

SOLVING ATOMIC STRUCTURE USING STATISTICAL MECHANICAL SEARCHES ON  
X-RAY SCATTERING DERIVED POTENTIAL ENERGY SURFACES

by

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## DEDICATION

## ACKNOWLEDGMENTS

# ABSTRACT

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# INTRODUCTION

This is the introduction to the thesis.

# CHAPTER 1

## ATOMIC STRUCTURE: EXTRACTION AND APPLICATION

### 1.1 ATOMISTIC GOALS

The only way to truly understand the fundamental source of material and chemical properties is through atomic structure. The goal of atomistic engineering is to produce novel structures and combinations of structures to engender new properties and functions. This includes producing stronger materials, more durable catalysts, more energy dense batteries, and many more engineering applications. The true power of atomistic engineering has been shown in biochemistry and pharmaceutical design. Although the production of drugs and biomedical treatments is usually considered to be rather far from the field of catalyst design and materials science, the atomistic nature of these fields can not be denied. The field of protein structural analysis stands as an example of structural science, elucidating the three dimensional coordinates of thousands of atoms. These structures are then used to describe how the molecular machinery of the biological world works, enabling the development of new drugs and treatments for diseases and a deeper understanding of how we evolved. The development of protein inhibitor drugs, which are important to so many treatments, would have not been possible without very detailed atomic structures. The aspiration of this work is to create this level of accuracy and utility, generating structures which allow for the understanding of how materials work on a fundamental level.

## 1.2 ATOMISTIC EXPERIMENTS

### **Single Crystal Diffraction**

### **Electron Microscopy**

### **X-ray Total Scattering**

## 1.3 ATOMISTIC SIMULATIONS

The goals of atomistic simulations are usually to produce atomic structures from quantum mechanical first principles, as in the case of Density Functional Theory (DFT), or classical approximations to quantum mechanics.

### **Density Functional Theory**

### **Classical Force Field**

### **Monte Carlo and Statistical Mechanics**

Maybe put the ensemble and PES work here, since it is more general than the PDF per say. Also the rational for the gradients and fast computation make much more sense knowing we are going to be very sample happy and follow the gradient of the PES.

# CHAPTER 2

## STATISTICAL MECHANICAL ENSEMBLES AND POTENTIAL ENERGY SURFACES

### 2.1 INTRODUCTION

The approach taken in this work for solving the atomic structures of materials is one of optimization. The positional variables of the system are optimized so as to minimize the value of a potential energy surface (PES). The

### 2.2 POTENTIAL ENERGY SURFACES

A PES simply describes the potential energy of the system as a function of all its relevant coordinates in phase space, essentially providing a mapping  $\mathbb{R}^n \rightarrow \mathbb{R}$ . Usually these coordinates are the positions of the atoms  $q$  and their conjugate momenta  $p$ . Note that there could be more variables associated with the system, for instance the magnetic moments of the atoms could play a role in describing the system. In this magnetic system there would be positional variables for the atomwise spin vectors and their "momenta". Application of the term "momenta" might seem odd here, as the magnetic spin does not have a mass or a velocity. However, since the magnetic "position" is defined on the PES we need to describe its conjugate variable to properly formulate Hamiltonian dynamics and the kinetic portion of the PES.

## Experimentally Derived Potential Energy Surfaces

Generally PESs are obtained from purely computational experiments including: ab-initio DFT, classical approximations via the embedded atom method, or even parameter driven models with experimentally fitted parameters. However, one can derive a PES from an experiment which describes how well the model reproduces the experimental data. In this case one needs a theoretical and computational framework mapping the atomistic variables of the simulation to the same space of the data obtained from the experiment. This allows the experiment to be compared directly against the predicted data via an experimentally derived PES.

### Potentials

For an experiment which produces 1D data, like powder diffraction, EXAFS or XPS, the implemented potentials are:

$$\chi^2 = \sum_{a=a_{\min}}^{a_{\max}} (A_{\text{obs}} - \alpha A_{\text{calc}})^2 \quad (2.1)$$

$$Rw = \sqrt{\frac{\sum_{a=a_{\min}}^{a_{\max}} (A_{\text{obs}} - \alpha A_{\text{calc}})^2}{\sum_{a=a_{\min}}^{a_{\max}} A_{\text{obs}}^2}} \quad (2.2)$$

$$\alpha = \frac{\sum_{a=a_{\min}}^{a_{\max}} A_{\text{obs}} A_{\text{calc}}}{\sum_{a=a_{\min}}^{a_{\max}} A_{\text{calc}}^2} = \frac{\vec{A}_{\text{obs}} \cdot \vec{A}_{\text{calc}}}{|\vec{A}_{\text{calc}}|^2} \quad (2.3)$$

where  $A_{\text{calc}}$  and  $A_{\text{obs}}$  are the calculated and observed 1D experimental data. Note that  $A_{\text{calc}}$  has a dependence on  $q$ , the positions of the system.

### Forces

$$\vec{\nabla} \chi^2 = -2 \sum_{a=a_{\min}}^{a_{\max}} \left( \alpha \frac{\partial A_{\text{calc}}}{\partial q_{i,w}} + A_{\text{calc}} \frac{\partial \alpha}{\partial q_{i,w}} \right) (A_{\text{obs}} - \alpha A_{\text{calc}}) \quad (2.4)$$

$$\vec{\nabla} Rw = \frac{Rw}{\chi^2} \sum_{a=a_{\min}}^{a_{\max}} \left( \alpha \frac{\partial A_{\text{calc}}}{\partial q_{i,w}} + A_{\text{calc}} \frac{\partial \alpha}{\partial q_{i,w}} \right) (\alpha A_{\text{calc}} - (A_{\text{obs}})) \quad (2.5)$$

$$\frac{\partial \alpha}{\partial q_{i,w}} = \frac{(\sum_{a=a_{\min}}^{a_{\max}} A_{\text{obs}} \frac{\partial A_{\text{calc}}}{\partial q_{i,w}} - 2\alpha \sum_{a=a_{\min}}^{a_{\max}} A_{\text{calc}} \frac{\partial A_{\text{calc}}}{\partial q_{i,w}})}{\sum_{a=a_{\min}}^{a_{\max}} A_{\text{calc}}^2} \quad (2.6)$$

INCLUDE INVERT. DISCUSS INVERT A BUNCH. ALSO COMPARE RW AND CHI\*\*2, POTENTIALY WITH A FIGURE.

### 2.3 ENSEMBLES

While PESs describe which atomic configurations are the most desirable and how the atoms would like to get there, the ensemble describes how the atoms move on the PES. The abstraction of the PES from the ensemble is an important one, as it allows for the reuse and exchange of both PESs and ensembles for a wide array of problems. Statistical mechanical ensembles can be described in two ways, analytically and stochastically. For long simulation times and fine enough numerical or analytical integration these two descriptions should be identical. In either case one starts by defining the Hamiltonian  $\mathcal{H}$  as the total energy of the system. Thus, the Hamiltonian is described as the sum of the potential  $U(q)$  and kinetic  $K(p)$  energies, where  $q$  is the positions of the atoms and  $p$  is their momenta

$$\mathcal{H}(q, p) = U(q) + K(p) \quad (2.7)$$

where  $K(p) = \frac{1}{2} \sum_i \frac{p_i^2}{m_i}$  and  $i$  denotes the  $i$ th particle. Analytically one generally defines a partition function, which describes the sum of probabilities over all potential atomic states.

$$\Xi = \sum_i P_i(q, p)$$

where  $P_i$  is the probability of the  $i$ th state and is a function of the total energy of that state. This partition function can then be used to obtain the probability of any specific state.



Hamiltonian Monte Carlo

No-U-Turn-Sampling

Grand Canonical Monte Carlo

Configurational Biasing

# CHAPTER 3

## ATOMIC PAIR DISTRIBUTION FUNCTION: THEORY AND COMPUTATION

### 3.1 THEORY

To properly understand the PDF and its limitations we need to derive its mathematics. The following derivation has been performed numerous times but most recently and completely by Farrow and Billinge, it is reproduced here for clarity and completeness.

#### **Derivation**

Consider a wave incident on a volume of variable density...

#### **Analytical Gradients**

Many optimization algorithms and simulations methodologies, including HMC, require not only the potential energy of a given configuration but also the forces acting on that configuration. These forces are described by the gradient of potential energy of the system.

### 3.2 COMPUTATION

Simply deriving the equations for the PDF is not enough. The many body nature of the PDF equation make analytical solution of the structure from the PDF impossible.

Thus, the PDF must be computed from a structural candidates and compared against experimental results to evaluate the reliability of the model.

## **HPC and GPUs**

To properly solve the structure of materials the PDF will need to be computed many times and checked against experimental results. This requires computation of the PDF, potentially over many atoms. Calculating these PDFs requires a fast, highly parallized, computational framework.

### **GPUs and Parallelization**

Computing the PDF is an embarrassingly parallel problem. The basic procedure is to calculate the reduced structure factor  $F(Q)$  for each atom pair and momentum transfer vector, sum over all the atom pairs, and Fourier transform the structure to the PDF. The first part of this procedure is perfectly parallizable, as each atom pair is seperate from the others. The summation over all the atomic reduced structure factors can be parallelized via distributed summing. Lastly the FFT can be parallelized using existing parellel FFT algorithms.

GPUs are particularly well suted to the task of computing PDFs. GPU chip architecture is designed to perform many task simultaneously by having potentially thousands of cores.

### **Map from ij space to k space**

The above equations, although formally correct, are very ineffiecent.  $F(Q)$  and its gradient are indexed over all the atoms twice, however there are symmetries that allow us to only compute over the atom pairs esentially mapping from an  $n \times n$  space,  $ij$  space, to a  $\frac{n(n-1)}{2}$  space,  $k$  space. For  $F(Q)$  we apply the following mapping

$$\begin{array}{ccccc}
E & \xrightarrow{\psi} & E' & \xrightarrow{\Sigma} & Z \\
\phi \downarrow & & & \nearrow \tilde{\phi}\Sigma & \\
B & \xrightarrow{\psi'} & B' & & 
\end{array}$$

$$\begin{array}{ccccc}
E & \xrightarrow{\psi} & E' & \xrightarrow{\Sigma} & Z \\
\phi \downarrow & & & \nearrow \Sigma' & \\
B & \xrightarrow{\psi'} & B' & & 
\end{array}$$

where  $E$  denotes the atomic coordinates in  $ij$  space,  $E'$  denotes  $F(Q)$  before the summation in  $ij$  space,  $B$  denotes the atomic pairs in  $k$  space,  $B'$  denotes  $F(Q)$  in  $k$  space, and  $Z$  denotes the final summed  $F(Q)$ . For the operators,  $\phi$  denotes the mapping from  $ij$  space to  $k$  space  $k = j + i * \frac{i-1}{2}$ ,  $\psi$  and  $\psi'$  denote the  $F(Q)$  operation in  $ij$  and  $k$  space, respectively.  $\Sigma$  denotes the sum over all the atoms.

To properly define  $\Sigma'$  we must establish whether  $F(Q)$  is an even function. We can accomplish this by examining each of the portions of  $F(Q)$ ,  $\alpha, \beta, \tau, \Omega$ .  $\Omega$  is even, since  $r_{ij}$  is the interatomic distance, which is the same despite a flip of indicies,  $Q$  does not depend on the atomic indicies, and since  $Qr_{ij}$  is even so is  $\sin Qr_{ij}$ . Thus,  $\Omega$  is even. Providing similar analysis to  $\tau$  we can see that while  $\vec{u}_{ij}$  is odd, so is the unit displacement vector between the two atoms, thus the two odds cancel out. Intuitively this makes sense, since the  $F(Q)$  equation is fundamentally interested in the interatomic distances which is even. Thus, switching atom indicies does not change  $F(Q)$ . Due to the even nature of the  $F(Q)$  operator the  $\Sigma'$  operator sums over all the atom pairs, and multiplies by two to reflect the double counting of the  $\Sigma$  operator.

For the gradient a similar mapping is used:

In this mapping, however, we use the  $\tilde{\phi}\Sigma$  operator. This operator simultaneously performs a reverse mapping from  $k$  to  $ij$  space, and a summation with the correct symmetry. In this case the  $\psi$  and  $\psi'$  operators, which denote the  $\vec{\nabla}F(Q)$  operator

in  $ij$  and  $k$  space, are antisymmetric. Intuitively this makes sense as an extension of Newton's Second Law, since each particle's interaction is felt oppositely by its partner.

## Periodic Boundary Conditions

Periodic boundary conditions can be helpful when simulating extended solids or large nanoparticles. In this case all the non-crystallinity is contained within the simulation box and the box is repeated to create the longer distance peaks observed in the PDF. To perform this we can break up the Debye equation into two main parts, the part that describes the interatomic distances within the simulation box and those between boxes. Neglecting the thermal motion portion:

$$F(Q) = \frac{1}{N\langle f \rangle^2} \left( \sum_{j \neq i} f_i^*(Q) f_j(Q) \frac{\sin(Qr_{ij})}{r_{ij}} + \sum_{i,j} f_i^*(Q) f_j(Q) \frac{\sin(QR_{ij})}{R_{ij}} \right) \quad (3.1)$$

where

$$R = |\vec{r} + \vec{u}| \quad (3.2)$$

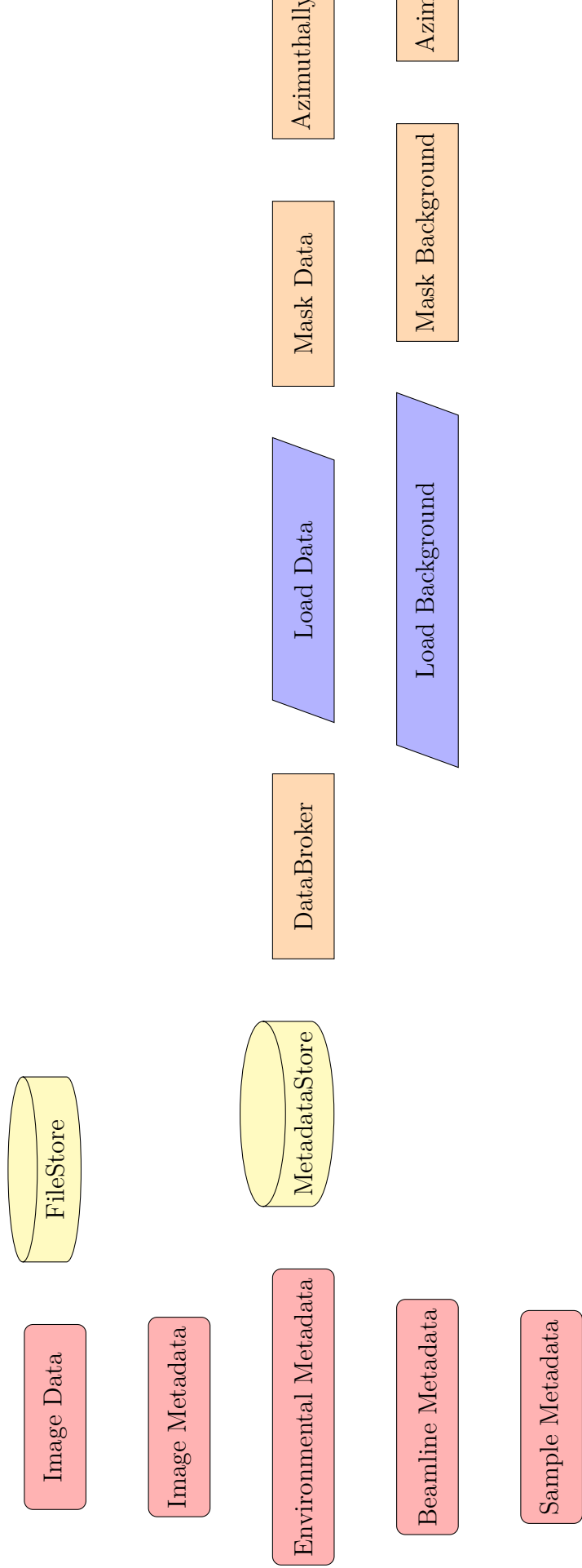
$$\vec{u} = \gamma_1 * \vec{a} + \gamma_2 * \vec{b} + \gamma_3 * \vec{c} \quad (3.3)$$

## 3.3 EXPERIMENT

PDF experiments are generally performed at synchrotron light sources, as only these sources can provide the need flux, energy, and high momentum transfer vectors needed to obtain reliable PDFs.

## 3.4 DATA PROCESSING WORKFLOW

Processing the raw pixel intensities to the PDF is very important as we are extracting most of our interesting information out of very high  $Q$  data. This data relies on good statistics and sound background subtraction. Talk about papers from Billinge Group with thin film PDF and dilute NP solutions. Diagram of the overall data processing workflow. Discuss the NSLS-II data stack.



## MetadataStore Side Loading

Design of sidewinder-spec for loading the data into metadatastore. Most of the design considerations went into the loaders, which are different for each experiment.

## Automated Image Azimuthal Integration

Mux data as needed. Use pyFAI to get the radial distance array. Mask the image.a

## Automated Mask Generation

Enforce azimuthal symmetry by performing azimuthal integration and collecting ring statistics. We then mask data points which are  $x$  standard deviations away from the mean. Additionally the standard deviation threshold can be a function of the pixel distance from the center, allowing the mask generator to be more forgiving at certain points and stricter at others. This is particularly helpful as the small number of pixels near the point of incidence combined with the very sharp peaks causes some pixels to be improperly masked. Similarly it is important to remove dead pixels at the edge of the detector as these have an outsized effect on the integration as the pixel intensity is low to begin with. In practice this results in the removal of almost all dead pixels and potentially the beamstop holder. Removal of the holder depends on its individual properties, since a holder which is more x-ray opaque will cause a larger shift in the pixel intensity distribution. The method was benchmarked on synthetic data, with both hot and cold pixels added. Additional benchmarking was performed with synthetic beamstop holders of various x-ray transmittance. Anomalous corner masking most likely due to the small number of pixels out at the corners.

## CHAPTER 4

### BENCHMARKING

#### 4.1 PDF

**Au55: surface relaxed**

**Au55: surface disordered**

**Au55: amorphous**

**Au102: triple phase**

**Au147**

**C60**

#### 4.2 PDF WITH ADPS



# CHAPTER 5

## ANNEALING AND AGGREGATION OF 2NM

### AU NANOPARTICLES

#### 5.1 EXPERIMENTS

##### **NP Synthesis**

##### **X-ray Total Scattering Measurements**

#### 5.2 DATA PROCESSING

#### 5.3 DATA ANALYSIS

#### 5.4 SIMULATION

#### 5.5 STRUCTURAL ANALYSIS

#### 5.6 CONCLUSIONS

# CHAPTER 6

## PHASE CHANGES AND ANNEALING DYNAMICS OF $\text{Pr}_2\text{NiO}_4$ AND ITS DERIVATIVES

### 6.1 EXPERIMENTS

#### **$\text{Pr}_2\text{NiO}_4$ Synthesis**

#### **X-ray Total Scattering Measurements**

### 6.2 DATA PROCESSING

### 6.3 DATA ANALYSIS

#### **Intra Sample Comparison**

#### **Inter Sample Comparison**

### 6.4 SIMULATION

#### **Small Box**

#### **Large Box**

### 6.5 STRUCTURAL ANALYSIS

### 6.6 CONCLUSIONS

CHAPTER 7

CONCLUSION