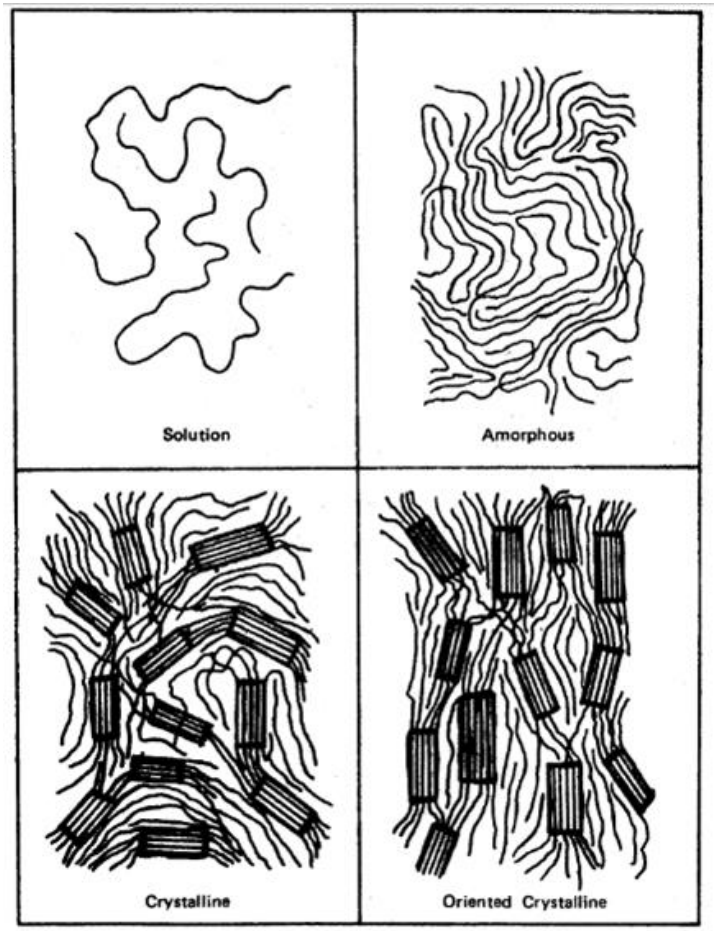
MIC PSP linkages of polymers using SAXS data

Marie DEKOU and Andrew Castillo

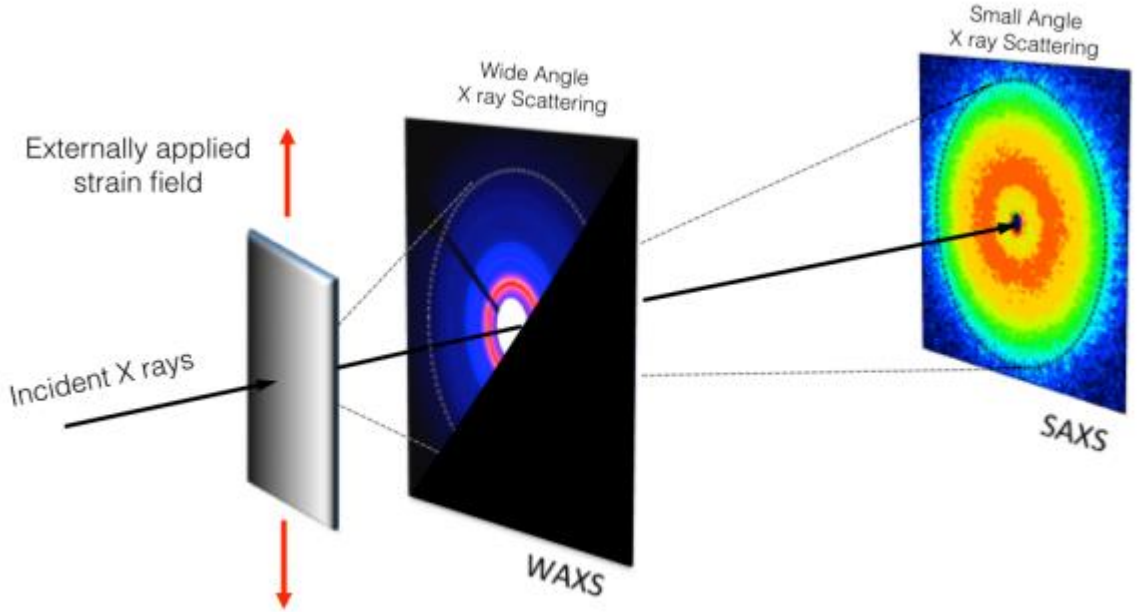
12/10/2015

Material Informatics Class Fall 2015

Introduction



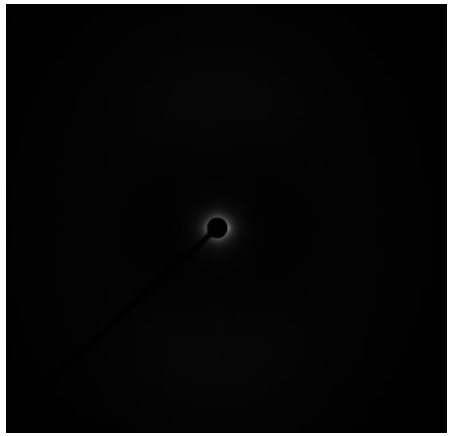
Material system: semi-crystalline polymer



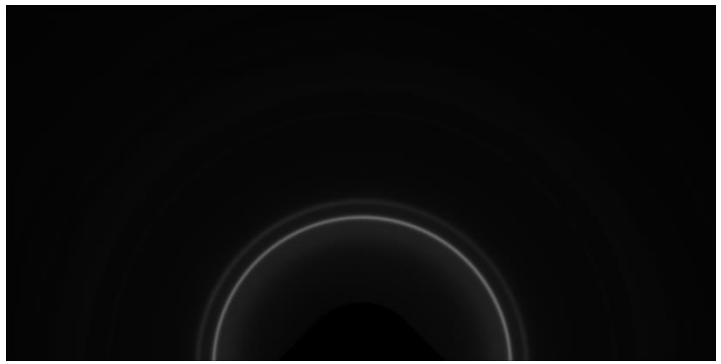
Experimental procedure: X-Ray Scattering

DataSet

SAXS (960x960)

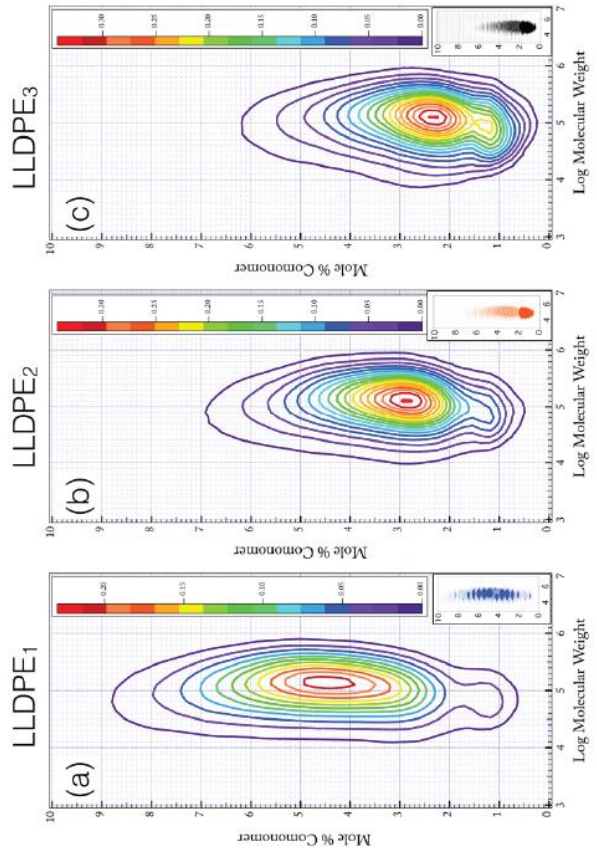


WAXS (960x1920)

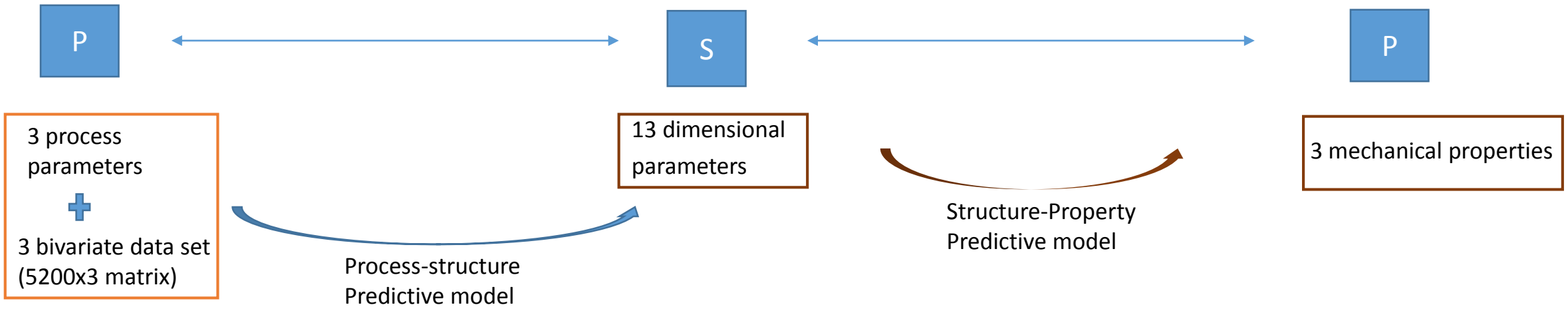


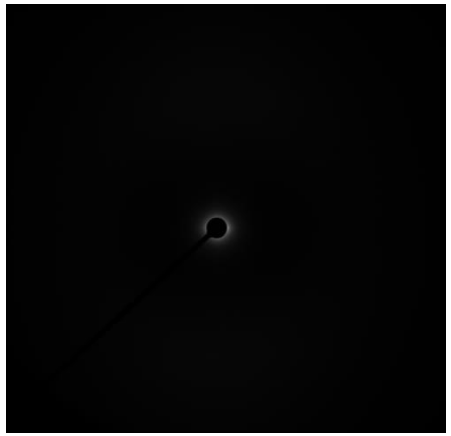
Sample Details					Dimensionality in Angstroms				Orientation								Mechanical Property		
	Density	Film Thickness in microns	MD Draw Ratio	% Crystallinity	Lsaxs Angstrom	dac Angstrom	dc Angstrom	da Angstrom	LAR	Hermans Lamellae	fa md	fb md	fc md	fa td	fb td	fc td	dart drop in gms/mil	elmendorf TD gms/mil	elmendorf MD gms/mil
average	0.918	37.500	19.875	40.698	136.577	136.000	38.146	91.463	1.943	0.085	0.060	-0.093	0.033	-0.054	0.133	-0.080	714.031	373.769	236.767
standard deviation	0.005	22.079	8.774	3.516	23.168	9.421	2.958	7.419	0.754	0.050	0.046	0.066	0.029	0.032	0.080	0.049	403.124	64.404	44.214
minimum	0.912	20.000	7.000	33.317	108.363	124.000	30.630	81.700	1.110	0.018	0.010	-0.213	0.006	-0.121	0.026	-0.192	135.000	287.520	146.480
maximum	0.923	75.000	32.000	47.338	181.340	149.000	41.850	100.600	3.700	0.186	0.163	-0.015	0.101	-0.002	0.312	-0.024	1380.000	527.210	326.000
18 samples					13 variables												3 mechanical properties		

3 bivariate distributions (molecular composition)

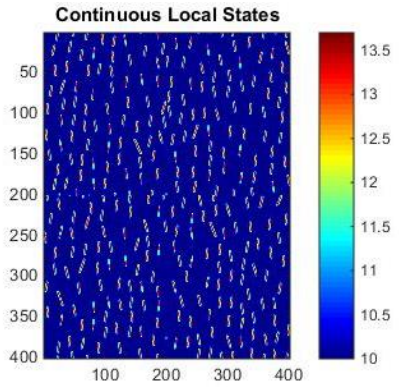


Project definition





Phase recovery challenge



Structure-Property Predictive Models

S

P

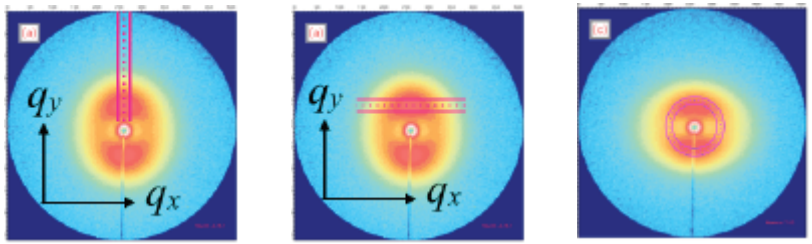
13 dimensional parameters

3 mechanical properties

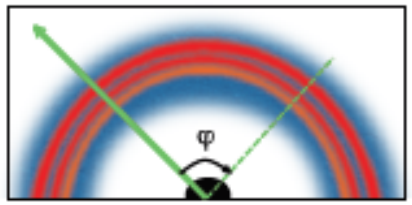
Structure-Property Predictive model

Dimension and orientation parameters

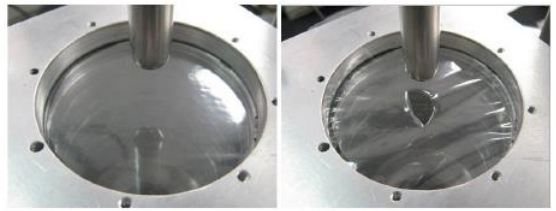
- 1D SAXS data (dac, lamellar width, tilt angle…)



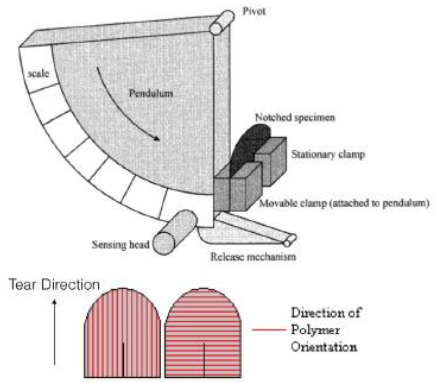
- 1D WAXS data (crystallinity, crystalline orientation, amorphous chain orientation …)



Puncture resistance (dart drop test)



Tear resistance (Elmendorf tear test)



Structure-Property Predictive Models

- Property to predict: puncture resistance (dartdrop)
- Predictors: structure parameters

Loocv RMPE: Root Square Percentage Error
MAPE: Mean Absolute Percentage Error

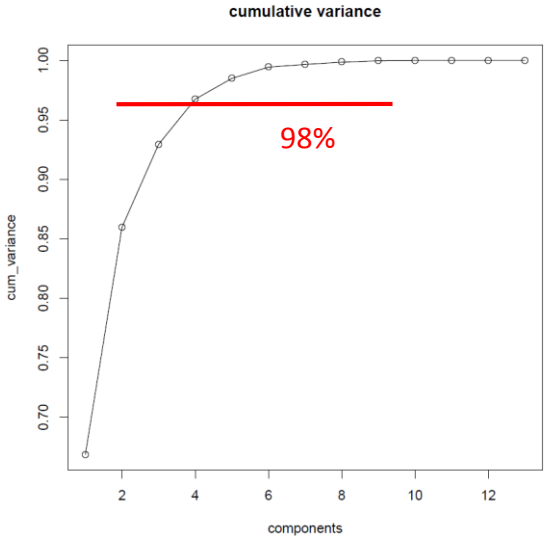
INPUTS | DATA REDUCTION | REGRESSION: PREDICTIVE MODELS

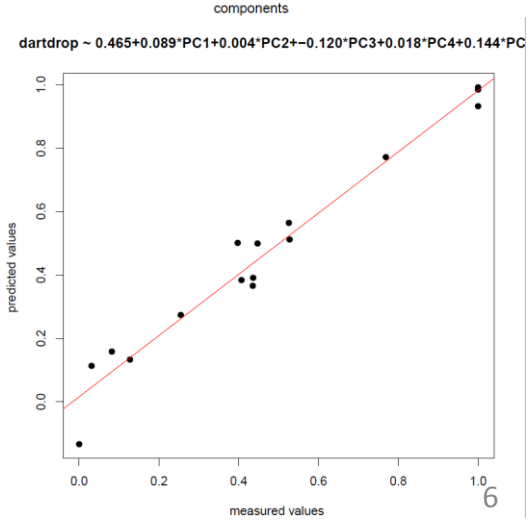
13 structure variables → loocv → Linear model
R-squared: 0.79
Loocv RMPE: 0.496
MAPE: 20%

13 structure variables → Stepwise regression → 4 variables → loocv → Linear model
R-squared: 0.885
Loocv RMPE: 0.148
MAPE: 37%

13 structure variables → PCA → PC1,PC2,PC3,PC4,PC5 → loocv → Linear model
R-squared: 0.965
Loocv RMPE: 0.1237
MAPE: 30%

PC1,PC2,PC3,PC4,PC5 → loocv → Degree 2 polynomial model
R-squared: 0.901
Loocv RMPE: 0.208
MAPE: 51%





Process-Structure Predictive Models

P

S

3 process
thickness
Crystallinity
MDRatio

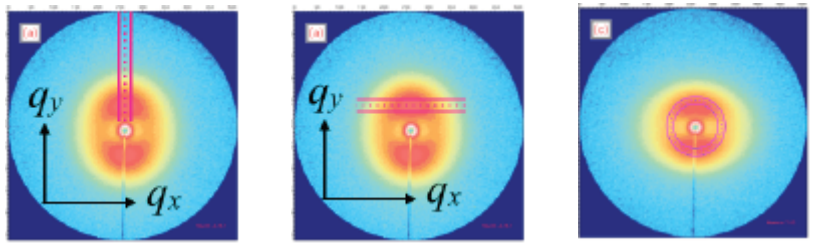
+

3 bivariate data set
(5200x3 matrix)

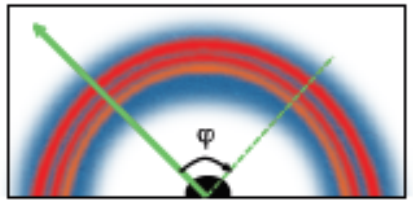
13 dimensional
parameters

Dimension and orientation parameters

- 1D SAXS data (dac, lamellar width, tilt angle…)



- 1D WAXS data (crystallinity, crystalline orientation, amorphous chain orientation …)



3 bivariate
distributions
vectors
(3x5200)

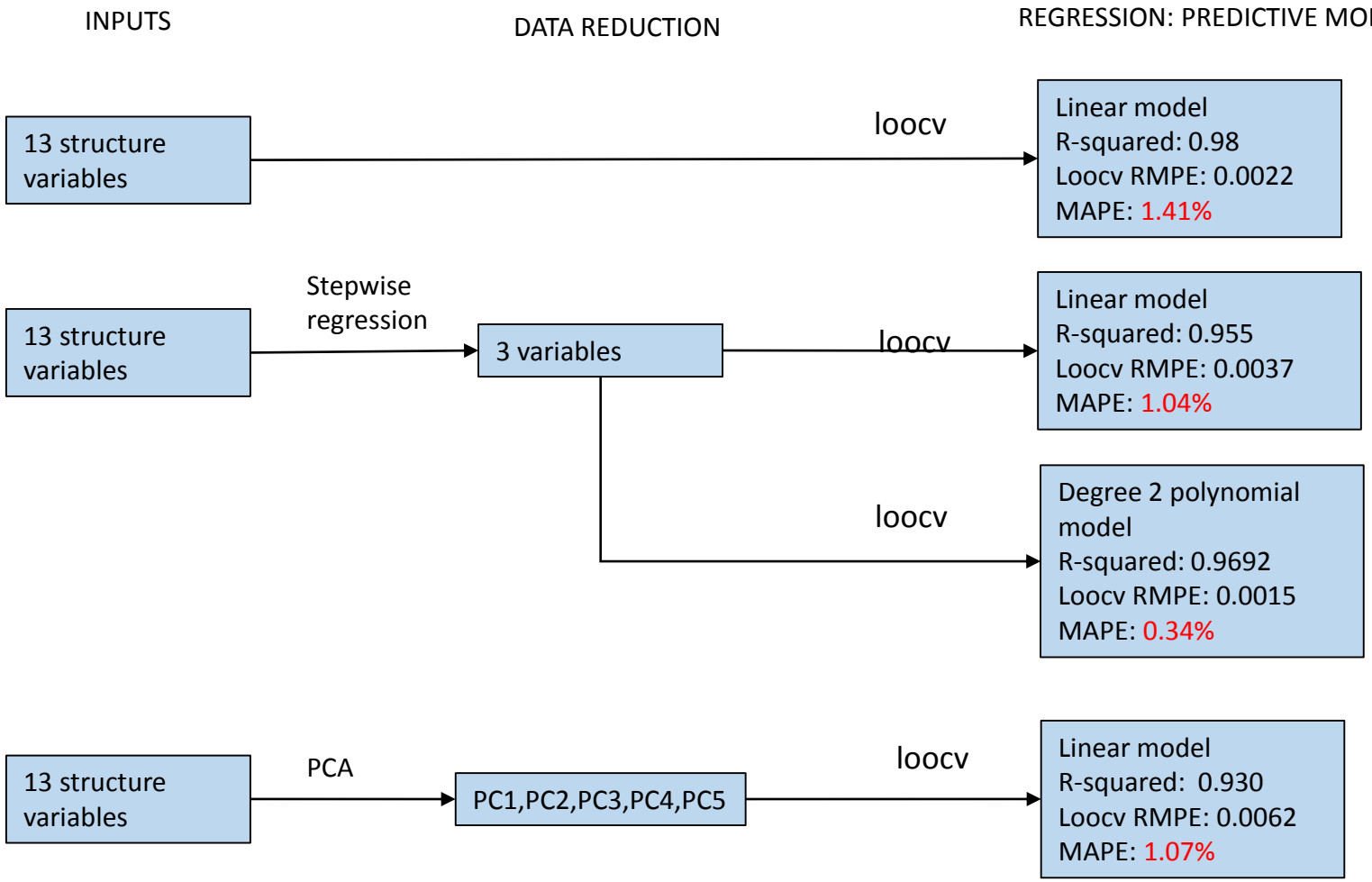
PCA

1 Component
(96% of the
variance)
PC1MolComp

Process-Structure Predictive Models

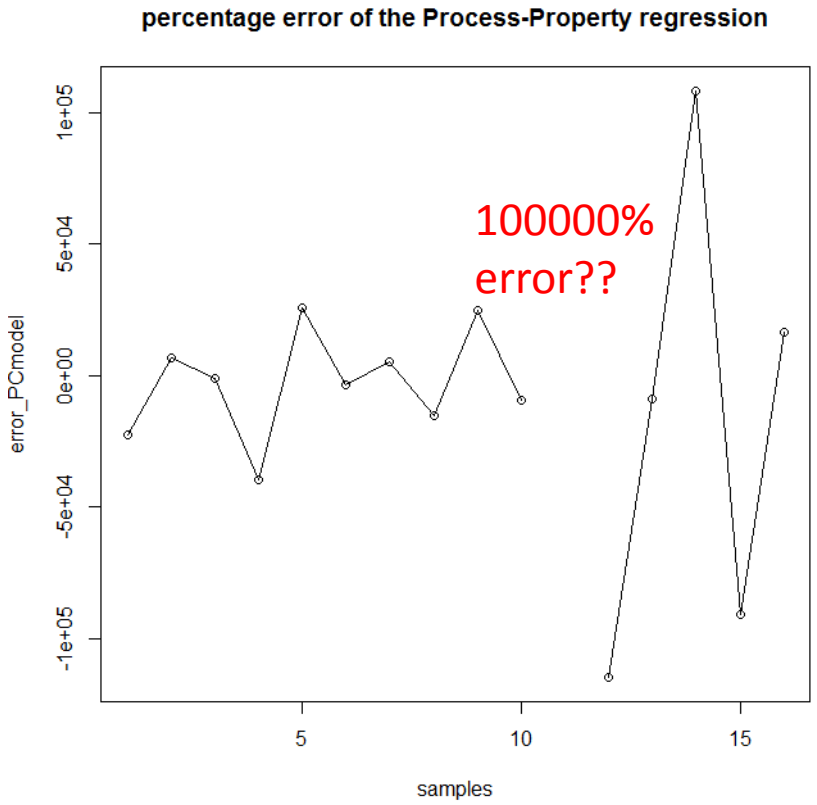
Process to predict: molecular composition reduced to 1 component

Loocv RMPE: Root Square Percentage Error
MAPE: Mean Absolute Percentage Error

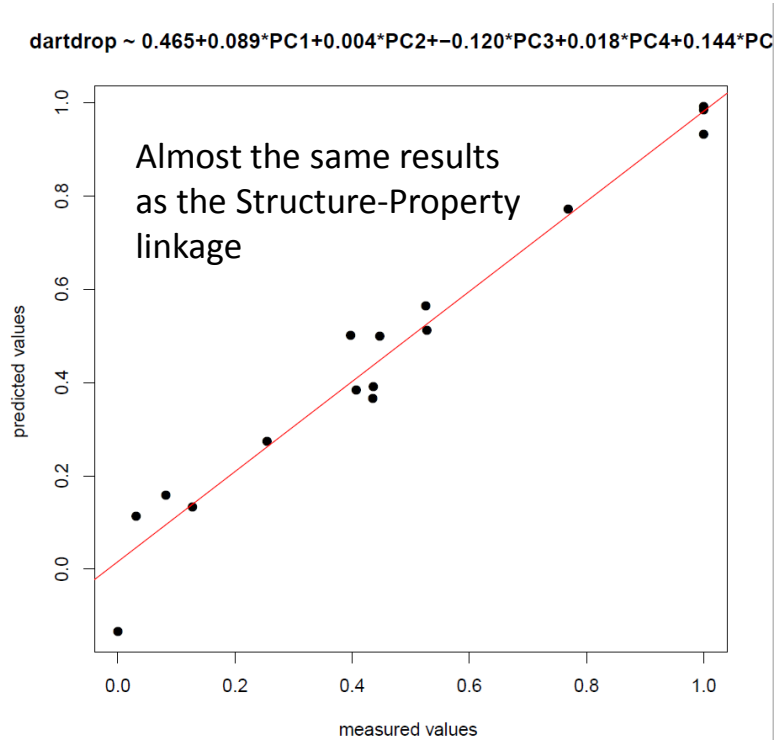


PSP linkage?

Mechanical Property ~ Process parameters (Density, Thickness, PC1MolComp)



Mechanical Property~ Process (molecular comp)+Structure(PC1,2,3,4,5)

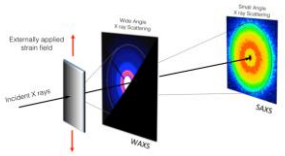


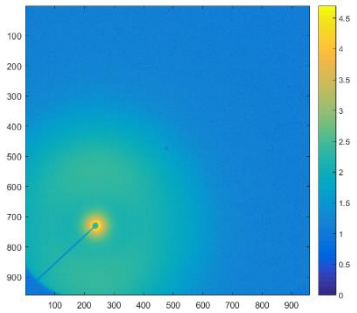
Good Process-Property linkage
Not accurate Structure-Property linkage
Impossible linkage between Process and Property

Initial Approach

SAXS Images

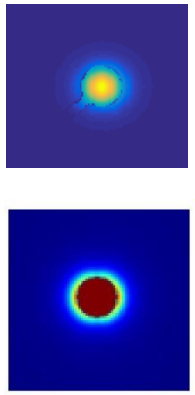
Fourier Space
960 x 960 Uint16
intensity maps (0-65535)





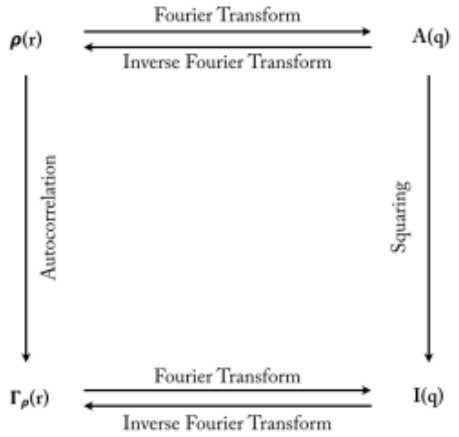
Cleaned SAXS Images

Fourier Space
400 x 400 Uint16 intensity maps
Beam Stop Corrections



Characteristic Equation

Real Space
Based off Normalizing by
an invariant of the material system



Recovered 2-pt Statistics

Phase Recovery

Recover Microstructure

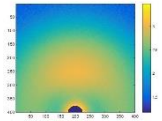
Database Approach

SAXS Images

Fourier Space
960 x 960 Uint16
intensity maps (0-65535)

Cleaned Experimental Data

400x400 Uint16
intensity maps, BS removed

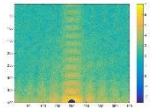


Simulated Micro structures

Real Space
.mat files (0s and 1s)
Control over various parameters

Simulated Scattered Images

Fourier Space
Autocorrelation of electron densities



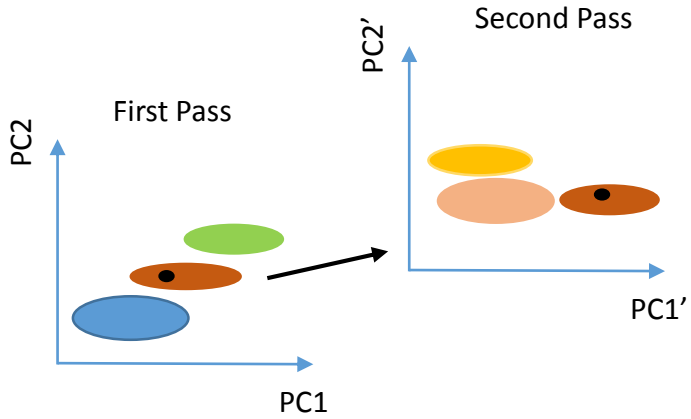
Mixed Simulated Scatter Images

Half of Autocorrelation of Simulated Scatter images,

Available, symmetric half of Experimental image

PCA Mixed Images

Observed clustering and use PCA as a directional guide

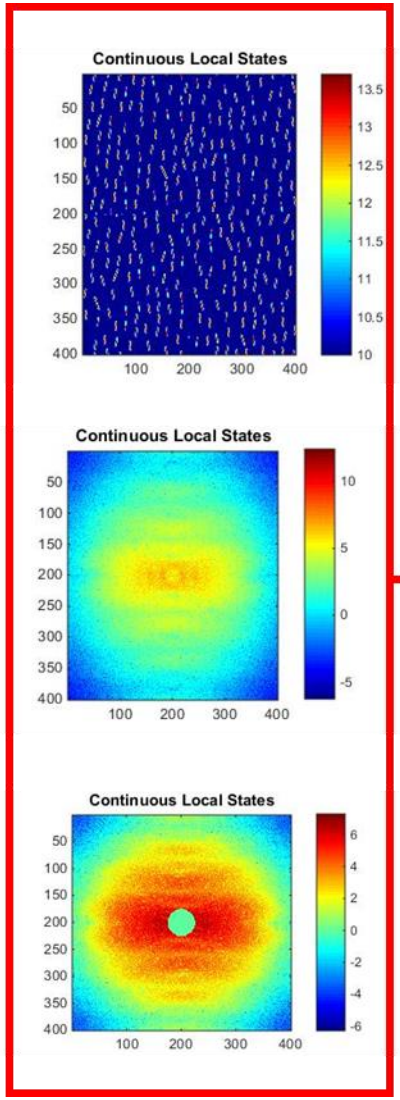


Parameters of Closest Neighboring Simulated Microstructures

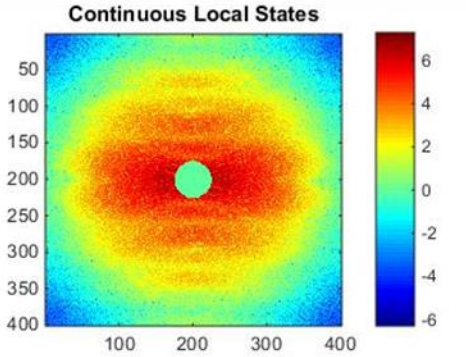
Increase Simulated microstructures within clustering region

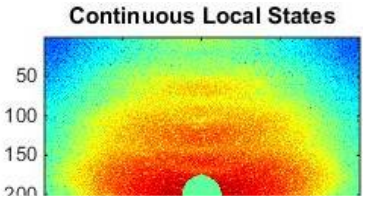
Exploratory PCA

- PCA
  - Goal: Establish feasibility to make matches for microstructure in fourier space
  - Data
    - Autocorrelation in Fourier Space
    - 12 Experimental images (reduced to 400 by 400 pixels)
    - 180 simulated images (400 by 400 pixels)
    - Vf, Particle Height, Particle Width set for segmented images
      - Gaussian fields than applied to simulate non-eigen microstructures
  - PCA Figures
    - Beam Stop On
    - Beam Stop Off
    - Parameters that were controlled are color coded



Simulated Scatter Plot





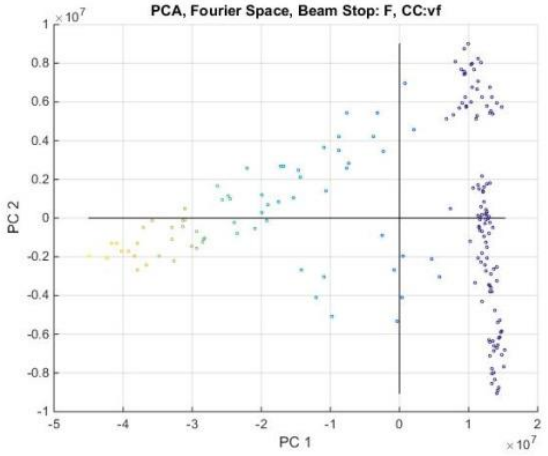
Data Used for Comparison

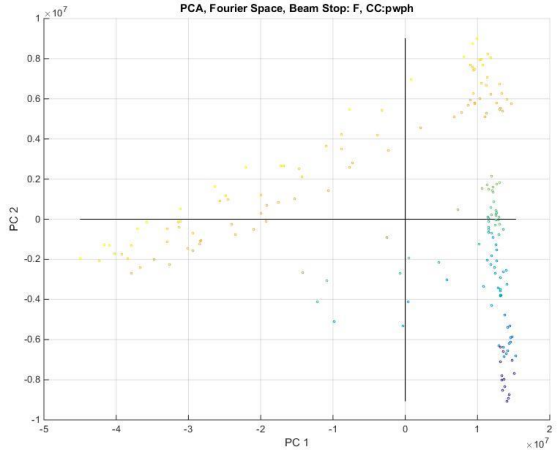
Exploratory PCA Results

Vf Colorcoded

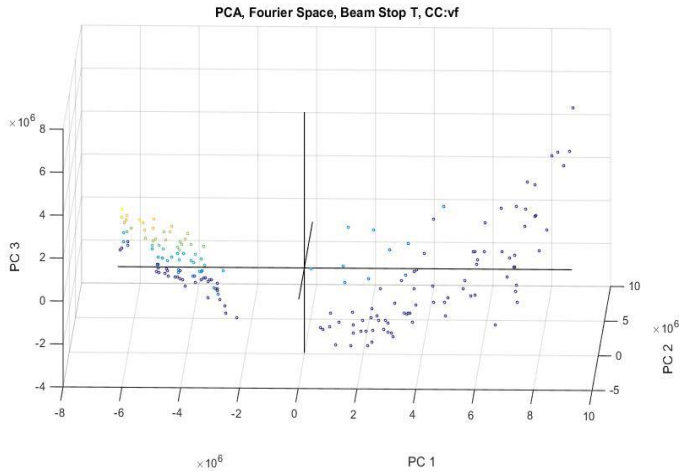
Size Colorcoded

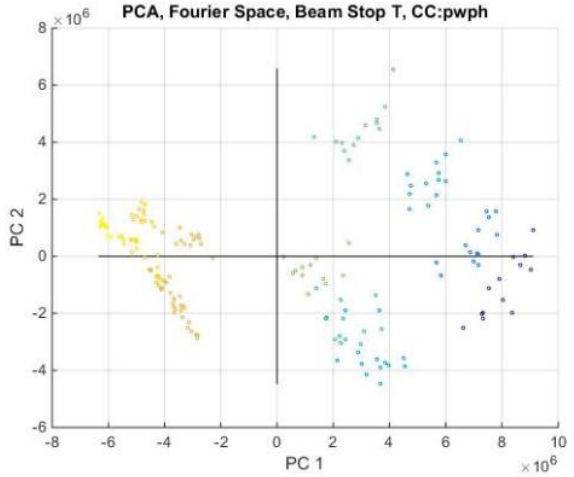
Beam Stop
Not included





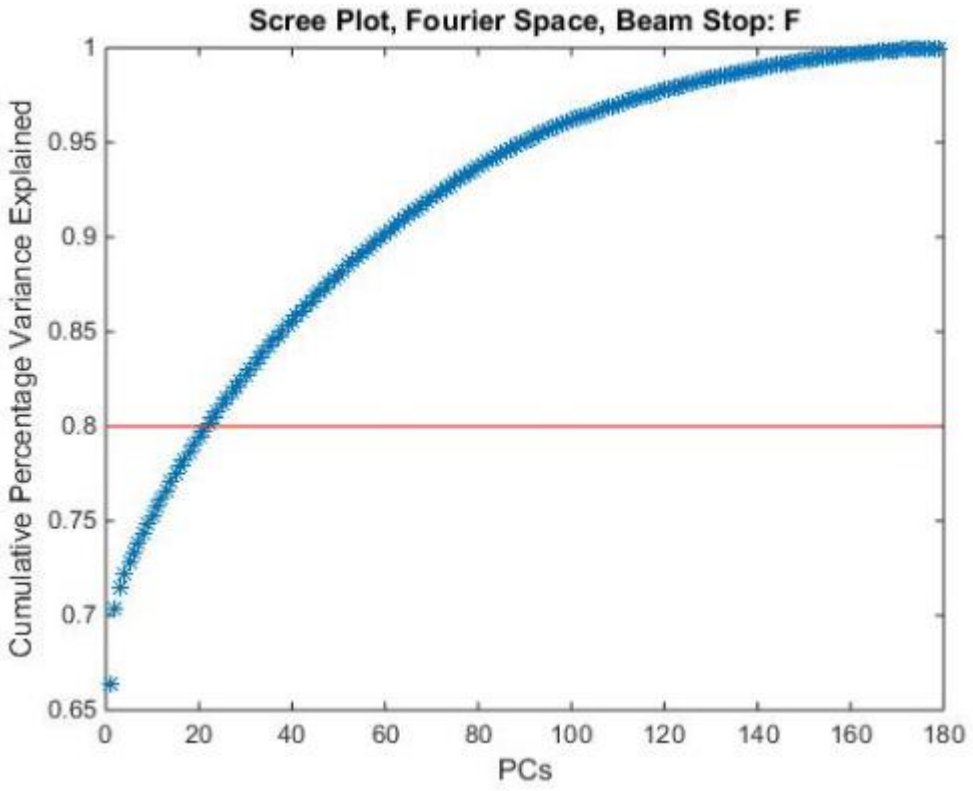
Beam Stop
included

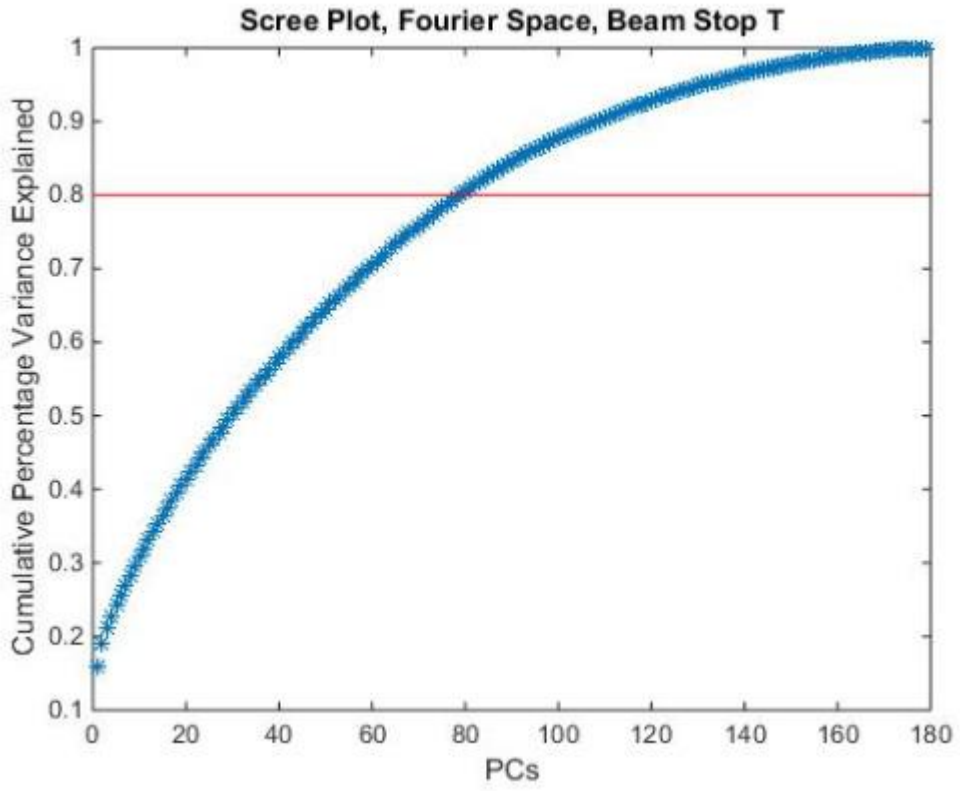




- Observe if clustering occurs even if information at beamstop is removed

Observing effects of the Beam Stop

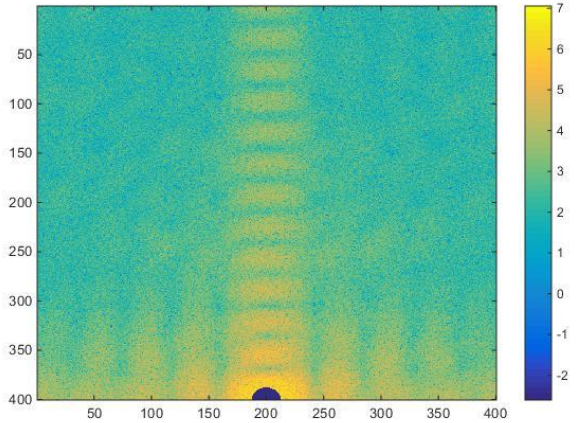


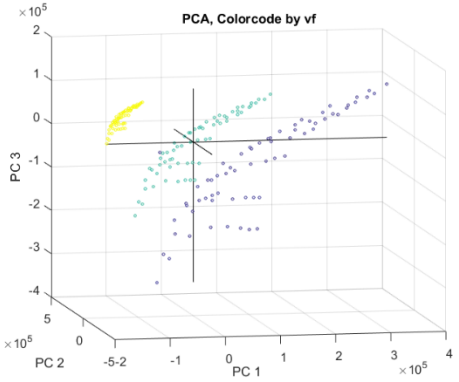


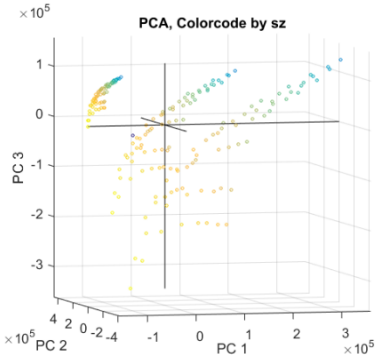
- Results suggest that large amount of variance between microstructures where beam stop is located (lose a lot of unique information)
- However, our PCA results stills show clustering of the microstructures in accordance with the parameters we have chosen, suggesting this a viable method to trace back to microstructure features

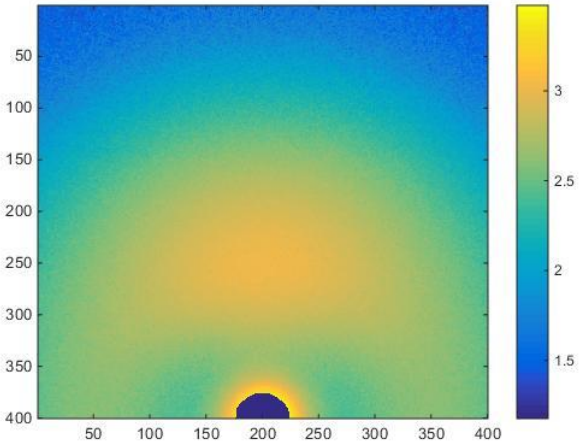
Final steps of forward problem

- Problem
  - Way to normalize images to match experimental images
    - Possible solution: Set range of electron density
      - Find possible electron density range (in arbitrary measurement units)
      - Or convert micrographs to absolute intensity scale
        - Use bounds of electron density from literature/extracted from experiments









Conclusions and perspective

- Dataset too reduced to generate accurate PSP linkages.
- Possible to use the complete SAXS and WAXS data for the PSP linkage once the normalization problem is solved.
- Built method to develop forward problem in recovery
  - Clustering suggest that this method could be used to narrow down microstructure parameters.
- Identified major issues with recovery
- Direct approach for recovery very difficult.

Appendix Equations

- Scatter Equations

$$I_k = \left| \int_V \rho_s e^{-iks} ds \right|^2$$

$$A_k = \int \rho_s e^{-iks} ds$$

$$I_k = |A_k|^2$$

$$I_k = A_k A_k^*$$

$$I_k = \left(\int \rho_{s'} e^{-iks'} ds' \right) \left(\int \rho_s e^{iks} ds \right) \qquad s' = s + r$$

$$I_k = \int \left(\int \rho_s \rho_{s+r} ds \right) e^{-ikr} dr$$

$$I_k = \Im \left(\int \rho_s \rho_{s+r} ds \right)$$

$$I_k = \Im^{-1}(f_r^{\rho\rho}) = F_k^{\rho\rho}$$

$$f_r^{\rho\rho} = \int \rho_s \rho_{s+r} ds$$

$$f_0^{\rho\rho} = \langle \rho^2 \rangle V$$

$$f_\infty^{\rho\rho} = \langle \rho_s \rangle \langle \rho_{s+r} \rangle V = \langle \rho \rangle^2 V$$

$$f_r^{\rho\rho} = \int (\eta_s + \langle \rho \rangle)(\eta_{s+r} + \langle \rho \rangle) ds \qquad \eta_s = \rho_s - \langle \rho \rangle$$

$$f_r^{\rho\rho} = \int \eta_s \eta_{s+r} ds + \langle \rho \rangle^2 \int ds + \langle \rho \rangle \int \eta_s ds + \langle \rho \rangle \int \eta_{s+r} ds$$

$$I_k = \int f_r^{\rho\rho} e^{-ikr} dr = \int f_r^{\eta\eta} e^{-ikr} dr + \langle \rho \rangle^2 V \int e^{-ikr} dr \qquad f_r^{\eta\eta} = \int \eta_s \eta_{s+r} ds$$

$$f_\infty^{\eta\eta} = \langle \eta \rangle^2 V = 0$$

$$f_0^{\eta\eta} = \langle \eta^2 \rangle V$$

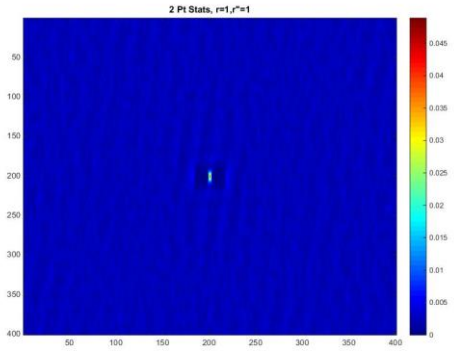
$\langle \rho \rangle^2 V \delta_k$, refers to scattering of the sample as a whole if there were uniform density, since at k=0 the intensity is swamped by the beam intensity and experimentally not measured this term is ignored if we ignore this term we can define the scattering intensity as

$$I_k = \int f_r^{\eta\eta} e^{-ikr} dr = \Im(f_r^{\eta\eta})$$

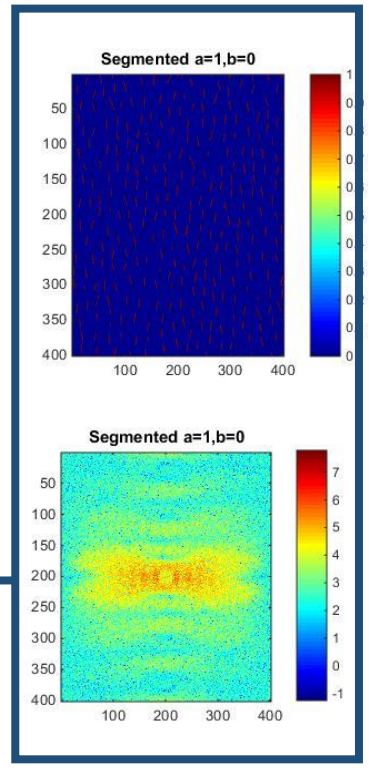
$$\gamma_r = \frac{f_r^{\eta\eta}}{f_0^{\eta\eta}}$$

$$\gamma_r = \frac{\int \eta_s \eta_{s+r} ds}{\int \eta_s \eta_s ds}$$

Understanding the intensity maps

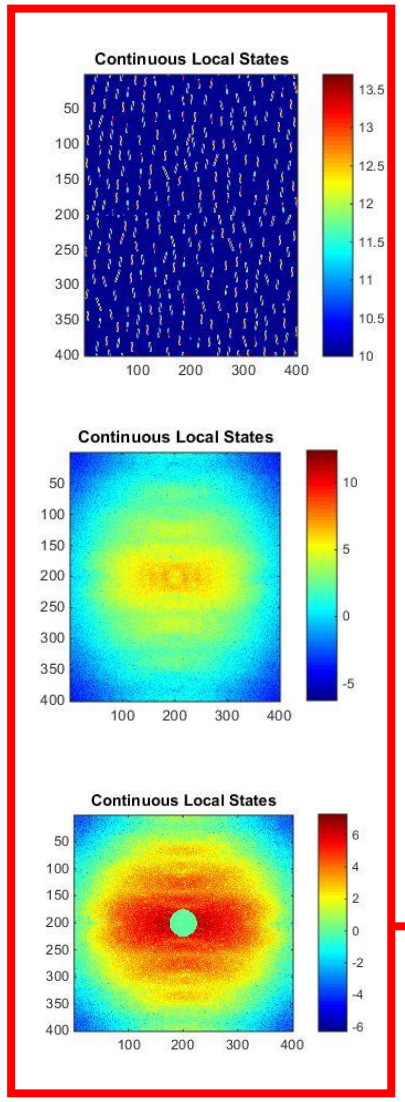


2-pt stats of simulated microstructure (real space)

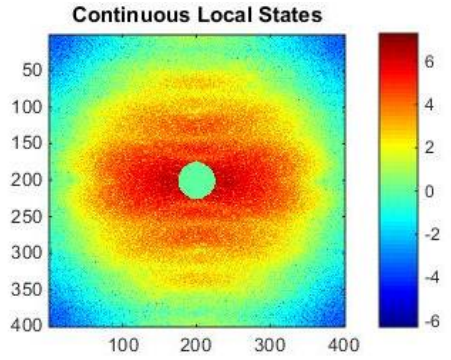


Microstructure

Autocorrelation in Fourier Space



Simulated Scatter Plot (similar to received experimental data)

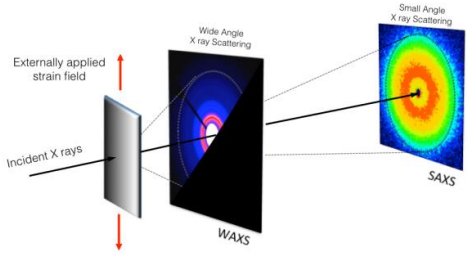


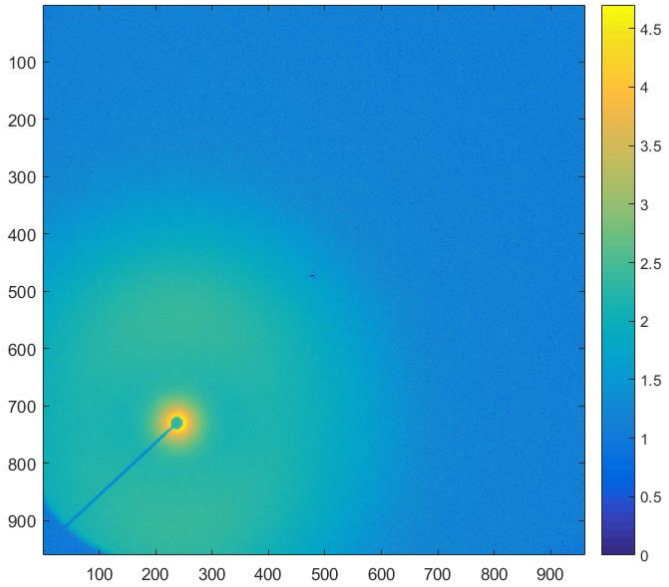
Early Trials

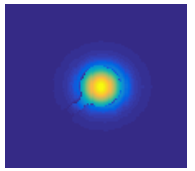
$$A_k = \int \rho_s e^{-iks} ds$$

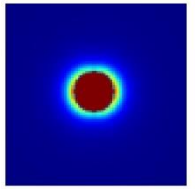
$$I_k = |A_k|^2$$

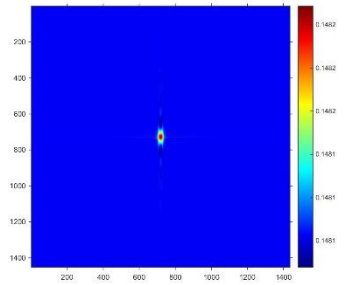
$$I_k = \int \left(\int \rho_s \rho_{s+r} ds \right) e^{-ikr} dr$$











- Initial Approach proved difficult
  - Handling of information within beam stop non-trivial
  - No reference point or measurement to scale with to get to absolute intensity
  - Manipulating data in Fourier space not straight forward
    - Fourier representation means amplitudes are independent
  - Recovery of phase information ultimately needed as well as recovery of microstructure