Autonomous analysis of synchrotron X-ray experiments with applications to metal nanoparticle synthesis

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Outline

1. Pipeline for nanoparticle optimization based on Small-Angle X-ray Scattering (SAXS) data (Anthony/Lenson)
   - Automatic analysis of SAXS data
   - Bayesian optimization of reaction conditions

2. Automatic analysis of powder diffraction / Wide-angle X-ray scattering (WAXS) data
   - Lattice parameter estimation using CNNs
   - Effects of experimental non-idealities on predictions
   - Approaches for tackling multiphase data

Introduction

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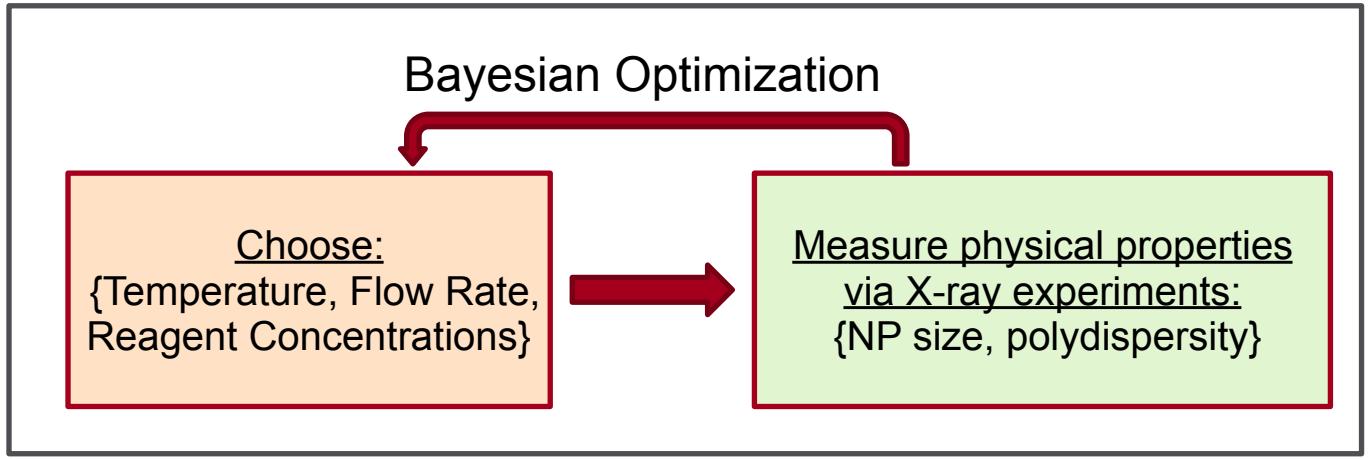
Project Goals

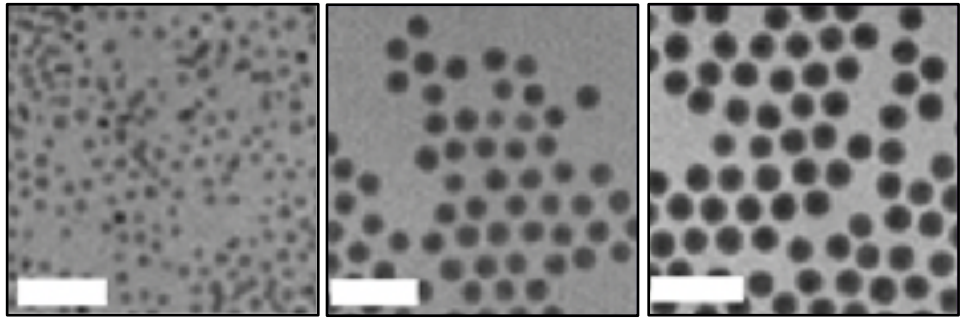
1) Synthesize libraries of monodisperse Pd nanoparticles with user specified sizes

2) Determine synthetic conditions for desired nanoparticle sizes

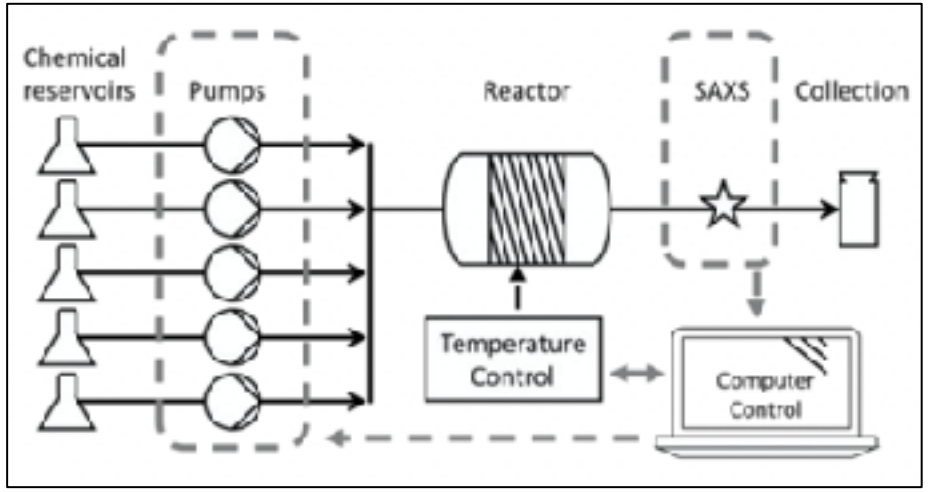
3) Perform these experiments in an autonomous fashion using a flow-reactor setup



TEM of Pd NPs with different sizes



Automatic Synthesis Schematic

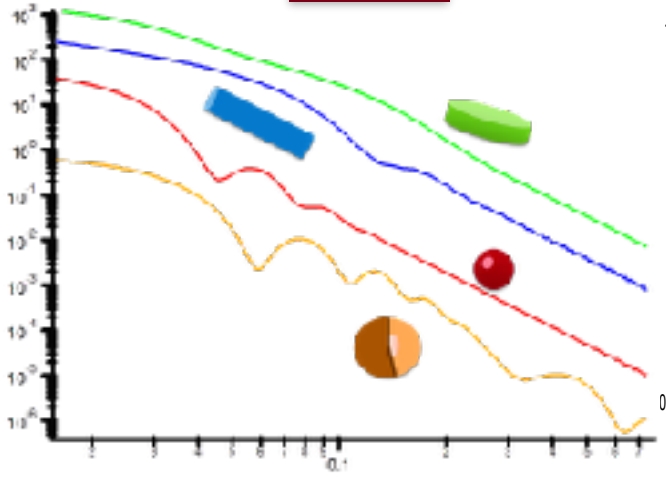


Fong, A et al. Utilization of machine learning to accelerate colloidal synthesis and discovery (in review).

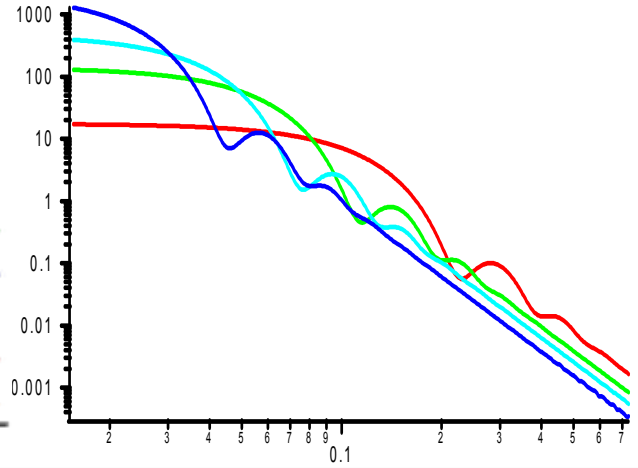
Matching the Probe to the Metric

Small Angle X-ray Scattering (SAXS) characterizes

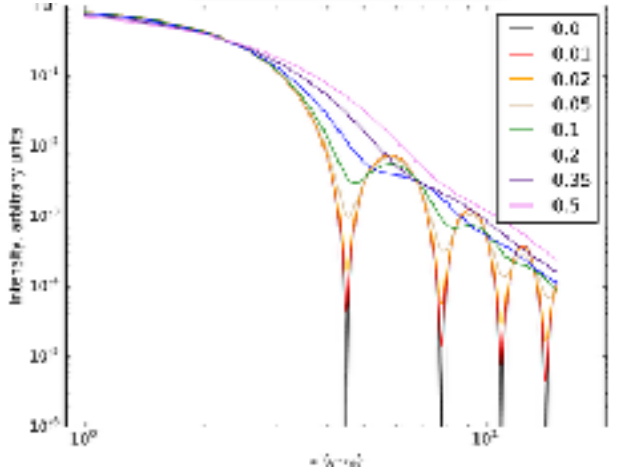
Shape



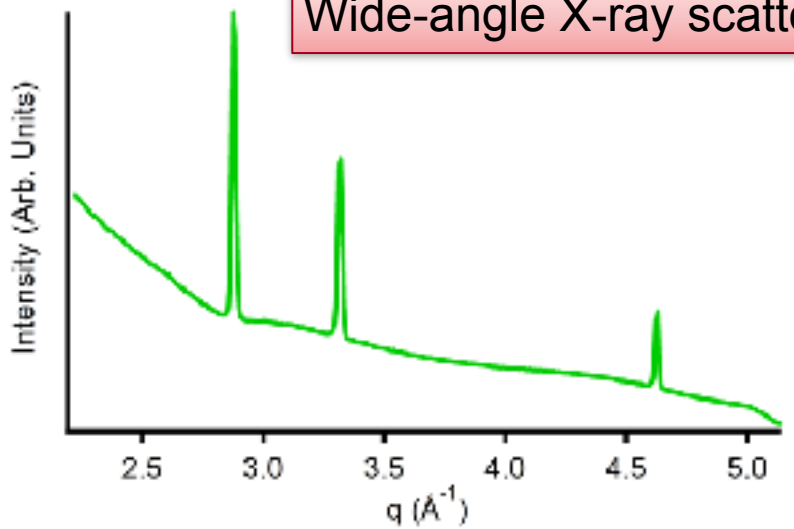
Size



Polydispersity

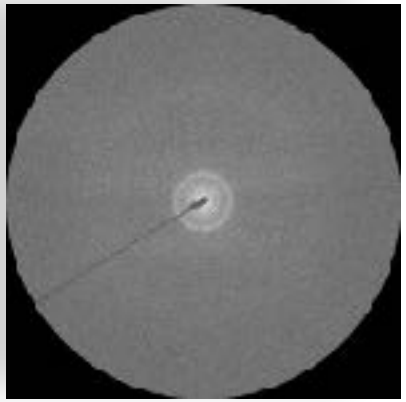


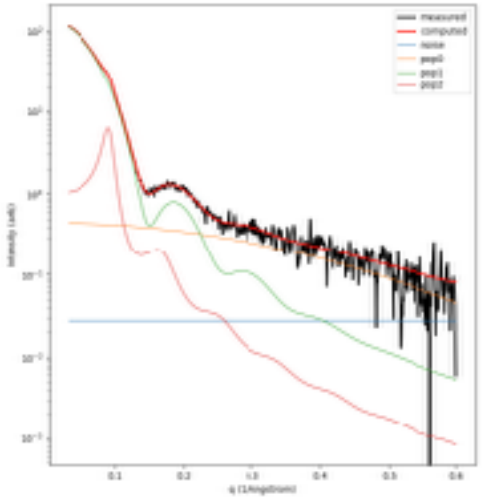
Wide-angle X-ray scattering (WAXS) characterizes



- Phase
- Composition
- Degree of Crystallinity
- Strain
- Crystallite Size

Automated Fitting of SAXS data





$$\mathbf{s} = \begin{bmatrix} I_{\text{noise}} \\ I_{0,\text{pre}} \\ I_{0,\text{dil}} \\ I_{0,\text{cond}} \\ r_{\text{g,pre}} \\ r_{\text{dil}} \\ \sigma_{\text{dil}} \\ r_{\text{cond}} \\ \sigma_{\text{cond}} \\ r_{\text{h,cond}} \\ \phi_{\text{cond}} \end{bmatrix}$$

SAXS data populations

-- Dilute spherical NPs (desired)
-- Condensed / disordered
-- Superlattice
-- Precursor (metal ligand)

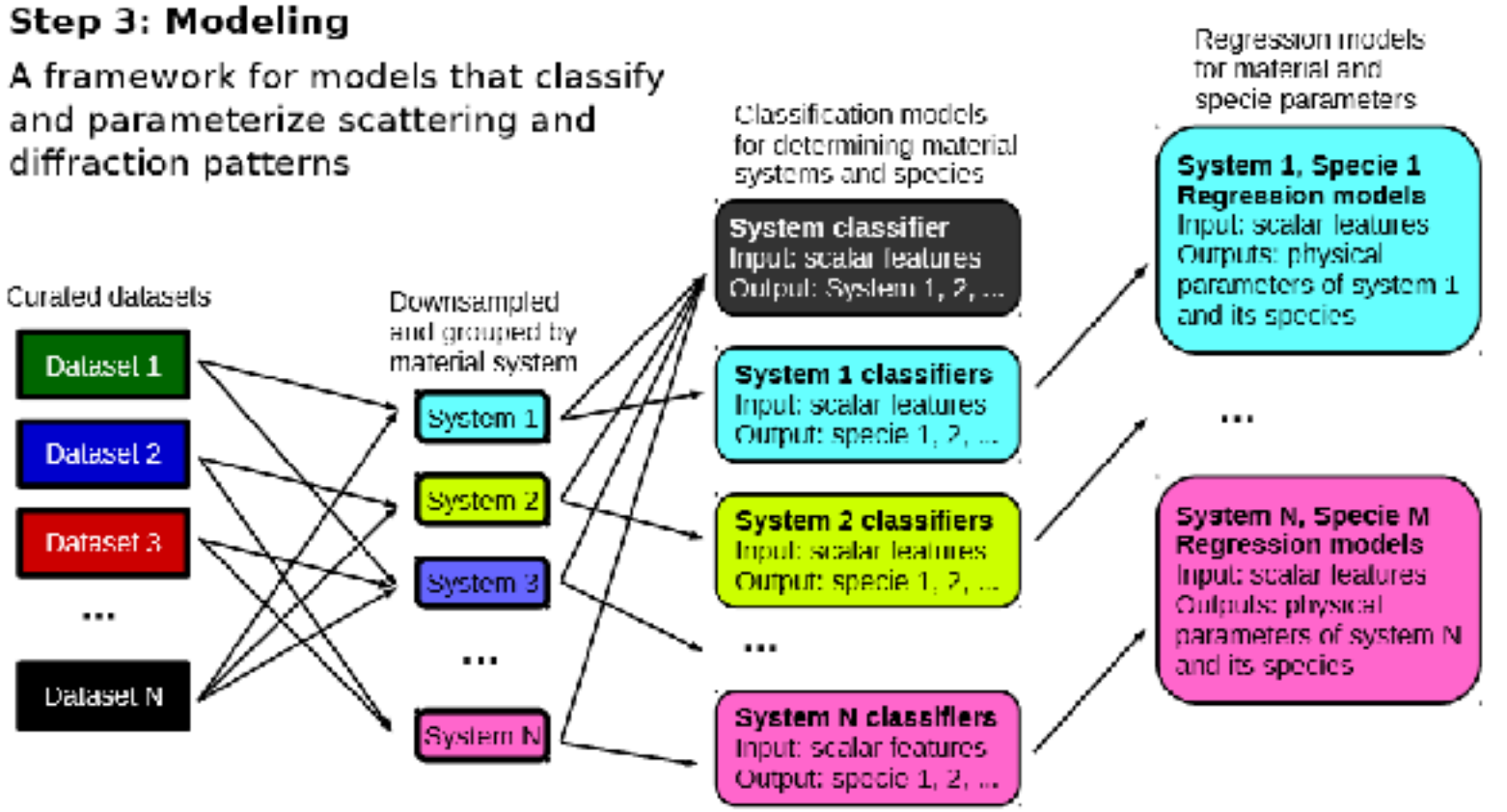
Data Fitting Approach

$$\begin{aligned} I_{\mathbf{s}}(q) = I_{\text{noise}} &= I_{\text{noise}} \\ &+ I_{\text{pre}}(q) &+ I_{0,\text{pre}} * \overline{\langle f^2_{\text{G-P}} \rangle}[r_{\text{g,pre}}, D_{\text{pre}}](q) \\ &+ I_{\text{dil}}(q) &+ I_{0,\text{dil}} * \overline{\langle f^2_{\text{sph}} \rangle}[\bar{r}_{\text{dil}}, \sigma_{\text{dil}}](q) \\ &+ I_{\text{cond}}(q) &+ I_{0,\text{cond}} * \overline{S_{\text{hs}}}[r_{\text{h,cond}}, \phi_{\text{cond}}](q) * \overline{\langle f^2_{\text{sph}} \rangle}[\bar{r}_{\text{cond}}, \sigma_{\text{cond}}](q) \end{aligned}$$

$$c(\mathbf{s}) = \frac{1}{\Omega_q} \int_q \mathrm{d}q \left[\frac{1}{\sigma_I(q)^2} \left[\log(I_{\text{exp}}(q)) - \log(I_{\mathbf{s}}(q)) \right]^2 \right]$$

$$\mathbf{s}^* = \underset{\mathbf{s}}{\operatorname{argmin}}\, c(\mathbf{s})$$

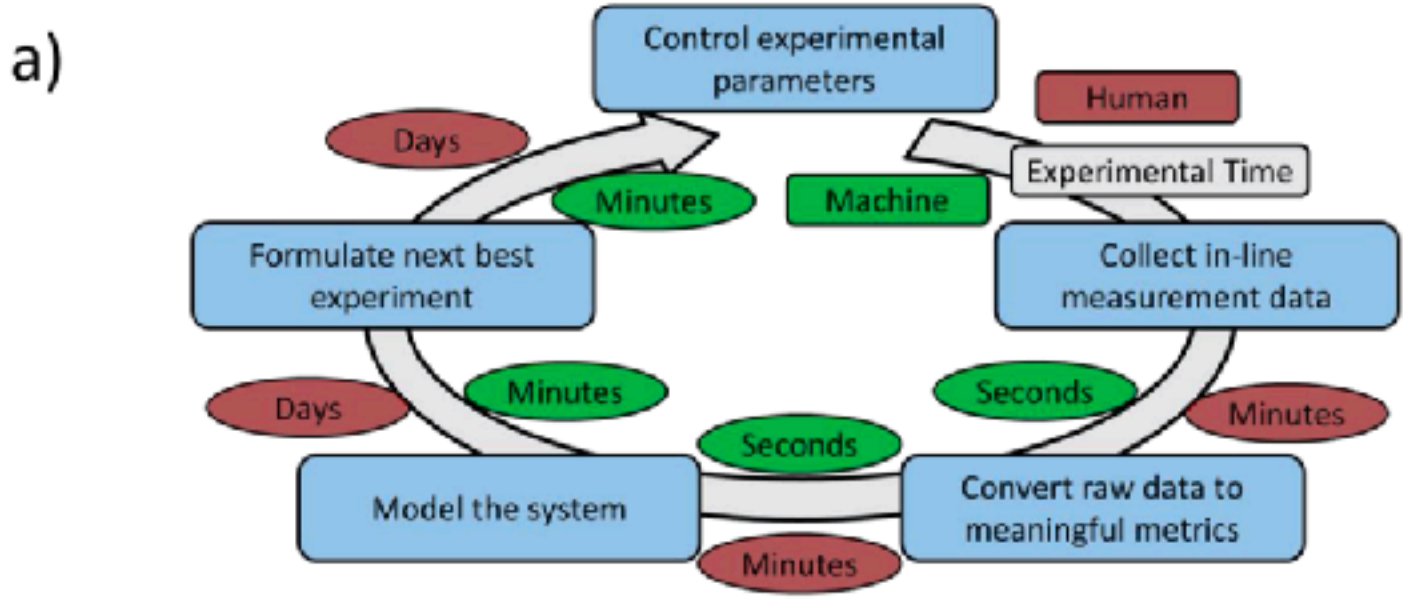
Using ML to improve SAXS Fitting

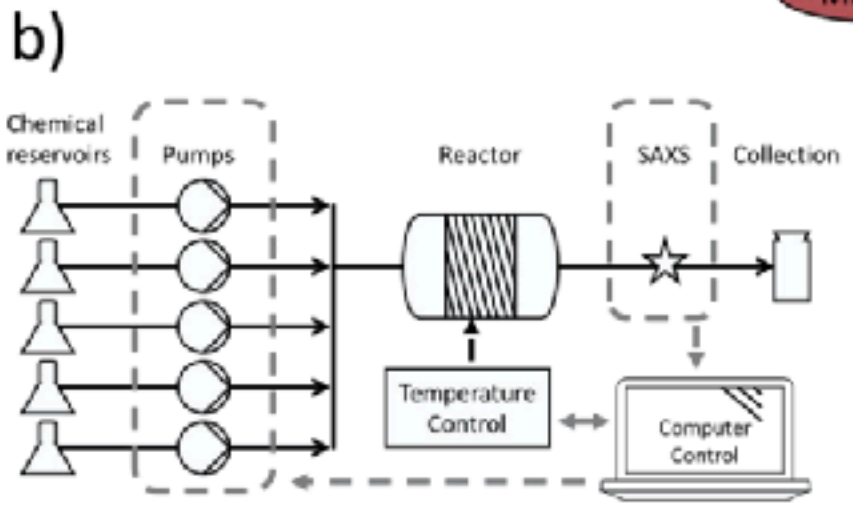


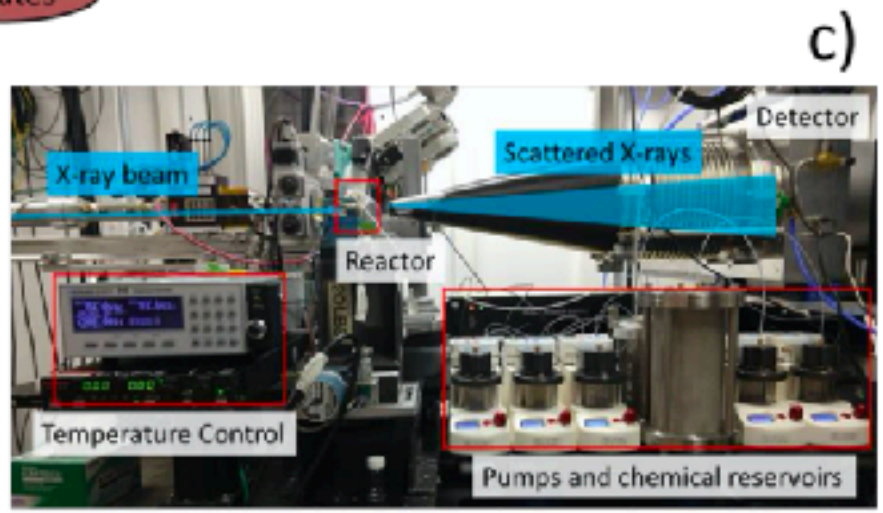
Code: xrsdkit

https://github.com/scattering-central/xrsdkit

Bayesian Optimization to find synthesis conditions







Bayesian Optimization to find synthesis conditions

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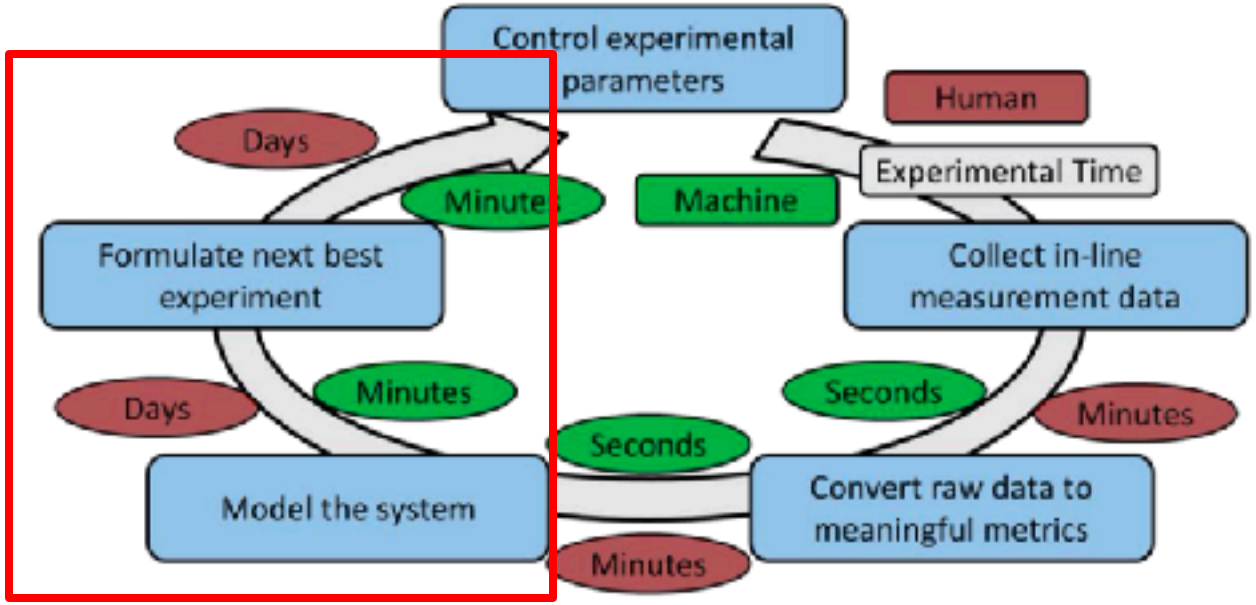
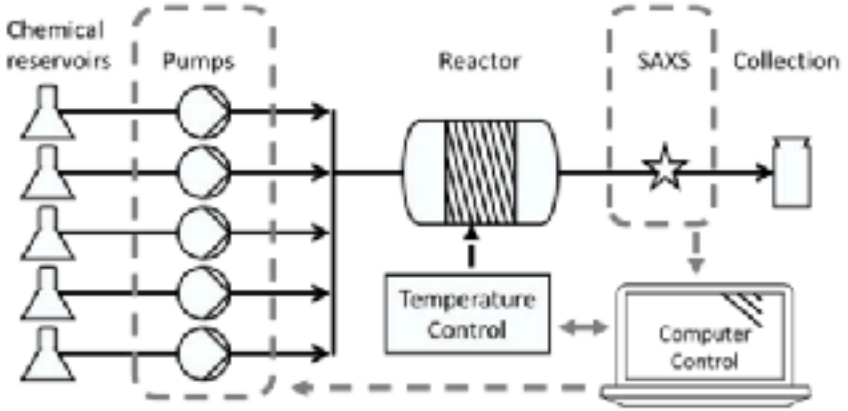
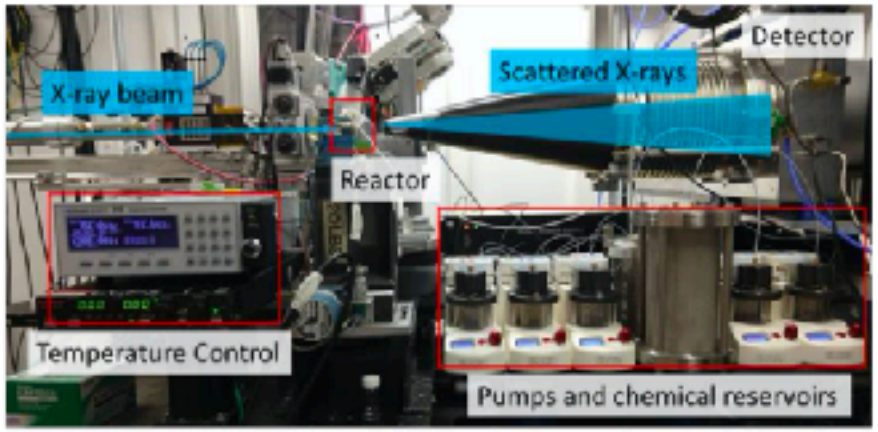
a)



b)



c)



Details of Bayesian Optimization

$$x = \begin{bmatrix} T_{reac} \\ F_{tot} \\ x_{ODE} \\ x_{TOP} \\ x_{oley} \end{bmatrix}$$

$$\mathbf{y} = \begin{bmatrix} p_{\mathrm{dil}} \\ p_{\mathrm{cond}} \\ p_{\mathrm{cryst}} \\ I_0 \\ \tilde{I}_{0,\mathrm{dil}} \\ \bar{r}_{\mathrm{dil}} \\ \sigma_{\mathrm{dil}} \end{bmatrix}$$

1. Presence of dilute nanoparticle products (binary): $p_{\mathrm{dil}} \in \{-1, 1\}$
2. Presence of condensed (disordered) nanoparticle products: $p_{\mathrm{cond}} \in \{-1, 1\}$
3. Presence of crystalline (superlattice) nanoparticle products: $p_{\mathrm{cryst}} \in \{-1, 1\}$
4. Intensity at $q = 0$: I_0, in $[0, \infty)$
5. Fraction of I_0 attributable to dilute nanoparticle products: $\tilde{I}_{0,\mathrm{dil}} = I_{0,\mathrm{dil}}/I_0$, in $[0, 1]$
6. Mean radius of dilute nanoparticle products: $\bar{r}_{\mathrm{dil}}$, in $(0, \infty)$
7. Fractional standard deviation of radii of dilute nanoparticle products: σ_{dil}, in $(0, \infty)$

Individual GPs

Enforce

- Size
- Monodispersity
- Large Yield
- Desired Population (dilute)

$$g(\bar{y}, \sigma_y^2) = \prod_j [g_j(\bar{y}_j, \sigma_{yj}^2)]$$

$$x^* = \underset{(x)}{argmax}\, g(\bar{y}, \sigma_y^2)$$

$$g_j(\bar{y}_j, \sigma_{yj}^2) = P(|y_j - y_j^*| < |y_j^+ - y_j^*|)$$

Acquisition Function Details

$$\mathbf{y} = \begin{bmatrix} p_{\text{dil}} \\ p_{\text{cond}} \\ p_{\text{cryst}} \\ I_0 \\ \tilde{I}_{0,\text{dil}} \\ \bar{r}_{\text{dil}} \\ \sigma_{\text{dil}} \end{bmatrix}$$

Constraints Coded into Acquisition Functions

$$g_0(\bar{p}_{\text{dil}}, \sigma^2_{p\text{dil}}) = P(p_{\text{dil}} > 0)$$

$$g_1(\bar{p}_{\text{cond}}, \sigma^2_{p\text{cond}}) = P(p_{\text{cond}} < 0)$$

$$g_2(\bar{p}_{\text{cryst}}, \sigma^2_{p\text{cryst}}) = P(p_{\text{cryst}} < 0)$$

$$g_3(\bar{I}_0, \sigma^2_{I0}) = P(I_0 > 10)$$

$$g_4(\bar{\tilde{I}}_{\text{dil}}, \sigma^2_{\tilde{I}\text{dil}}) = P(\tilde{I}_{\text{dil}} > 0.9)$$

$$g_5(\bar{\bar{r}}_{\text{dil}}, \sigma^2_{\bar{r}\text{dil}}) = P(|\bar{r}_{\text{dil}} - \bar{r}^*_{\text{dil}}| < |\bar{r}^+_{\text{dil}} - \bar{r}^*_{\text{dil}}|)$$

$$g_6(\bar{\sigma}_{\text{dil}}, \sigma^2_{\sigma\text{dil}}) = P(\sigma_{\text{dil}} < 0.2)$$

Closest training example

target

Automating Understanding of Synthesizability

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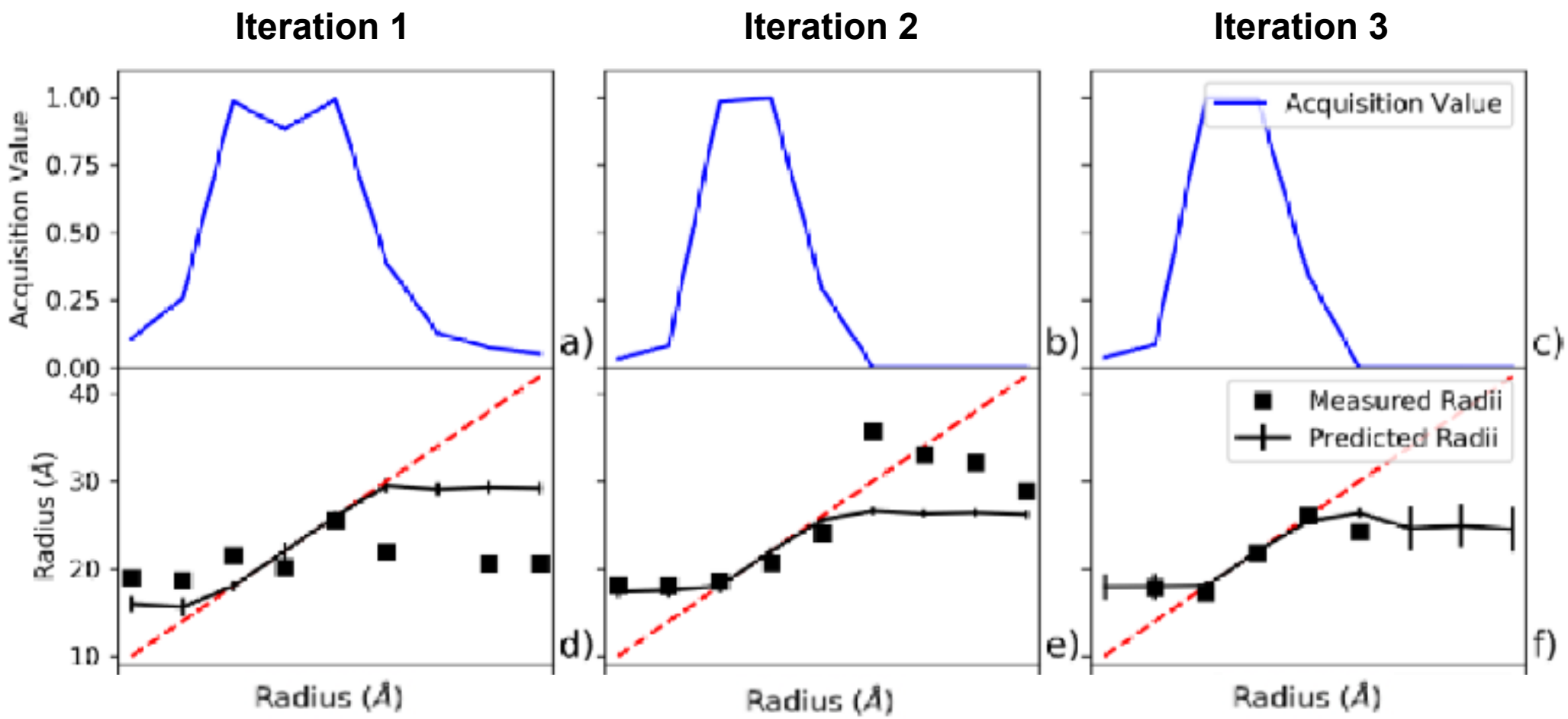
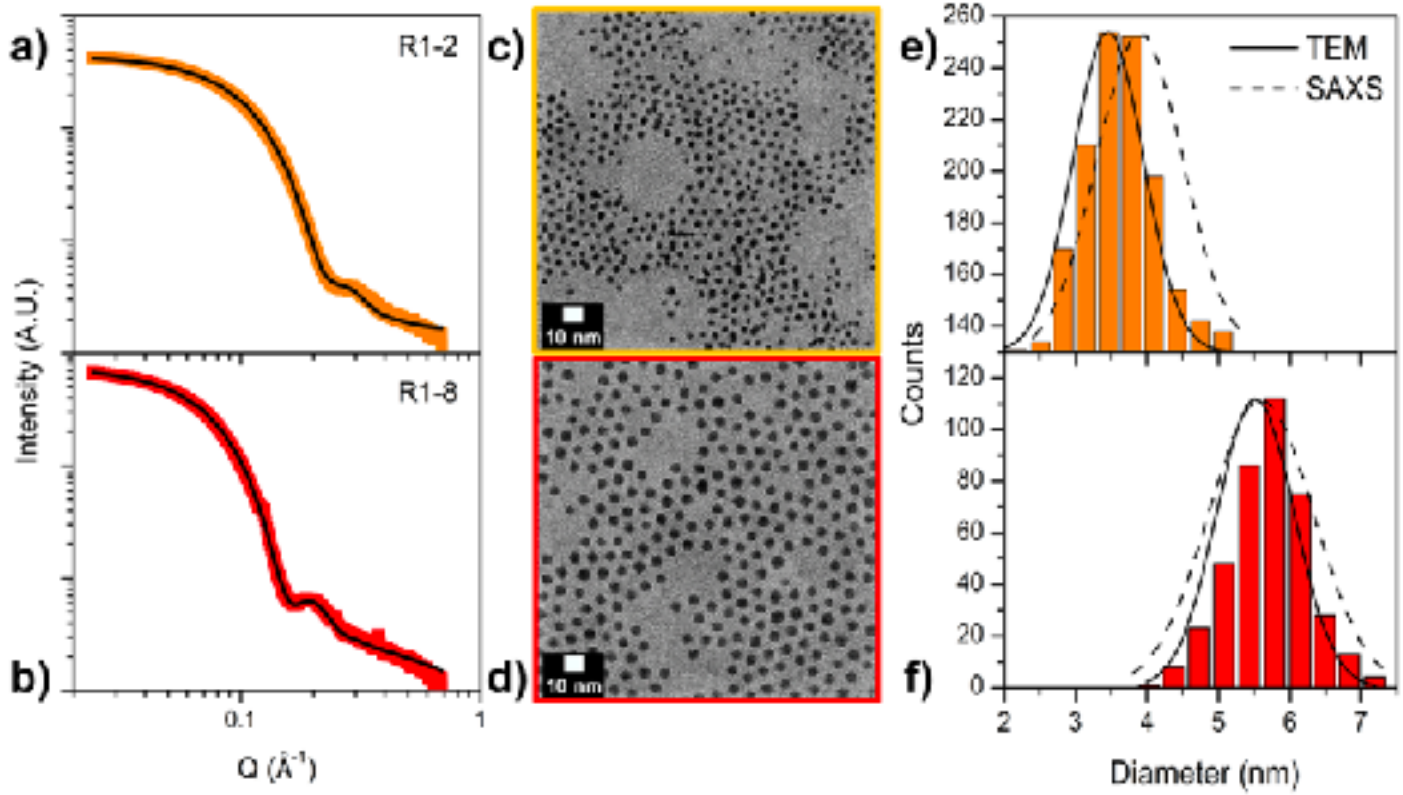
We don't want to synthesize a single catalyst, we want to synthesize a library



Sample Results for NP synthesis

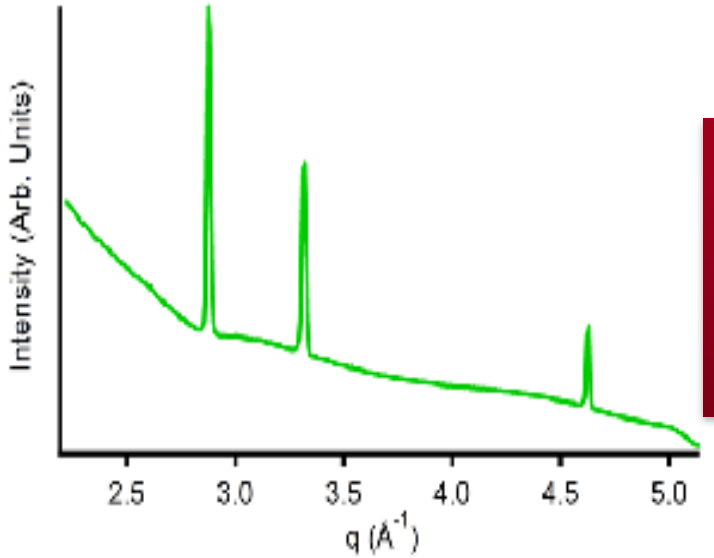


Reaction	SAXS [nm]	TEM [nm]	Flowrate [µL]	Temp. [°C]	$Pd(acac)_2$ [M]	TOP [M]	oleylamine [M]
R1-2	3.9 ± 0.6	3.5 ± 0.5	116	275	0.0168	0.0719	0.0036
R1-8	5.6 ± 0.7	5.5 ± 0.5	20	284	0.0198	0.0845	0.5117

Future Directions: Binary and Ternary Systems

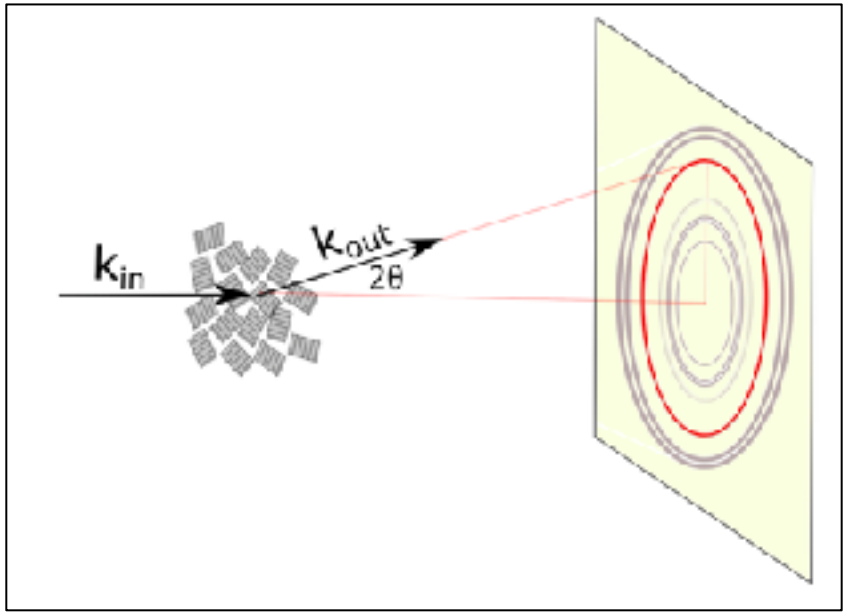
- Multimodal SAXS/WAXS experiments
  - Optimize for desired phase, composition and particle size
  - E.g. make NPs of Pt4Sn alloy
- Automate analysis of 1D powder/WAXS data using ML
  - Crystal System / Lattice parameters
  - Predict phases in data based on known priors

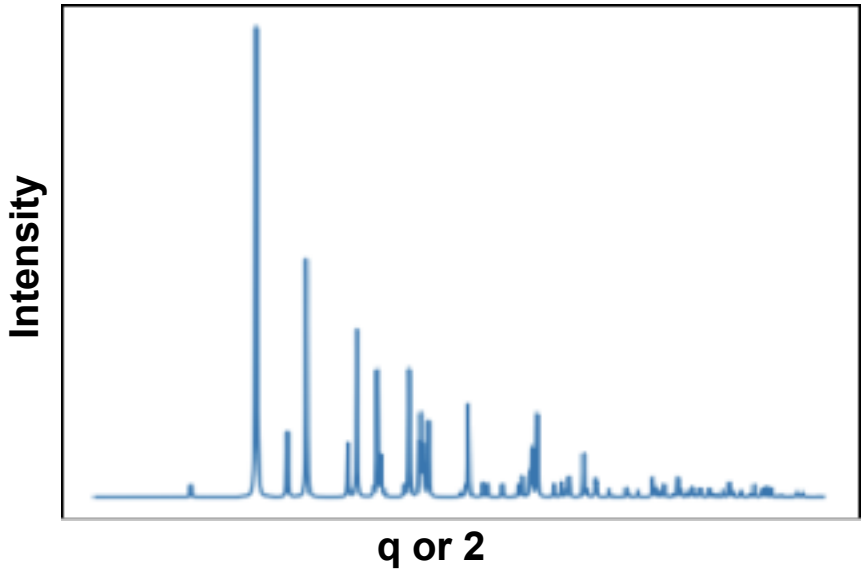
Wide-angle X-ray scattering (WAXS) characterizes



- Phase
- Composition
- Degree of Crystallinity
- Strain
- Crystallite Size

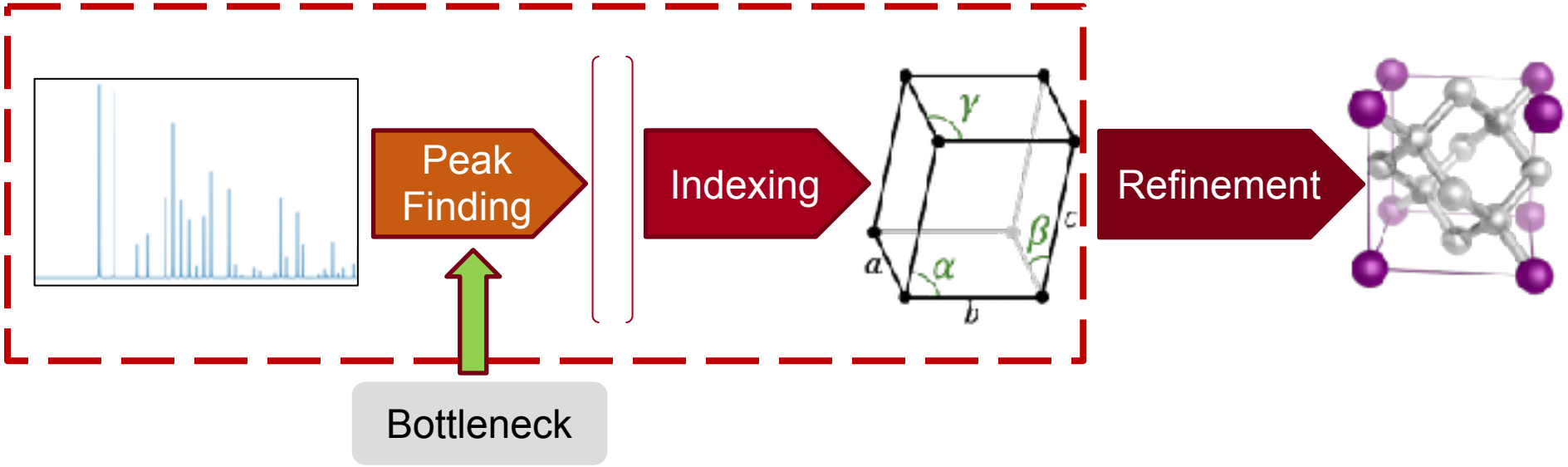
Introduction to WAXS / Powder Diffraction

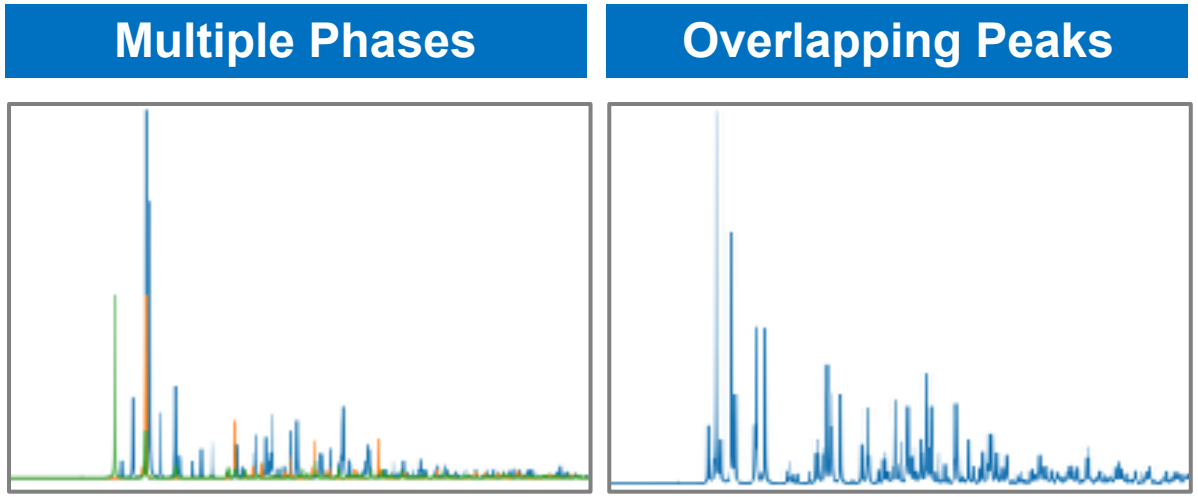




- **Peak locations**: crystal system / lattice parameters
- **Peak intensities:** space group / position of atoms, texturing
- **Peak shape:** sample / instrument effects
- **Phase Identification:** fingerprinting

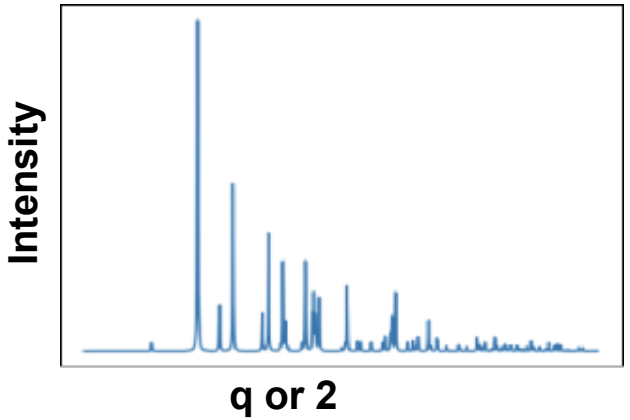
Conventional Analysis Pipeline

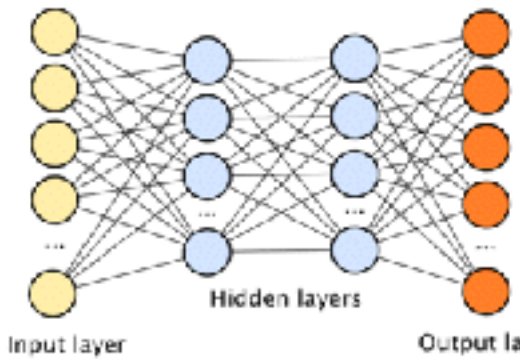


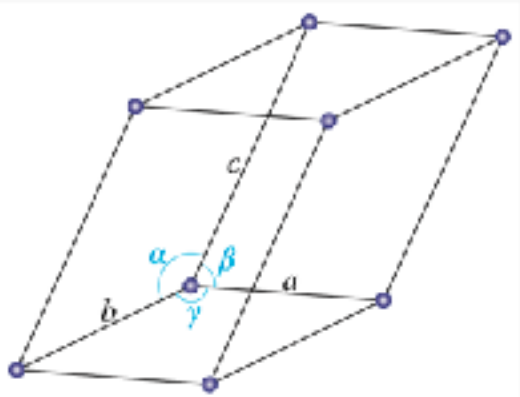


Problem Formulation

Goal: Develop machine learning models to directly **estimate lattice parameters** from powder diffraction data







Previous Work

- [1]Automatic space group and crystal system prediction
- [2]Lattice parameter prediction for neutron diffraction data

Potential Advantages

- Robust to Noise
- No Intervention Needed
- Fast

1. Park, W. B. et al., IUCrJ (2017).
2. Doucet, M. et al., Machine Learning: Science and Technology 2.2 (2020).

Previous ML Analysis of Powder Diffraction Data

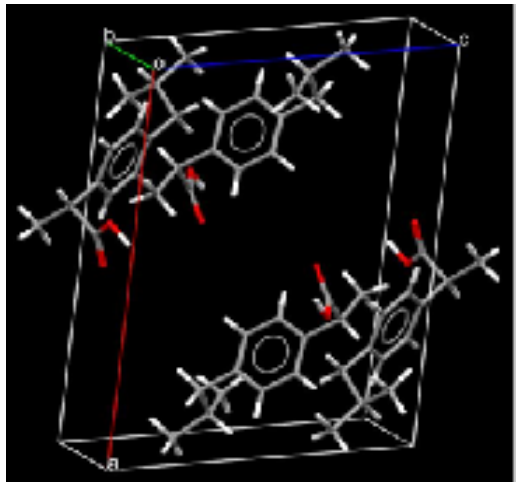
- Determination of **Space Group** and **Crystal System** directly from diffractogram
  - 230 Space Groups, 7 Crystal Systems

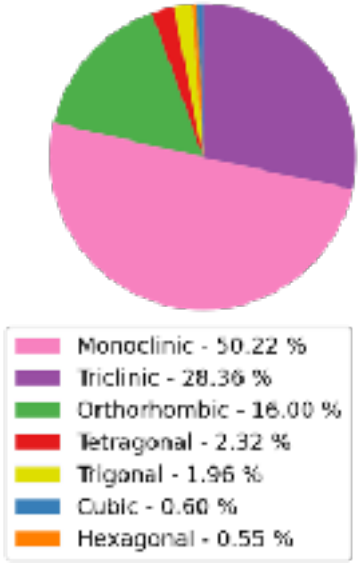
	Method	Accuracy	Type	Output	Dataset Size	Datasets
Park et al. 2017	CNN	81.14%	Sim	230 space groups	150000	ICSD
Oviedo et al. 2018	CNN + physics augmentation	89%	Sim/Exp	7 Crystal Systems	164 + 115	ICSD/Exp
Vecsei et al. 2018	FCNN	57%	Sim/Exp	230 space groups	128404 + 800	ICSD/RRUFF
Suzuki et al. 2018	RF - 10 peak positions	83.62%	Sim	230 space groups	188607	ICSD

Simulation Details

➢ **~ 1 million patterns simulated** from CIF structure files from Inorganic Crystal Structure Database and Cambridge Structural Database

Cambridge Structural Database

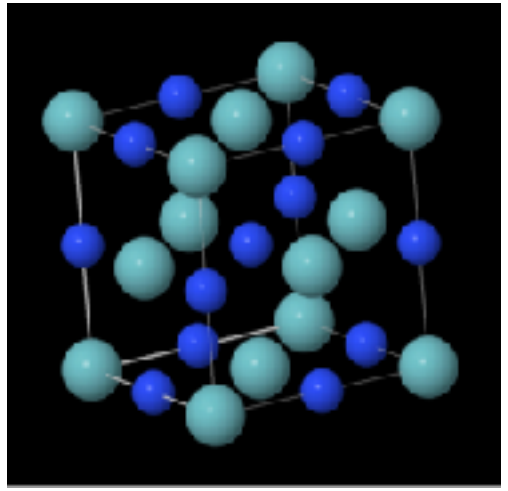


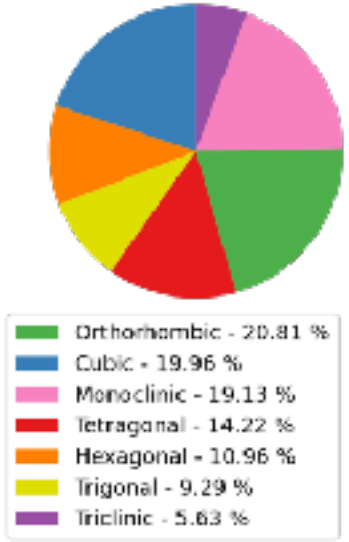


Ibuprofen

~ Large Unit Cells
~ Low symmetry

Inorganic Crystal Structure Database





NaCl

~ Small Unit Cells
~ High symmetry

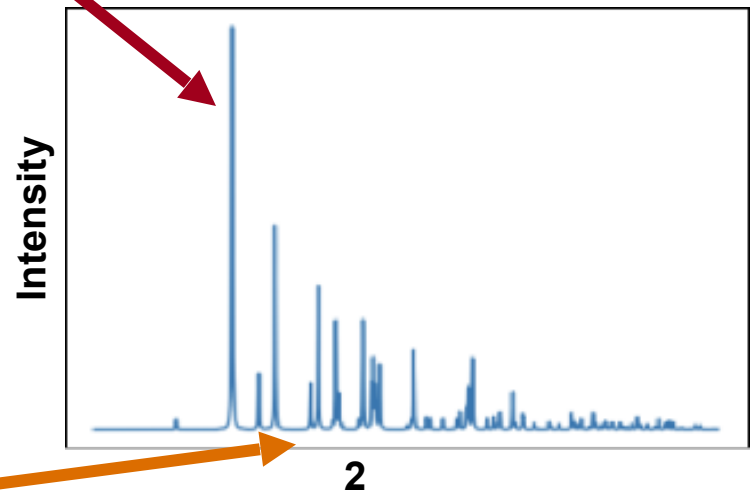
Simulation Details

$$I = \alpha(m_{hkl})\left(|F_{hkl}|^2\right)\frac{\left(1+\cos^2 2\theta\right)}{\left(\sin\theta \sin 2\theta\right)}$$

Multiplicity

Crystal Structure Factor

Lorentz-Polarization



$$\lambda = 2d_{hkl}\sin\theta$$

Performance of Baseline Models on Simulated Data

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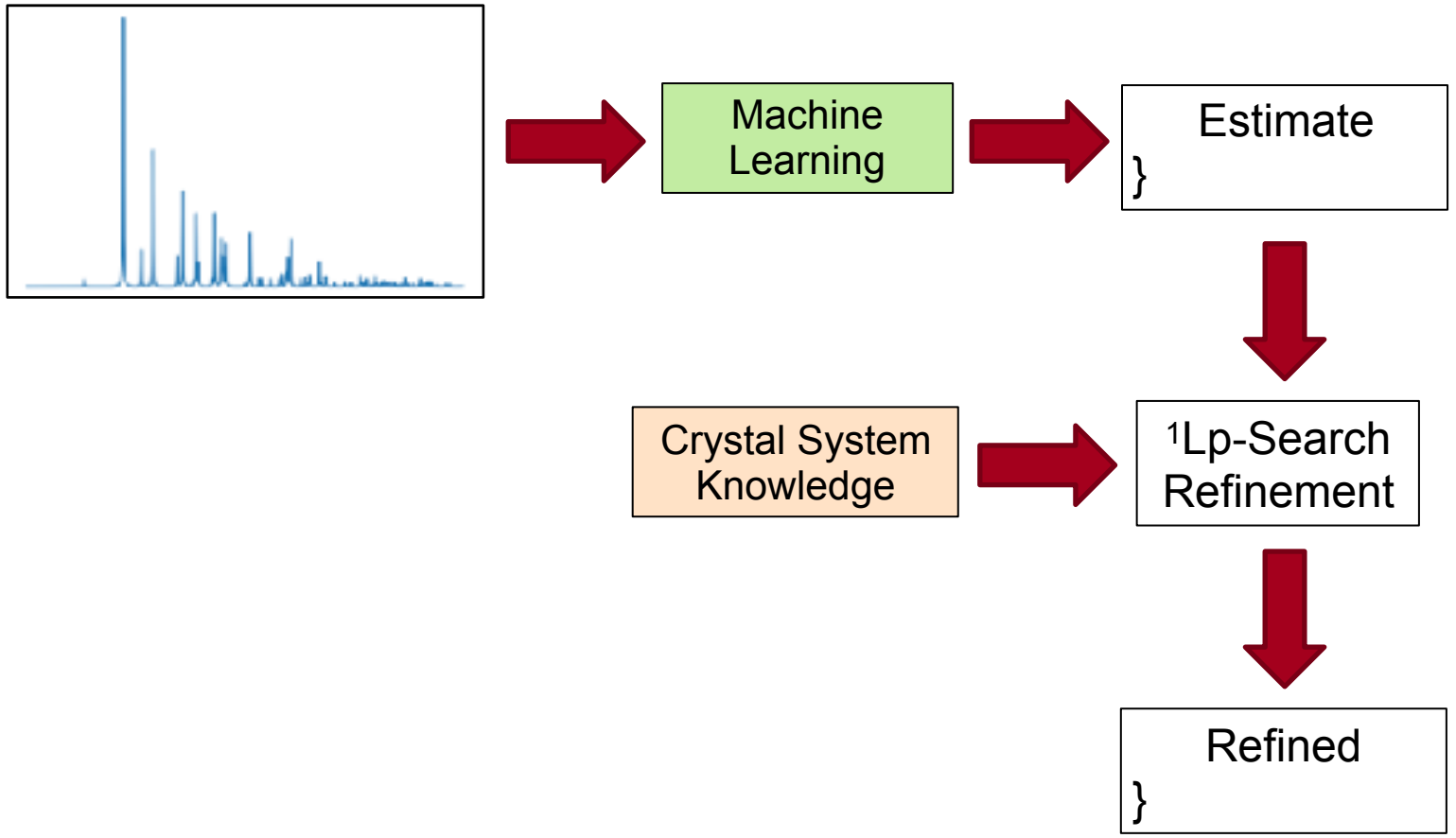
ML Models: 1D Convolutional Neural Networks trained and tested on simulated intensity arrays for each crystal system

Crystal System	Independent Parameters	Mean Percentage Error (%)
Cubic		7.4
Hexagonal		6.4
Trigonal		14.8
Tetragonal		11.6
Orthorhombic		10.0
Monoclinic		11.8
Triclinic	,	3.1

Are these predictions good enough?

Machine Learning + Refinement Pipeline



ML can provide the **initial guess** required for refinement

1. Coelho, A. A., Journal of Applied Crystallography (2017).

Monte Carlo Pawley Refinement (Lp Search)

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Pawley Refinement

- Minimize difference between calculated and observed (experiment) diffractogram
- Method does not rely on the structure factor

$$M = \sum_i W_i \left\{ y_i^{obs} - \frac{1}{c} y_i^{calc} \right\}^2$$

Parameters	Interpretation
Lattice Parameters	Dictates peaks via Bragg Equation
$I(hkl)$	Intensities for each (hkl)
$2\theta_{zero}$	Zero-offset (instrument)
U,V,W	Peak-width
η	Other detector, peak shape parameters

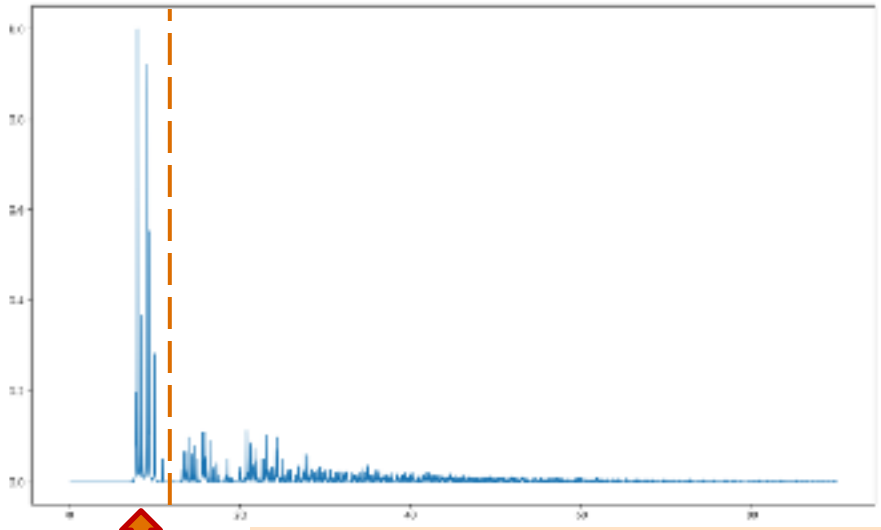
Lp Search is a Monte Carlo minimization of the objective:

- Not used so much due to large parameter range
- Lattice parameter ranges for {}
  - 3 <
  - < 120
- Space Group

Automatic Unit-Cell Refinement

Chemical Formula: $^{1}C_{48}H_{62}Er\ N_7O_2Si_2$ **Crystal System**: Hexagonal

Lattice Parameters: {a = 13.11, b = 13.11, c = 57.64, = 120}



Peaks for c lattice parameter

CNN Estimate

{a = 13.71, b = 13.71, c = 57.74}

After Refinement

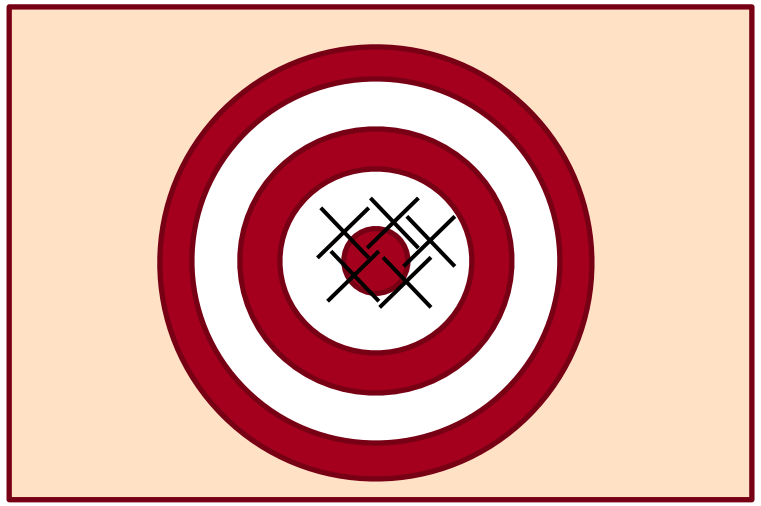
✓ {a = 13.11, b = 13.11, c = 57.64}

Possible to **fully automate** the analysis of challenging powder diffraction patterns

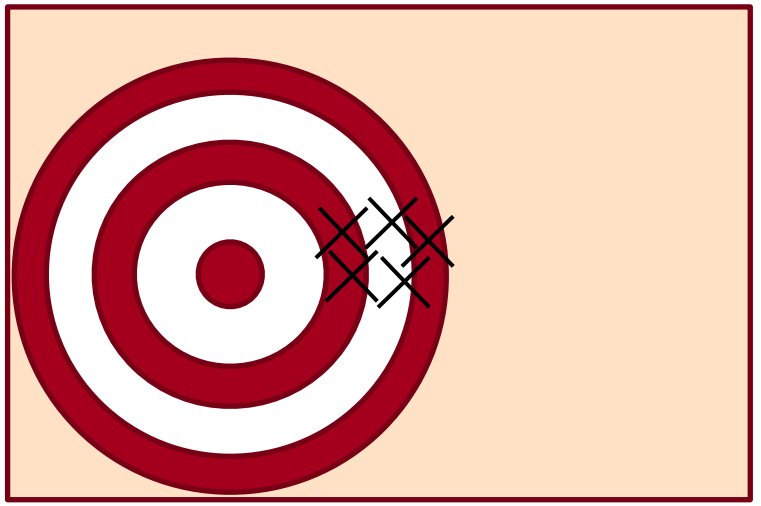
1. Huang, Z. et al., Inorganic chemistry (2018).

Modelling Realistic Non-idealities

- There is normally exists a generalization gap between training on simulated data and predicting on experimental data



Train on Simulated / Test on Simulated



Train on Simulated / Test on Experimental

- Experimental data has extra non-idealities that may need to modelled
  - ➢ Peak Intensity Variation
  - ➢ Zero-Offset Error
  - ➢ Peak Broadening
  - ➢ Impurity Phases
  - ➢ Baseline Noise

Modelling Realistic Non-idealities

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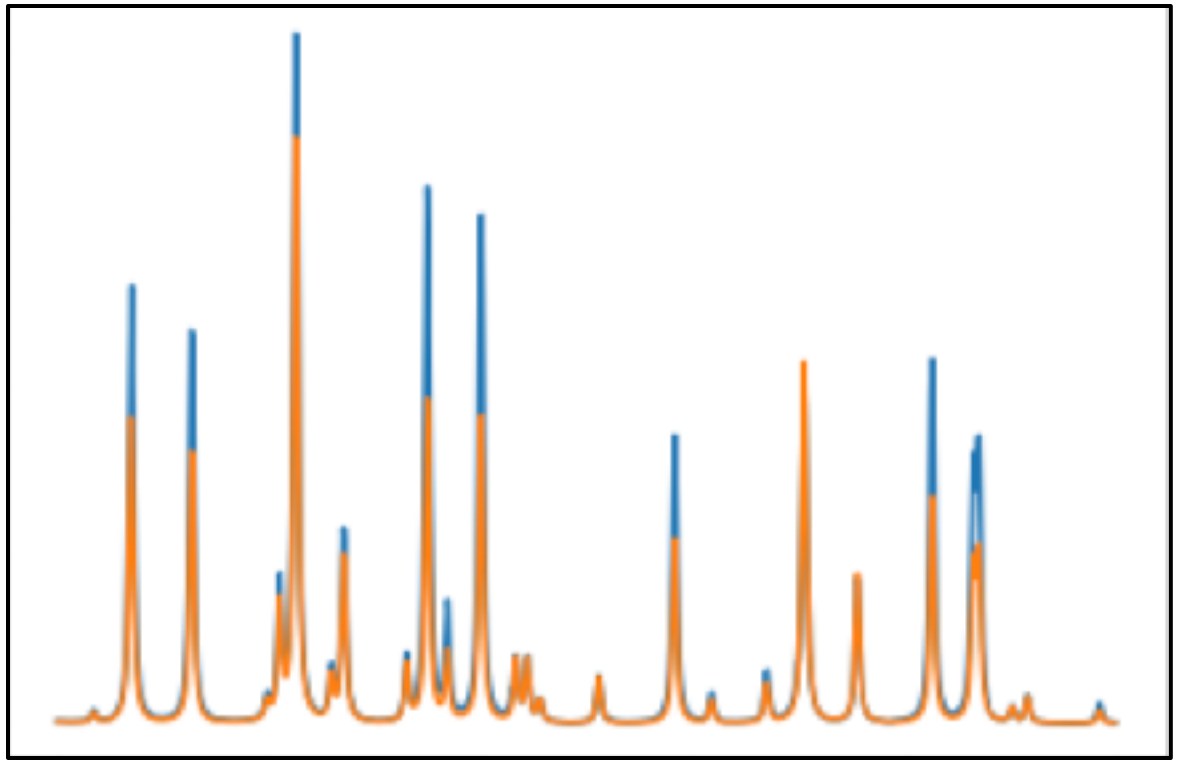
Intensity Variation



Non-ideality models preferential orientation effects

Modelling Realistic Non-idealities

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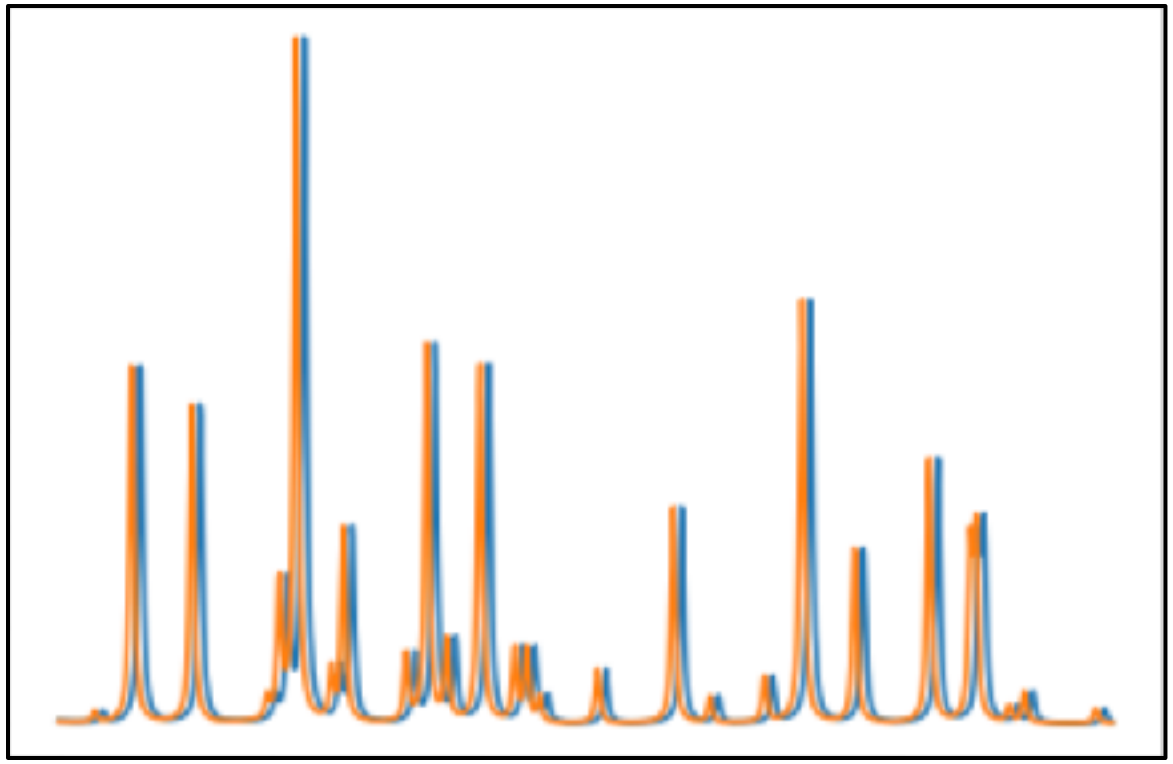
Zero-Offset Error

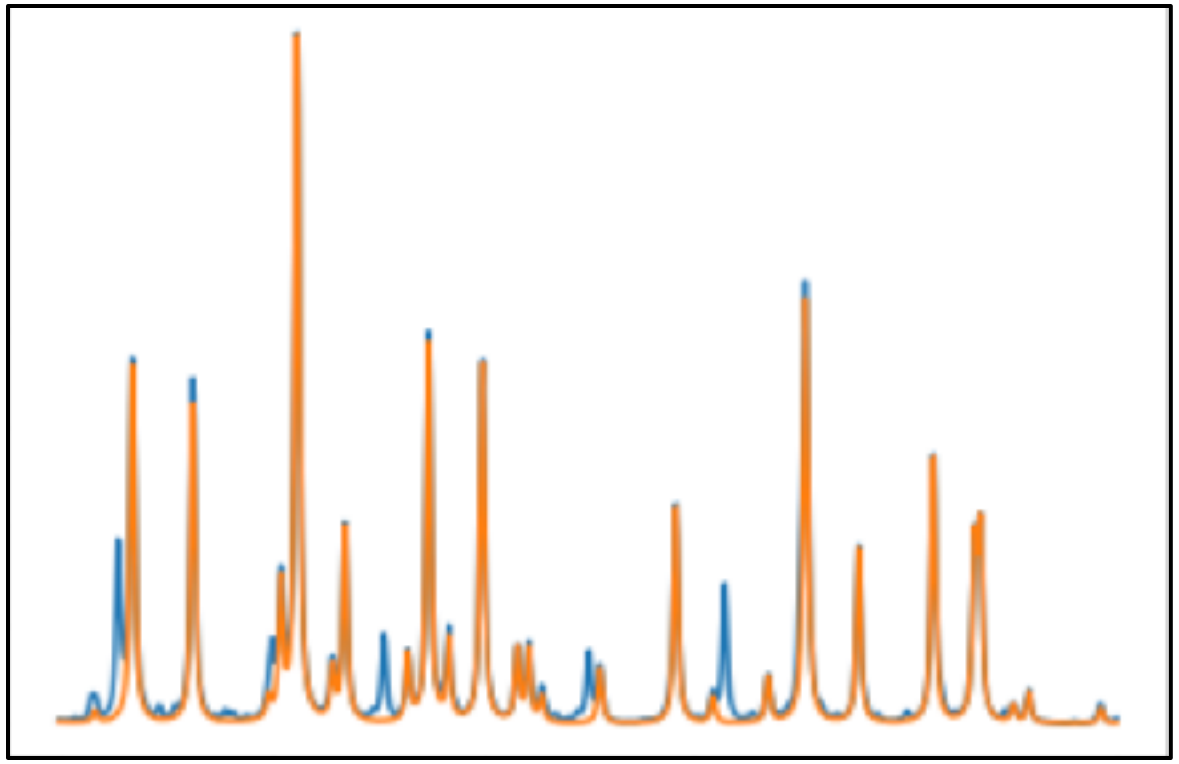


Non-ideality models detector drift

Modelling Realistic Non-idealities

SLAC

Impurity Phases

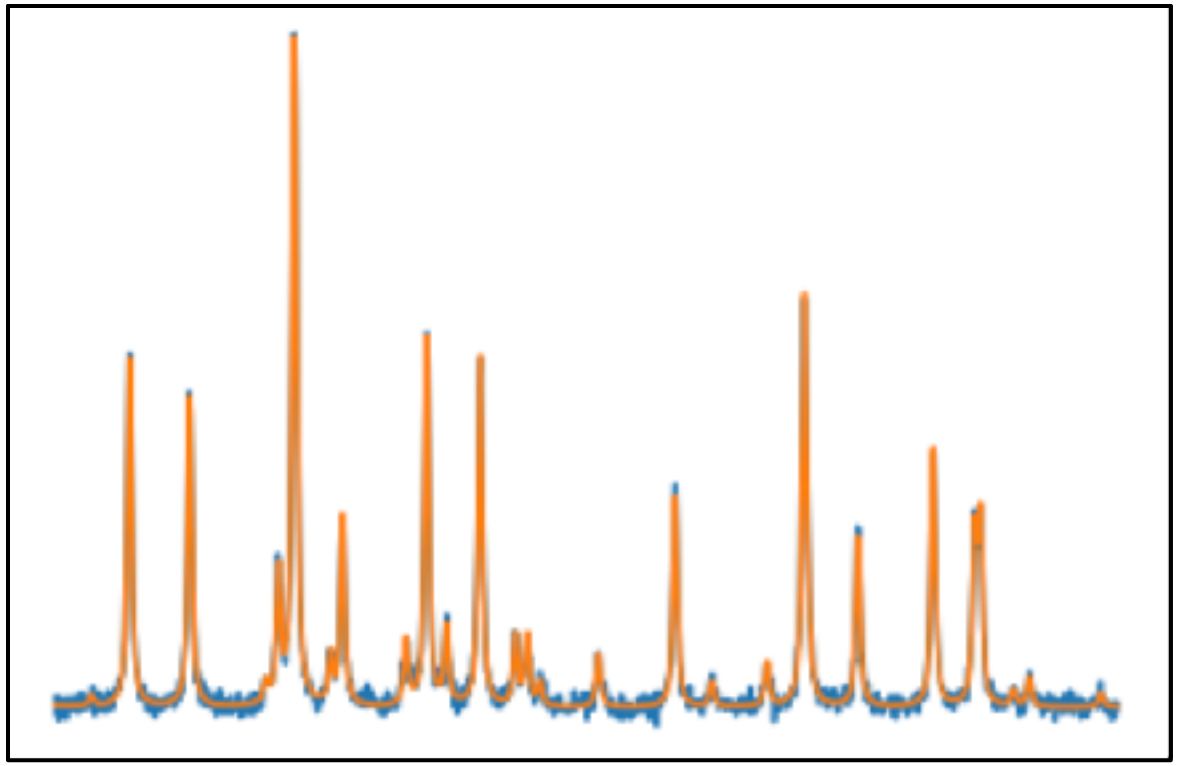


Non-ideality models the addition of extra impurity phases

Modelling Realistic Non-idealities

SLAC

Baseline Noise

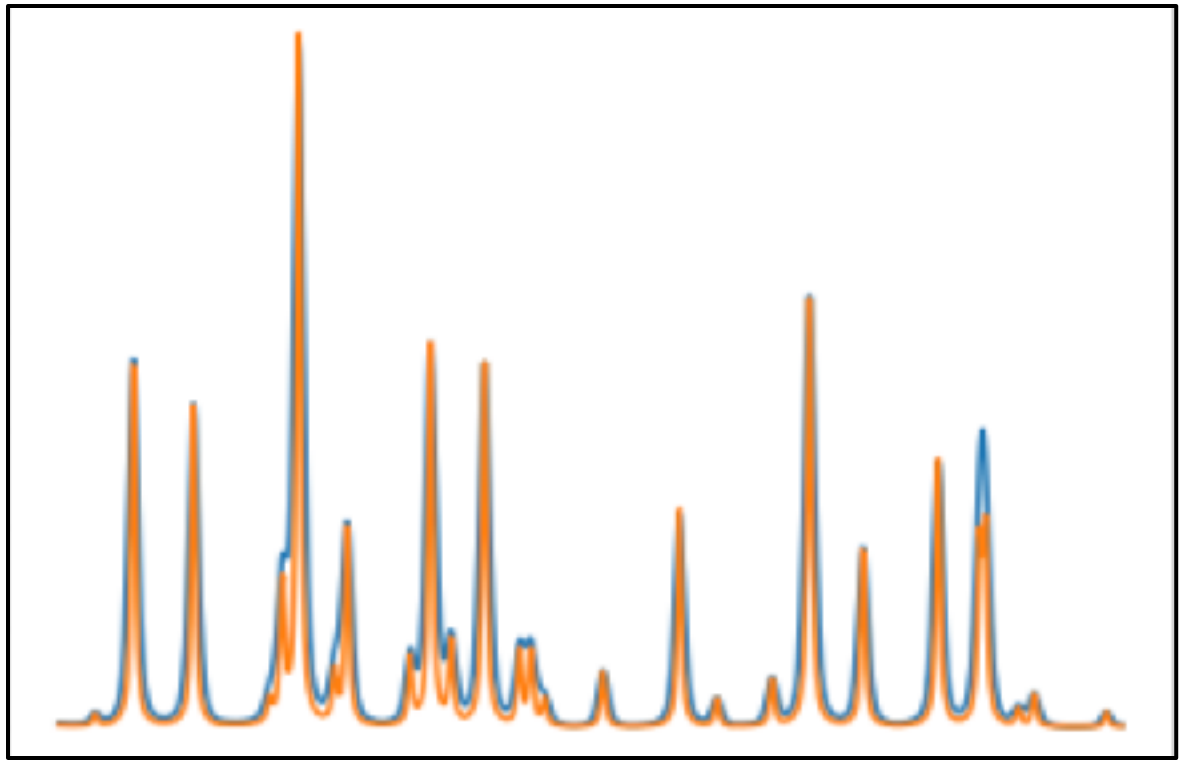


Non-ideality models various sources of baseline noise

Modelling Realistic Non-idealities

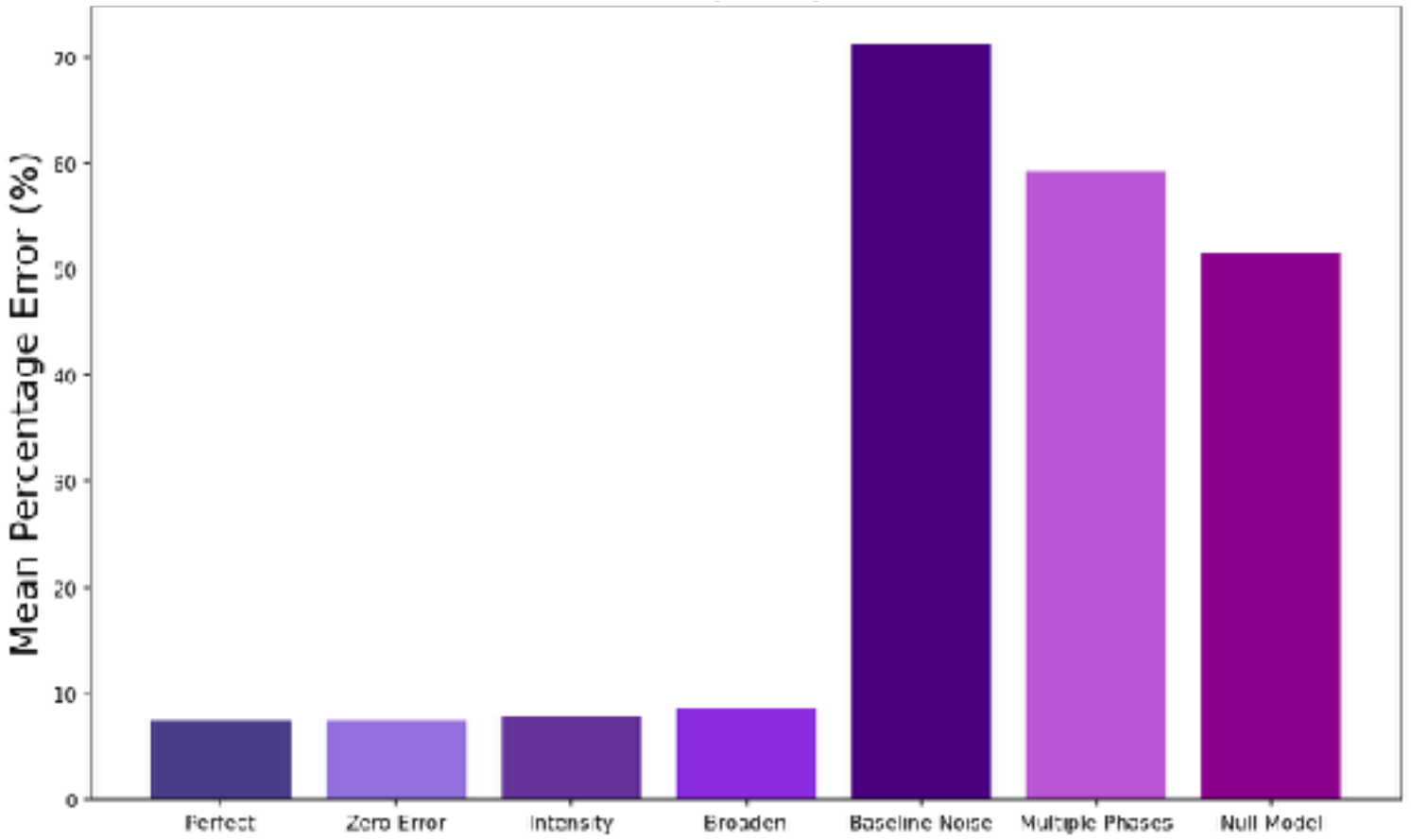
SLAC

Peak Broadening



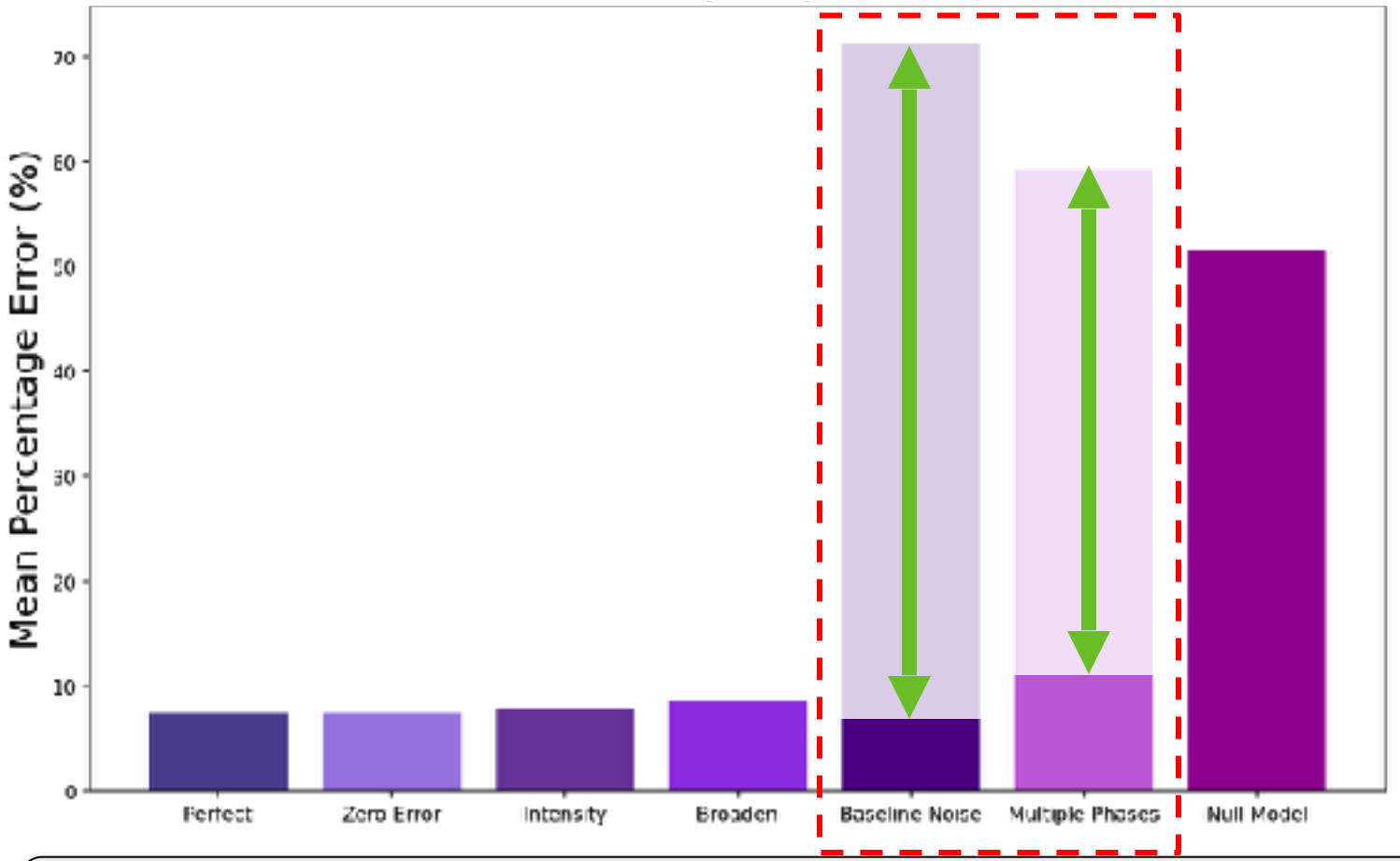
Non-ideality models broadening due to size and microstrain effects

Effect of Realistic Non-idealities



Baseline CNN models are **unstable** against some non-ideal conditions

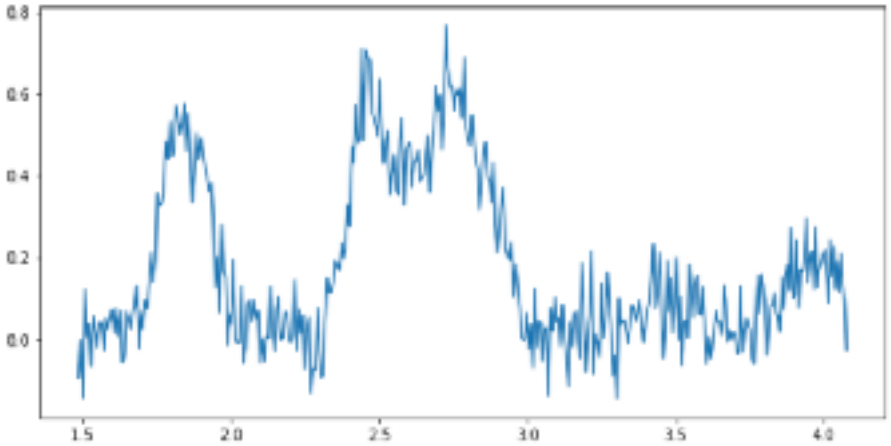
Stabilization against Realistic Non-idealities

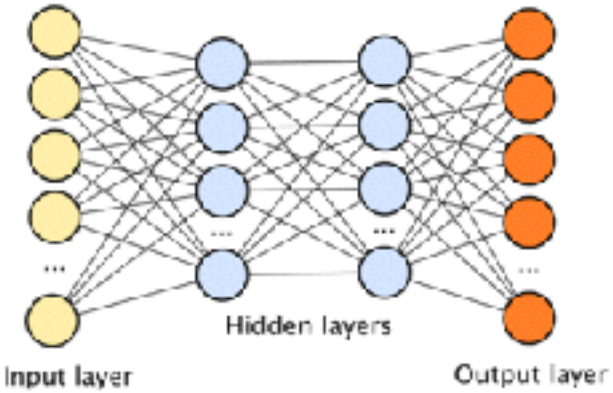


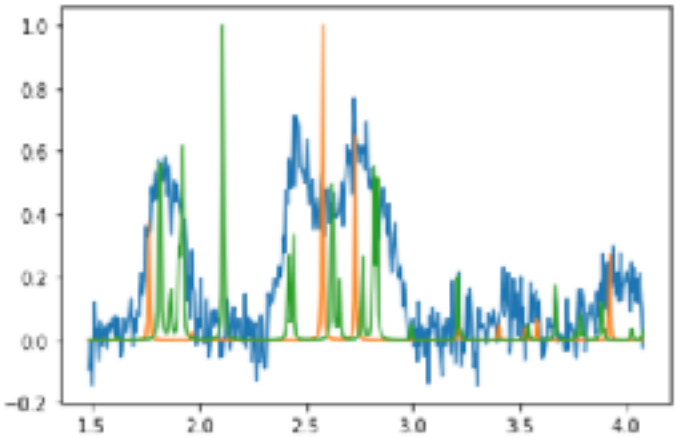
Using non-idealities **during training** greatly improves performance

Multiphase analysis: Predicting phases and phase fractions

Phase identification/fraction using CNNs







['PtSn', 'PtSn4']

+

Prior knowledge of possible phases

Future Work

- **Nanoparticle Optimization**
  - Other systems beyond Pd
  - Extension to multicomponent systems using SAXS/WAXS
  - Analysis of other optimization methods beyond Bayesian optimization

- **Powder Diffraction Anaysis**
  - Incorporation of more realistic physical models for preferred orientation, microstrain, crystallite size and temperature dependence
  - Adding atomic / geometrical features based on plausible compositions
  - Capturing additional information in the 2D area data
  - Using prior information to analyze multiphase data

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Supplementary Slides

Learning Nanoparticle Design Rules

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- TOP, oleylamine, oleic acid are ligands which can bind and control nucleation and growth
  - TOP slows nucleation kinetics by increasing Pd precursor
  - Oleylamine can enhance nucleation kinetics
  - ODE is just a diluting solvent

- Higher Temperatures + Lower Flow Rates give bigger NPs
  - Large T accelerates growth kinetics
  - Low Flow-rate increase growth duration