-92 & 2.06 & 4.18 \\ EH-95 & 0 & 6.00 \end{bmatrix}$$

\(\square\) = New zero found with the addition of the next parameter
The fit of the reconstruction to the original data improves with the addition of parameters.

NMA Connectivity Results

\[ A_o = \begin{bmatrix} TP1 & TP2 & TP3 \\ EB-83 & 0 & 1 & 1 \\ EB-86 & 1 & 0 & 1 \\ EB-89 & 1 & 0 & 1 \\ EB-92 & 1 & 1 & 0 \\ EB-95 & 0 & 1 & 0 \\ EH-83 & 1 & 1 & 1 \\ EH-86 & 1 & 1 & 1 \\ EH-89 & 1 & 1 & 1 \\ EH-92 & 1 & 1 & 0 \\ EH-95 & 0 & 1 & 0 \end{bmatrix}, \quad A = \begin{bmatrix} TP1 & TP2 & TP3 \\ EB-83 & 0 & 1.61 & 6.19 \\ EB-86 & 2.54 & 0 & 6.24 \\ EB-89 & 5.37 & 0 & 3.70 \\ EB-92 & 7.07 & 1.99 & 0 \\ EB-95 & 0 & 5.96 & 0 \\ EH-83 & 2.13 & 0.53 & 5.49 \\ EH-86 & 4.78 & 0.37 & 3.60 \\ EH-89 & 2.74 & 3.54 & 1.26 \\ EH-92 & 2.32 & 4.60 & 0 \\ EH-95 & 0 & 5.97 & 0 \end{bmatrix} \]

\[ \text{□ = New zero found with the addition of the next parameter} \]
Optimal Topology Matrix - 1 or 2 TP’s

- Column values of the optimal matrix are plotted as a function of $T_c$
- Absolute values not as important as observing trends

Ex: using 2 TP’s we see that TP1 has zero contribution to the 95° samples, while TP2 has a significant contribution.
Optimal Decomposition - 3 TP’s

- Disordered, smaller crystals (Distribution Function)
- Amorphous, non-lamellar material
- Crystals organized into lamellar stack

\[ L_{avg} = \frac{2\pi}{q_{max}} \]
Reconstruction, Optimal Topology

• Reconstruction shows excellent agreement with experimental data for all samples

Blue = $E$

Red = $A \cdot P$
Validation: Crystallization Mechanism

1) Initial crystallization (isolated crystals)

2) Peak max height reached when well-defined lamellar stacks form

3) Peak broadens and shifts due to contribution from smaller crystals distributed around thicker crystals in the lamellar stack

The decomposition generated by NMA separates the scattering curve at the last time step into these two parameters (TP1 and TP3)

Effect of Processing Conditions:

Ex: Contribution to the SAXS curve by stacked lamellar crystals (TP1) decreases with increasing $T_c$ while that for smaller crystals (TP2) increases.
Summary & Conclusions

• NMA approach can extract different contributions to the overall scattering data signature directly from experimental data without assuming a model, and determine the effect of processing conditions on these contributions across multiple length scales.

Experimental Data: $\mathbf{E}$  

- Effect of Processing Conditions: $\mathbf{A}$  
- Contributions to Structure: $\mathbf{P}$

• These scattering contributions can then be compared to existing models to determine how best to describe the structure/morphology, possibly resulting in the development of new models.

Future work:

• Develop generalized models to describe influence of process on structure/morphology

• Decomposition of time-resolved data into parameters to investigate polymer crystallization

• Determine how NMA approach can improve the prediction of properties using micromechanical models
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Thank you! Questions?